TOWARDS LIGNIN VALORIZATION: PYROLYTIC AND ELECTROCHEMICAL UPGRADING OF LIGNINS EXTRACTED FROM PRETREATED BIOMASS TO VALUABLE INTERMEDIATES

Ву

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ABSTRACT

TOWARDS LIGNIN VALORIZATION: PYROLYTIC AND ELECTROCHEMICAL UPGRADING OF LIGNINS EXTRACTED FROM PRETREATED BIOMASS TO VALUABLE INTERMEDIATES

By

Mahlet Garedew

Hydrocarbons, made from fossil petroleum, currently remain the most practical energy sources for transportation. But with current energy crisis and the implication of burning fossil fuels as one of the major contributors to climate change, the production of fuels from biomass has become a possible alternative to displace fossil-based fuels. Unfortunately, biomass suffers from two flaws: (1) Inefficiency: at best, plants only capture and store about 1% of the sun's energy in chemical form; and (2) Energy density: biomass has about one third of the energy that of hydrocarbons. So, deriving value from all components of biomass including lignin, optimizing conversion processes that can harness the chemical energy stored in biomasses efficiently, and converting biomass to fuels that are energy dense is essential.

To this end, conventional biomass to ethanol conversion strategies utilize pretreatment methods such as extractive ammonia pretreatment (EA) and alkaline hydrogen peroxide pretreatment (AHP), to improve the rates and extents of subsequent hydrolysis of sugars and maximize biofuel yields. As part of the pretreatment method, EA and AHP also enable the recovery of lignin which is often combusted for heat and power production. Lignin however accounts for 40% of the energy of biomass and is one of the largest natural sources of renewable aromatic compounds so it can be an ideal candidate for the production of higher-value products that would otherwise be derived from petrochemical feedstocks. The challenges in lignin valorization however come from lignin's complex structure that is naturally designed to be resistant to biological degradation. Thermochemical conversion processes such as fast pyrolysis offer a strategy for lignin depolymerization.

During fast pyrolysis the feedstock (biomass, lignin, etc.) is liquefied by heating in an oxygen free environment to form biochar, combustible gas and bio-oil. The biochar co-product has potential for use in soil amendment and carbon sequestration. The combustible gas is often burned for heat and power production. The major product, bio-oil, has the potential to displace liquid hydrocarbon fuels. However, bio-oil's reactive and corrosive nature along with its low energy content are major barriers for the adaption of this system. Classical catalytic upgrading is usually used to hydrogenate and deoxygenate bio-oil, often at high temperature and very high pressure. These severe conditions can result in barriers, such as catalyst deactivation. To avoid these conditions, electrocatalytic hydrogenation (ECH) can be used to stabilize bio-oil via hydrogenation and deoxygenation of reactive components under mild conditions (25–80 °C and 1 atm).

As lignin is converted to phenolic monomers, dimers, and oligomers upon pyrolysis, the transformation of lignin model compounds exhibiting similar bonding arrangements indicates the potential for lignin valorization using ECH. In this study, conversion, yield, and faradaic efficiency of ECH of model compounds derived from pyrolysis of lignins extracted from pretreated biomass are examined. ECH of these compounds is carried out using an activated carbon cloth supported ruthenium cathode. Having uncovered surprisingly easy aryl ether cleavages, the outcome of this research will provide understanding to further integrate biomass pretreatment, pyrolysis, and electrocatalysis systems for bio-oil stabilization and lignin valorization.

Dedicated to my partner Nick Garedew-Ballard

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Chapter 1 : Introduction and Background

Introduction

Since the industrial revolution, petroleum and other fossil-based fuels have powered human activities by providing raw materials for fuel and chemical manufacture.¹⁻⁵ Currently, these non-renewable, fossil-based resources continue to be the primary source of energy and chemicals. However, global fossil resource consumption comes at great cost to the environment as reported by the Intergovernmental Panel on Climate Change (IPCC).¹ Rising levels of greenhouse gases (GHG) in the atmosphere contribute to global warming and severe weather patterns along with ocean acidification, and sea level rise which further lead to loss of biodiversity and disruption of the oceanic ecosystems.¹ Furthermore, energy dependence and limited access to fossil fuels can lead to economic and political conflicts. Addressing these concerns requires the development of sustainable technologies that can displace fossil-based fuels with renewable alternatives.

On the energy front, although solar and wind are very attractive, their intermittent nature and their inability to produce liquid transportation fuels introduces a barrier.⁶ The use of nonedible biomass and waste sources derived from agricultural, forestry and food waste is considered a viable alternative.⁷ Biomass, formed by photosynthesis, incorporates carbon from the atmosphere and stores solar energy in the form of chemical bonds making it a renewable source of hydrocarbons. Biomass conversion simply recycles existing carbon from the biosphere instead of releasing carbon sequestered for millennia (as in the case of fossil-derived fuels). Additionally, new plant growth can capture CO₂ and help offset the impacts of its emission on the environment.^{7,8} To this end, biomass conversion technologies have experienced rapid advancement in recent decades.⁹ Biomass and waste streams composed of polysaccharides, lignins, lipids and proteins can be converted to valuable chemical and fuel intermediates via processes such as hydrolysis, thermochemical conversion, transesterification, and anaerobic digestion (Figure 1.1). These intermediates, often composed of monosaccharides, aromatics, triglycerides, methane, hydrogen gas, and CO have potential for energy storage and production of value-added products by further upgrading strategies such as fermentation and catalysis.¹⁰



Figure 1.1. Conversion of Biomass and waste components to valuable products.

Such technologies have enabled the use of biomass as fuel sources in recent decades. For example, per the U.S. Energy Information Administration, 95% of the 143.37 billion gallons (highest ever recorded) of the fuel consumed in motor vehicles in the U.S. in 2016 was 10% ethanol blended.¹¹ However, even typical biofuel production systems can access and effectively utilize only a fraction of the biomass carbon and can provide only a fraction of the energy produced from petroleum. As shown in Figure 1.2, the billion ton study projects that about 1

billion dry tonnes of biomass could be sustainably produced without impacting the food/feed markets by 2030.¹² This amount is comparable to the 0.86 billion tonnes of petroleum that is projected to be consumed by the year 2030 (this projection is made using amount of petroleum consumed in the U.S. in 2017 and assuming minimal change in consumption by 2030).¹³ However, even assuming the best-case scenario, only 0.4 billion tonnes of carbon and 21 EJ/kg of energy can be derived from the 1 billion tonnes of biomass. This falls short of displacing the 0.7 billion tonnes of carbon and 41 EJ of energy that can be derived from petroleum.¹⁴



Figure 1.2. Comparison of mass, carbon content, and energy content of petroleum and biomassderived fuel based on 0.9 billion tonnes/year of petroleum and 1 billion tonnes/yr of biomass. Carbon mass calculated assuming an empirical formula of CH_2 ($M_{carbon} = 86\%$ of mass 14) for petroleum and CH_2O ($M_{carbon} = 40\%$ of mass 30) for biomass-derived fuels. Energy calculated based on specific energy of petroleum (48 MJ/kg) and biomass (20.6 MJ/kg) (adapted from Lam et al.¹⁵).

This carbon and energy deficiency of biofuels can be attributed to the fact that when converting biomass to fuels such as ethanol using fermentation, a third of the carbon is lost as CO₂ during the fermentation process.¹⁴ Furthermore, in most cases, lignin, one of the three major components of biomass, is often burned for process heat or used as a component of animal feed. Lignin, however, is the largest natural source of renewable aromatic compounds and is ideal for

producing higher-value aromatics that would otherwise be derived from petrochemical feedstock.¹⁰ But the complex structure of lignin and its resistance to biological degradation is a major barrier for both sugar hydrolysis and its own valorization. The key to deriving value from lignin lies in the effective cleavage of its ether linkages, so conversion processes that achieve such cleavage are needed to fully valorize all components of biomass.^{14, 16, 17}

Biomass fast pyrolysis is one such alternative biomass conversion process whereby heat (400-600 °C) is used in the absence of oxygen to convert biomass into three major products: bio-oil, biochar and combustible gas. Although bio-oil has potential to produce liquid transportation fuels, its reactive properties during storage, corrosive properties due to its acidity, high water content and low higher heating value (HHV) make is undesirable, incompatible with current infrastructure, and not ready for end use as a transportation fuel. Before bio-oil can be used as a viable fuel, stability and energy upgrading is needed. With further upgrading, bio-oil can be hydrogenated and deoxygenated and used to produce liquid transportation fuels and valueadded products. Electrochemical upgrading of bio-oil offers a way whereby mild conditions (low temperature and atmospheric pressure) can be used to achieve hydrogenation and deoxygenation.¹⁸ This method offers certain advantages over other methods such as catalytic hydrogenation; as the hydrogen needed for reduction is produced in situ in ECH, avoiding the kinetic barrier related to hydrogen dissociation and hydrogen gas mass transport.¹⁹ Even catalyst poisoning is avoided due to the cathodic potential that can prevent the adsorption of poisons.¹⁹ Furthermore, ECH also can facilitate product selectivity by controlling the charge supplied to the cathodic electrode.^{19, 20}

By combining pyrolysis with electrocatalytic hydrogenation, liquid fuels and value-added products result from biomass. The production of biofuels and bio-based chemicals from bio-oil could have the potential to help reduce petroleum use in the U.S.²¹ Biochar and the combustible gas, on the other hand, can be used for heat and power production. Land application of biochar can sequester carbon, enhance soil water holding capacity, reduce fertilizer use and increase crop yields.²¹ The carbon sequestration properties of biochar, carbon dioxide capture by plant growth and displacement of fossil fuels by biofuels can reduce fossil fuel related GHG emissions by up to 10% and deter the impacts of fossil fuel use on the environment.²¹ By using pyrolysis and electrocatalysis, to fully valorize all components of biomass at centralized biorefineries, carbon and energy efficiencies of the biomass conversion process can be improved.

Project Description and Objectives

To solve the problems of low energy and carbon efficiencies, we propose deconstructing lignin using pyrolysis and further valorizing the depolymerization products of lignin pyrolysis using electrocatalysis. This project aims to investigate a combined system that utilizes lignins derived from pretreatment and extraction methods such as extractive ammonia (EA) and copper catalyzed alkaline hydrogen peroxide pretreatment (Cu-AHP) as feedstock for a pyrolysis system that effectively depolymerizes the lignin to produce bio-oil. This can further be upgraded using electrocatalytic hydrogenation and deoxygenation (ECH) to improve both the energy content and stability at centralized facilities. The upgraded stable bio-oil can then be hydroprocessed to hydrocarbon fuels (Figure 1.3). The combustible gas typically heats the pyrolysis system while biochar can be used as a soil amendment, for carbon sequestration, or burned for producing heat and power.



Figure 1.3. Herbaceous and woody biomass pretreatment and lignin extraction using extractive ammonia process or copper catalyzed alkaline hydrogen peroxide processes, conversion using pyrolysis, and upgrading electrocatalysis (adapted from Garedew, 2014).²²

Previous work by Li et al. and Lam et al., demonstrate the scheme presented in Figure 1.3. Li et al. used ruthenium loaded on activated carbon cloth (Ru/ACC) as a catalyst to transform model monomers derived from lignin pyrolysis such as guaiacol, phenol and syringol to cyclohexanol.²³ Additionally, Li et al. studied the effect of different ruthenium salt precursors, loadings, operating temperatures and current density effects on the conversion of guaiacol and electrochemical efficiencies of the system. Instead of Ru/ACC, Lam et al. investigated the effect of alkoxy position and length on alkoxyphenol conversions. Li et al. further studied the effectiveness of ECH using Ru/ACC to stabilize water-soluble bio-oil.²⁴ In this current study, we expand further in this area to more completely ascertain the potential for the pretreatment-pyrolysis-ECH system according to the objectives outlined next.

- 1. Obtain and characterize lignin streams extracted via EA and AHP processes.
 - Use elemental content and higher heating value to determine which lignin streams form the most viable feedstock.

- Investigate the thermal degradation properties of the feedstock (using thermogravimetric analysis)
- III. Compile a list of lignin-derived pyrolysis products for ECH upgrading (using pyrolysis GC/MS).

2. <u>Perform ECH on lignin model monomers using ruthenium on activated carbon cloth</u> <u>catalysts.</u>

- a. Test high temperature/pressure reduced ruthenium on activated carbon cloth (Ru/ACC) for ECH various substrates.
 - Based on results obtained from microscale pyrolysis of EA lignins and AHP lignins, compile a list of monomers, and subject them to ECH using Ru/ACC.
 Phenol, *p*-cresol, 4-ethylphenol, 4-propylphenol, guaiacol, creosol, 4ethylguaiacol, 4-propylguaiacol, eugenol, syringol, vanillin, and syringaldehyde were all subjected to ECH using Ru/ACC.
 - II. Further study the effects of alkyl group length, alky group and methoxy group position on the ECH of these phenolic monomers.
 - III. Investigate the effect of substrate concentration on faradaic efficiency in an attempt to improve previously reported modest efficiencies.
- b. Test electrochemically reduced ruthenium on activated carbon cloth (EC-Ru/ACC) for ECH of quaiacol.
 - Utilize electrochemical reduction for catalyst preparation which can bypass the high temperature, high pressure method used to prepare the catalyst previously and compare results of the two catalyst preparation methods.

- *c.* Investigate catalyst reusability for catalysts prepared using both methods to maximize catalyst life and insure maximum recovery of products.
- 3. <u>Perform ECH on lignin model dimer using ruthenium on activated cloth catalyst (Ru/ACC)</u>.
 - Perform ECH of various 4-O-5 linked dimers (3-phenoxyphenol, 4phenoxyphenol 3-phenoxyanisole and 3-phenoxytoluene) to investigate the effectiveness of the ruthenium catalyst on lignin relevant linkages.
 - II. Investigate the effect of electrolyte pH, substrate concentration, and current density on conversion and faradaic efficiency of 4-O-5 linked model dimers.
- 4. <u>Describe aspects of barriers to bioenergy technology adaptation using the wicked</u> problem framework and by looking at the social actors that influence this transition.

This is done in an effort to understand the social aspect of transitions to bioenergy use in addition to technological advancements that make bioenergy more accessible and viable.

The combination of pyrolysis and electrocatalysis for lignin depolymerization and upgrading at central biorefineries offers an approach to fully valorize biomass components to improve carbon and energy efficiencies of the biomass conversion process. The following section will briefly touch upon different aspects of lignin valorization via pyrolytic depolymerization and electrochemical upgrading.

Literature and Background

Biomass conversion is important for producing sustainable hydrocarbon products and displace fossil fuels. Conversion processes offer a way of valorizing important components of biomass such as lignin. Pyrolysis a thermochemical conversion process that can depolymerize biomass to fuel and valuable intermediates employs heat in the absence of oxygen to convert biomass to bio-oil, bio-char and non-condensable gas. Bio-oil (the liquid product) though a promising intermediate for liquid fuel production, has various undesirable properties such as high oxygen content, low pH, low energy content, and high reactivity of its oxygenated compounds during storage. Electrocatalytic hydrogenation (ECH) is employed to hydrogenate and deoxygenate these reactive compounds and improve bio-oil properties. Electrocatalytic hydrogenation offers a sustainable way to integrate, renewable sources of energy such as wind a solar with biomass-derived intermediates (such as lignin pyrolysis products) to produce valuable products. In the following sections, different aspects of the lignin valorization scheme such as lignin structure, biomass pretreatment and lignin extraction, lignin pyrolysis, and electrocatalysis will be discussed.

Lignin Biosynthesis and Structure

Lignin is the second most abundant biopolymer, and together with lignans, accounts for nearly 30% of the organic carbon.²⁵⁻²⁷ Lignin is the component of the cell wall in vascular plants mainly involved in structural integrity.²⁸ It is an essential component of the cell wall distributed throughout the secondary xylem, providing mechanical support and enabling long-distance water conduction in the tracheary elements.²⁹ Lignans are mostly dimers and sometimes oligomers that are present in various parts of the plant and can have antibacterial, antiviral antifungal, antioxidant, and cytotoxic properties that are mainly responsible for defense.^{28, 30, 31} Lignins and lignans are both derived from the phenylpropanoid pathway and are formed through phenolic oxidative coupling process.²⁹ But their metabolic fates are different since they have different physiological roles.²⁹ It is universally accepted that lignin and lignans are biopolymers

derived from monolignols *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol (Figure 1.4a).³²⁻³⁵ For the most part, the phenylpropanoid pathway and biosynthetic mechanisms for monolignol formation are relatively well defined and agreed upon while the successive monolignol coupling and modifications after coupling are a topic of much debate that spans more than two decades.^{29,36} Especially, the process of lignification that forms the 'collective phenylpropanoid macromolecule' (lignin) has been a source of disagreement for many scientists in the field.³⁷



Figure 1.4. a) Three monolignols p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol b) lignin linkages β -O-4, α -o-4, 4-O-5, β -5, β -1, 5-5 and β - β .

There are two major conflicting hypothesized models regarding the lignification process; the dirigent protein and the combinatorial model. The dirigent protein hypothesis states that lignification is made possible by proteinaceous control and template replication.^{25, 28, 29, 38-42} This hypothesis originates from the idea that the lack of structural control in lignification, as proposed by the conflicting combinatorial model, is a 'biochemical anomaly'.³⁸ According to the dirigent protein linear template replicate model, it is hypothesized that lignification occurs after the

formation of different layers of the cell wall at which time monolignols are transported through the plasma membrane, differentially targeted towards specific sites (lignin initiation sites), then starting at these sites the lignin polymer extends backwards into the plasma membrane.²⁸ This polymerization has further been hypothesized to happen via a template mediated replication process.^{25, 41} This model basically states that the primary lignin polymer is assembled with the help of an array of dirigent proteins that serve as binding sites for monolignol radicals; this lignin polymer then acts as the template where identical or mirror images of lignin polymers can be assembled to form an antiparallel double stranded lignin macromolecule.^{40,42} But there are already some criticisms of this model. If lignification is a truly regulated process, accounting for all the varieties of radical coupling between "two monolignols or between a monolignol and a growing lignin chain" would require up to 50 specific dirigent proteins to account for all the possible linkage combinations.³⁷ Furthermore, the control of the growing lignin polymer in the case of the template/replicate model would require specific proteins that can bind not only monolignols but also dimers and oligomers.³⁷ Additionally it is also noted that lignin fragments studied are often racemic but the dirigent protein would presumably form products with high regioselectivity and stereoselectivity in order to accommodate the racemic nature of lignin found in nature, there would need to be twice as many dirigent proteins or the template polymer would need to somehow be able to help form another polymer with opposite optical activity and in equal amounts.37

In contrast, the current widespread combinatorial model is mainly based on the work by Freudenberg which states that lignin biosynthesis involves a chemical process of random multidimensional crosslinking of monolignols via oxidative coupling.^{38, 43-47} According to this

combinatorial model, lignin is described as a complex racemic aromatic polymer produced from the oxidative coupling of the three major 4-hydroxyphenylpropanoid monolignols: paracoumaryl alcohol, coniferyl alcohol and sinapyl alcohol.⁴⁸⁻⁵⁰ Lignin biosynthesis starts with the synthesis of the monolignols which includes deamination of phenylalanine, followed by hydroxylation of the aromatic ring, then by phenolic O-methylation, and eventually by conversion of the side chain carboxyl to an alcohol group.⁴⁸ Once the monolignols have been synthesized they are then transported to the cell wall where they are dehydrogenated to form radicals (Figure 1.5) using oxidases, laccases, polyphenol oxidases and coniferyl alcohol oxidases.⁴⁸ 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 oligomer.⁵¹ More specifically, the radicals formed in the dehydrogenation step, which are relatively stable due to delocalized electrons (Figure 1.5), couple at the β position of the side chain to form linkages such as β -O-4, β -O-5 and β - β (Figure 1.4b).^{48, 52, 53} 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-O-5 and 5-5 (Figure 1.4b).⁴⁴



Figure 1.5. An example of monolignol radical formed by the dehydrogenation of coniferyl alcohol. It is well known that the most abundant and dominant linkage types tend to be β -O-4 linkages accounting for up to 60% of the linkages in some biomass species.⁵⁴ The lignin polymer is usually

deposited on secondary thickened cell walls and often has no regular repeating pattern like cellulose or other plant polymers.^{49, 54-56} Therefore, 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 types are different. Grasses, for example, contain all three monolignols while softwoods primarily contain coniferyl alcohol units and hardwood lignin is mainly made of sinapyl alcohol.^{57 58} Furthermore, the three dimensional lignin structure is often very rigid, resistant to biological degradation and contributes to biomass recalcitrance.⁴⁹

Biomass Pretreatment and Lignin Extraction Methods

Biomass recalcitrance is a major barrier that often limits the availability of sugars for biological conversion.⁵⁹ Several factors such as cellulose crystallinity, degree of polymerization, biomass porosity, and crosslinking between carbohydrates and lignin can all affect the activity of biological enzymes used in biomass conversion.⁶⁰⁻⁶² In addition to its contribution to limiting sugar availability, the complex lignin structure that provides structural stability and protection from pathogens for plants also contributes to enzyme inhibition during enzymatic hydrolysis.⁵⁹ If lignin is extracted from biomass, sugars can be hydrolyzed at improved efficiencies while lignin can further be valorized to valuable products. Various pretreatment and extractive methods involving physical, biological, physiochemical, and chemical processes have been explored in varying capacities to improve hydrolytic conversion efficiency of sugars by enhancing biomass porosity, transforming cellulose crystallinity, hydrolyzing hemicellulose, and isolating and extracting lignin.⁶³⁻⁶⁶

Physical methods such as mechanical comminution employ size reduction processes such as chipping, grinding and milling which "reduce cellulose crystallinity".^{64,67} Biomass milling, if

accompanied by organic solvent extraction can recover lignin.⁹ This lignin is very similar to native lignin, but the milling process can cause minor structural alterations such as the introduction of additional carbonyl and hydroxyl groups.^{9, 68} Pyrolysis is another physical method that uses heat to decompose cellulose, hemicellulose and lignin to mixtures of degradation products that can further be upgraded.^{64, 69} Biological methods utilize microorganisms such as soft-rot, brown-rot and white-rot fungi to selectively degrade lignin and hemicellulose.^{63, 64, 70} Physicochemical methods such as steam explosion, ammonia fiber explosion, CO₂ explosion, or SO₂ explosion expose biomass to steam, liquid ammonia, CO₂, and SO₂ respectively at high pressures followed by a reduction in pressure which results in explosive decompression of biomass fibers. ⁷⁰⁻⁷² These processes can result in cellulose decrystallization, hemicellulose degradation, and partial lignin depolymerization.^{64, 66, 69}

Chemical pretreatments include ozonolysis, acid hydrolysis, alkaline hydrolysis, oxidative delignification, and the organosolv process. Ozonolysis can result in lignin and some hemicellulose degradation.^{64,69} Organosolv process employs the use of organic or aqueous mixtures with organic acid catalyst to degrade cellulose and hemicellulose and break internal bonds between hemicellulose and lignin.⁶³ Acid hydrolysis pretreatment uses acids such as H₂SO₄ and HCl to hydrolyze cellulose and remove hemicellulose but is not as effective at removing lignin.⁷⁰ Furthermore the use of concentrated acids that are corrosive and toxic imposes barriers when it comes to the cost of the process.⁶⁹ Alkaline hydrolysis pretreatment uses bases such as NaOH to disrupt intermolecular forces between lignin and hemicellulose to improve biomass porosity.^{63,70} In oxidative delignification, biodegradation of lignin is achieved via the use of peroxidase enzymes in the presence of H₂O₂.^{64,69}

As previously mentioned, pretreatment methods offer a way to improve access to sugars for enzymatic hydrolysis. To further derive value from lignin, its effective extraction and recovery is needed. Acid pretreatment and extraction methods such as dilute acid and the organosolv process often suffer from repolymerization reactions in the presence of acids to produce condensed lignins with stable C-C linkages that are difficult to cleave.^{9,62,73,74} Alkaline- and ammonia-based pretreatments can be used to solubilize and extract lignin. Ammonia penetrates amorphous and crystalline cellulose and replaces OH-O hydrogen bonds with OH-N and results in rearrangement and transformation of cellulose I to cellulose III which has improved reactivity.^{65, 75-79} Furthermore, ammonia pretreatment enables the extraction of up to 50% of the lignin via the cleavage of ester and ether linkages that bind carbohydrates and lignin together.⁶² Alkaline hydrogen peroxide pretreatment (AHP), often used as a pulping and bleaching method in the pulp and paper industry, removes lignin while retaining cellulose. The process involves treatment of biomass with hydrogen peroxide in basic conditions using NaOH.⁷² Due to the tendency of lignin phenolic acids to dissolve in AHP solutions, AHP is also used as a delignification method for lignocellulosic biomass conversion.⁸⁰⁻⁸² This process chemically alters lignin and can partially depolymerize it to make cellulose more accessible to enzymatic hydrolysis while also degrading hemicellulose.⁸³⁻⁸⁵ Recent studies have shown that introduction of small amounts of copper 2,2'-bipyrydine (Cu(bpy)) can further enhance enzymatic hydrolysis compared to the conventional AHP process.⁸⁶⁻⁸⁸ Methods such as extractive ammonia process and alkaline hydrogen peroxide pretreatment are of interest to this group as they provide tools to separate and extract lignin for further valorization.

Lignin Depolymerization

Lignin degradation work has been conducted using methods such as oxidative degradation⁸⁹, reductive catalytic hydrogenation,⁹⁰ electrocatalytic reduction^{17,91-93} and pyrolysis^{58,94,95}. Oxidative methods have used ionic liquids, electrochemical approaches and catalytic methods. Generally oxidative methods depolymerize lignin at mild conditions to aldehydes and carboxylic acids. However, they may lack selectivity or result in radical formation and hence repolymerization.^{9, 17} Reductive methods using homogeneous or heterogeneous catalysis⁹⁰ and electrocatalysis^{17, 91-93} can result in selective C-O bond cleavage of lignin to form less complex aromatic compounds.⁹ The catalytic hydrogenation process can proceed either via hydrogenolysis of C-O bonds or hydrogenation of aromatic rings by addition of chemisorbed hydrogen at elevated temperatures and pressures. The challenge for this method is that if hydrogenation of the aromatic ring occurs before hydrogenolysis of the ether bond, lignin depolymerization can be impeded. Thermal degradation of lignin, as by fast pyrolysis can fragment lignin to provide monomers and dimers.⁹⁶ In this study, pyrolysis is proposed as one of the ways extracted lignin can be depolymerized.

Fast Pyrolysis of Lignin

Fast pyrolysis is a thermochemical processes whereby biomass is heated at high temperatures usually in the absence of oxygen to produce three major products: bio-oil (liquid), biochar (solid), and gas (Figure 1.6).^{97,98} The gas usually has a heating value of about 6 MJ/kg (compared to 54 MJ/kg for natural gas) and can be used for heat and power production.⁹⁹ Biochar, with a heating value of about 18 MJ/kg, not only has a potential to be used for heat and power production but it can also be used for soil amendment and carbon sequestration.¹⁰⁰ Bio-

oil is one of the products of pyrolysis and can be used as a liquid fuel or fuel intermediate. However, bio-oil has several undesirable properties such as its corrosive nature (~pH 2), its tendency to form a sludge during storage, high water content (~30%), and a relatively low HHV (~20 MJ/kg) compared to petroleum (~40 MJ/kg).¹⁰¹ For bio-oil to be an economically competitive fuel, catalytic upgrading is needed to enhance stability and energy content.¹⁰² The upgrading process itself is limited by the complexity of the bio-oil mixture and the large number of reactions that can occur between bio-oil components. Adding to this complexity, factors such as feed composition, reaction temperature, heating rate, and residence time all influence and can contribute to bio-oil's varied chemical composition. Studies of lignin's pyrolysis products from different biomass sources under varying conditions can give insight into the mechanism and composition of the bio-oil. Results from such studies will inform upgrading processes by tailoring them to specific lignin pyrolysis mixtures.



Figure 1.6. Biomass or lignin fast pyrolysis process and products (bio-oil, char, and combustible gas).

Lignins extracted from different biomass types have been pyrolyzed to understand their thermal degradation properties and products. Mechanistic studies by Liu et al. indicated that three major reactions occur during lignin pyrolysis. Initially, water evaporation takes place as physically bound water is liberated at temperatures above 100 °C. Water is again observed at elevated temperatures as chemical dehydration of aliphatic hydroxyl groups occurs.¹⁰³ The other reactions include the formation of primary volatiles (CO, CO₂, and CH₄) and the release of small molecules such as phenols, alcohols, aldehydes, and acids. Additionally, pyrolysis has been shown to decrease the presence of some oxygenated functional groups while making valuable aromatic monomers available for further valorization. NMR analysis of softwood Kraft lignin by ¹³C NMR showed that in the water-insoluble bio-oil fraction, carbonyl group content was reduced and methoxy groups were mostly eliminated after pyrolysis at elevated temperatures. Approximately 70-80% of the carbon found in this oil were aromatic carbons.^{104, 105} Additionally, side chain hydroxyl groups, aliphatic hydroxyl groups, and acid groups were significantly decreased.^{104, 105}

As previously noted, lignins derived from different biomass types can differ in their S, G and H content and thus will have varying products after pyrolysis. Saiz-Jimenez et al. reported that softwood lignin pyrolysis yields guaiacyl derivatives, coniferyaldehyde and coniferyl alcohol.⁵⁸ Hardwood lignin pyrolysis yielded guaiacyl and syringyl derivatives, syringaldehyde, coniferyl alcohol, and sinapyl alcohol.⁵⁸ Bamboo lignin pyrolysis on the other hand yielded primarily 4-vinylphenol.⁵⁸ Patwardhan et al. investigated the pyrolysis of organosolv lignin derived from corn stover under experimental settings that minimize secondary reactions.⁹⁴ Using pyrolysis GC/MS analysis to identify 24 primary pyrolysis products, this team noted the formation of phenolic monomers such as phenol, 4-vinylphenol, 2-methoxy-4-vinylphenol and 2,6-dimethoxy phenol.⁹⁴

It was also observed that the condensation of the vapor containing these products resulted in the formation of increased amounts of dimeric and oligomeric compounds suggesting oligomerization reactions of lignin monomers during storage.⁹⁴ While pyrolysis is applicable for a range of lignins derived from different biomass sources and pyrolysis conditions can be tailored to minimize secondary reactions, catalytic upgrading of lignin pyrolysis oils is still needed for lignin valorization.

Catalytic upgrading of pyrolysis products has been studied extensively and is used for the hydrogenation of lignin-derived model compounds and pyrolysis oils.¹⁰⁶ Catalytic studies have been performed on lignin-derived compounds such as phenol,¹⁰⁷⁻¹¹⁰ guaiacol,^{111, 112} cresols,¹¹²⁻¹¹⁴ pyrolysis oil,¹¹⁵⁻¹¹⁷ and many others. The main challenges of this process include the relatively elevated temperatures, the need to supply pressurized hydrogen, and the catalyst deactivation due to coke formation.^{18, 118} These challenges can increase capital costs and energy demands. Electrocatalytic hydrogenation and deoxygenation (ECH) of organic substrates is an alternative hydrogenation method that can be performed at mild conditions (room temperature and atmospheric pressure) while producing protons needed for hydrogenation *in situ* which helps avoid hydrogen gas solubility and mass transfer issues.⁹² Coke formation is also avoided in an ECH system, thus providing an economically feasible and relatively safe alternative to high-pressure/high-temperature catalytic hydrogenation processes.^{92, 119}

Electrocatalytic Hydrogenation and Deoxygenation

ECH is a multistep process that involves the generation of chemisorbed hydrogen $(M(H)_{ads})$ on the catalyst surface via the reduction of protons from water (Volmer reaction); the hydrogen then reacts with the adsorbed organic substrates $(M(X=Y)_{ads})$ to produce reduced species (M(XH-

YH) _{ads}). The organic product eventually desorbs from the catalyst surface and can be recovered from the bulk liquid.¹²⁰ Additionally, if the organic species have weak sigma bonds, hydrogenolysis of these bonds is possible.¹²⁰ Concurrently, hydrogen evolution reactions (HER) also occur by either Tafel or Heyrovsky reactions, thus competing with the substrate reduction reactions (Figure 1.7).^{92,17} The competition between the substrate reduction reaction and the hydrogen evolution reaction results in decreased faradaic efficiency (defined as the ratio of electrons used to generate desired product to total electrons passed) of the system and is one of the drawbacks of this process. However, it should be noted that hydrogen gas can be readily collected as a product with its own value.



Figure 1.7. Hydrogen chemisorption, electrocatalytic hydrogenation of organic substrate X=Y, and hydrogen evolution via Tafel or Heyrovsky reactions. (adapted from Dalavoy et al.¹⁸)

Adsorption/desorption mechanisms of substrates plays an important role in achieving successful ECH of organic substrates and also in limiting HER. Large surface area cathodes with multiple sites for adsorption of organic species and chemisorption of hydrogen can facilitate frequent interactions between the two.¹²⁰ Additionally, adsorption strength and mobility of adsorbed species also ensures frequent collision of organic species with chemisorbed hydrogen thus promoting hydrogenation.¹²⁰ Several factors such as electrode material, current density, temperature, substrate concentration, solution pH, the presence of competing organic solvents, and supporting electrolyte can all affect adsorption properties of organic substrates and the desorption of products and thus impact the faradaic efficiency.¹²⁰ Optimum temperature promotes high coverage of the catalyst surface with both hydrogen and substrate resulting in increased mobility of the substrate species and increasing the probability of their encounters with chemisorbed hydrogen.¹²⁰ Optimum current density ensures desired hydrogen chemisorption and low HER rates (due to lowered likelihood of chemisorbed hydrogens forming hydrogen gas).¹²⁰

There have been extensive studies in this regard, to achieve efficient organic molecule transformations and limit hydrogen evolution at the cathode surface by controlling reaction conditions, catalyst type and cell potential. Most of these studies have focused on the effects of these conditions on yield, selectivity, conversion and electrochemical efficiency. Varying cell setups and reaction conditions on different organic models such as phenolic compounds,¹²¹⁻¹²⁴ carbonyl compounds,^{4, 5, 125-130} organics acids,^{6, 18, 131} model lignin dimers,^{17, 91, 92} polycyclic aromatic compounds,¹⁹ lignin,¹³² bio-oil,²⁴ vegetable oil and dyes¹³³⁻¹³⁵ have been reported to be effective in hydrogenation of these various substrates.

Electrocatalytic Reduction of Organic Compounds

ECH of various oxygenated model compounds that exhibit carbonyl, methoxy, and hydroxyl functionalities are relevant for the electrochemical upgrading of lignin derived monomers and
dimers. As outlined in Table 1.1, electrochemical reduction of various organic molecules has been investigated dating back several decades. ECH of carbonyl compounds to alcohols has been investigated under varying conditions with varying substrates on varying catalyst materials and catalyst support matrices. Mahdavi et al. examined the ECH of conjugated enones to cyclohexanone and cyclohexanol in aqueous methanol using Raney nickel, nickel boride and fractal nickel. It was found that acidic pH and increased substrate concentration improved conversion and electrochemical efficiency but had no effect on selectivity. Additionally, it was reported that decreased current density resulted in increased conversion.²⁰ Similarly, Dabo et al. demonstrated that the improved conversion of 2-cyclohexenone to cyclohexanone and cyclohexanol in aqueous methanol could be achieved on cheaper cathode materials such as nickel and copper deposited on stainless steel compared to fractal nickel. ¹²⁷ Alternatively, Holt et al. investigated the ECH of 2-cyclohexen-1-one in a sulfur environment on a WS_2 catalyst loaded on vitreous carbon and found that the electrochemical efficiency increased with increasing WS₂ layer thickness of up 2 nm and decreased above that.² This study also demonstrated the resistance of this catalyst to sulfur poisoning.² Dube et al. ¹³⁶ and Cirtiu et al.¹³⁷ both investigated the ECH of cyclohexanone to cyclohexanol. Dube et al. compared various metals (platinum, palladium, ruthenium, rhodium, and nickel) on various support matrices (alumina, activated carbon powder and graphite) and found that the activated carbon matrix showed improved activity for cyclohexanone conversion compared to alumina.¹³⁶ Citriu et al. demonstrated that the catalytic activity of palladium on alumina catalyst towards cyclohexanone conversion to cyclohexanol was improved by the introduction of acetic acid as a supporting

electrolyte due to the formation of an organic layer on the catalyst surface (via a process known as *in situ* functionalization) that facilitated improved cyclohexanone adsorption.¹³⁷

The ECH of furanic compounds such as furfural and 5-hydroxymethylfufural have also been investigated. Li et al. ²³ demonstrated that furfural can be converted to furfuryl alcohol and 2methylfuran in an undivided cell using a nickel sacrificial anode. It is reported that furfuryl alcohol yield was optimum at pH 5 while 2-methylfuran yield was favored at pH 1. Additionally, increasing current density also resulted in increased furfuryl alcohol yield but decreased the electrochemical effciency.⁵ Green et al. studied ECH of furfural in a continuous membrane reactor and demonstrated that palladium on carbon was 4.4 times more active than platinum on carbon for the hydrogenation of furfural to furfuryl alcohol, 2-methylfuran, tetrahydrofurfuryl alcohol and 2-methyltetrahydrofuran.¹²⁸ Nilges et al. investigated the ECH of furfural and 5-hydroxymethyl furfural to 2-methylfuran and 2,5-dimethylfuran. It is reported that the combination of a copper electrode with acidic electrolyte solution yielded the highest product selectivity. The use of cosolvents, acetonitrile and ethanol improved product yield and electrochemical efficiency.¹²⁹ Zhao et al. also studied furfural ECH to furfuryl alcohol in various electrolytes using various electrodes and found that 3% platinum on activated carbon fiber prepared by the impregnation method gave the best conversion and current efficiency in 0.1 M HCl electrolyte.¹³⁰

Phenolic compounds have also been hydrogenated using ECH to form cyclohexanol as a major product. Amouzegar et al. investigated the ECH of phenol on highly dispersed Pt electrode and found that increased platinum loading (up to 2%) increased current efficiency to 85%.¹²⁴ Additionally, in their electrode support study they reported that platinum supported on carbon was significantly more active than platinum on platinum.¹³⁸ Laplante et al. found that among

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Pd/BaCO₄, Pd/BaCO₃, and Pd/Al₂O₃, alumina showed the best electrochemical efficiency and conversion of phenol to cyclohexanol.¹³⁹ Martel et al. studied the effect of pH, current density and electrode material on the ECH efficiency of phenol to cyclohexanol using various electrode materials (Pt/Pt, Rh/Ni, Ru/Ni, and Ru on stainless steel). The highest conversion and current efficiency were observed for Ru/Ni in acidic pH.¹²¹ Ilikti et al. studied the ECH of phenol¹²² and alkyl-substituted phenols¹⁴⁰ and demonstrated that the presence of low amounts of a surfactant, dodecyldimethylethylammonium bromide (DDAB), improved the conversion and current efficiency. Brisach-Wittmeyer at al. investigated the conversion of catechol on rhodium on alumina to 1,2-cyclohexanediol at pH 5, 7, and 13 and found that catechol conversion rate is improved in basic conditions.¹⁴¹ These studies showed that enhanced substrate adsorption and interaction with chemisorbed hydrogen can be achieved by optimizing catalyst loading, using appropriate support material, controlling the pH and using surfactants which all contribute, improving conversion and electrochemical efficiency.

Guaiacol has been investigated by Li et al. using ruthenium on activated carbon. Guaiacol was hydrogenated and partially deoxygenated. It is reported that higher temperature and low pH resulted in improved guaiacol conversion and current efficiency. Ru/ACC was also reported to be effective for the ECH of phenol and syringol.²³ Lam et al. investigated guaiacol and other alkoxyphenols and found that the ECH of these compounds on Raney Nickle cathodes proceeded via aryl-ether bond cleavage to form phenol followed by hydrogenation. Although size of the alkoxy group did not have a significant effect on conversion rate or current efficiency, both were affected by the proximity of the alkoxy group to the phenolic hydroxyl group.¹⁵ A more extensive

library of lignin monomer transformations is needed to better assess the efficacy of ECH for valorizing lignin-derived compounds.

The investigation ECH of dimers, especially those with lignin-type linkages are extremely relevant as they offer a way to depolymerize and upgrade lignin. In this regard, ECH has been investigated for using some lignin-derived model compounds. Mahdavi et al. also investigated ECH of β -O-4 model compounds including benzyl phenyl ether and substituted benzyl phenyl ethers on Raney nickel electrode and found that hydrogenolysis of benzyl phenyl ether can be improved to 100% by optimizing substrate concentration, current density, and temperature.¹⁷ Increasing substrate concentration and temperature improved conversion and current efficiency but had no effect on selectivity. However, decreased current density resulted in improved conversion due to the suppression of the hydrogen evolution reaction. The presence of methoxy groups on the aryl rings was not found to have a major effect on the efficiency of the system.¹⁷ Cyr et al. studied the ECH of various lignin model dimers with Raney nickel and palladium catalysts and successfully cleaved β -O-4 linkages in basic conditions and found that hydrogenolysis does not occur if the phenolic group is alkylated.⁹² 4-Phenoxyphenol, a 4-O-5 bonded lignin model dimer, was also cleaved to phenol on Raney nickel.⁹² Similarly, Dabo et al. investigated ECH of 4phenoxyphenol on various catalyst materials and demonstrated high current efficiencies (50-60%) on palladium on alumina, palladium on carbon and Raney nickel catalysts.⁹¹ Cirtiu et al. compared the catalytic hydrogenation and ECH of benzophenone on palladium catalyst and found that palladium supported on alumina was more efficient than finely divided palladium.¹⁴² Additionally treatment of alumina supported palladium catalyst with organic acids (acetic acid, propionic acid, and butyric acid) transforms the catalyst in to organically functionalized surface

and resulted in improved ECH efficiency due to improved substrate adsorption on the catalyst surface facilitated by the organic acids.¹⁴² The dimer cleavage studies outlined here show promising potential for the use of ECH as a lignin depolymerization and upgrading method. Additionally, as lignin derived bio-oils are susceptible to secondary reactions that can form dimers and oligomers,⁹⁴ lignin dimer ECH upgrading is extremely relevant. What is needed is a more extensive understanding of ECH's potential for linkage cleavage between lignin phenolics.

Citation Substrate Electrolyte Electrode Conditions Conversion Two-compartment H-cell Conversion: 60– Aqueous WE: nickel boride, fractal Conjugated enones methanol with with Nafion[®] 324. 100% (cyclohex-2-en-1-one nickel, Raney nickel Mahdavi et 250 mA/dm², 90 min (2 Current Efficiency: 0.1M NaCl and al. 1995 125 CE: glassy carbon and other conjugated 0.1M boric acid F/mol) – 180 min (4 F/mol). 55 - 143 % enones) (pH=5.3-9.3). WE: RVC with Pt, Pd, Ru, Rh (5% on Al_2O_3 and 5% Simple two-compartment dynamic cell with Nafion[®] on ACC), 10% Ni in Dube et al. Phosphate buffer Conversion: 5–96% 2003 126 Cyclohexanone graphite. 117. pH=7. CE: Stainless steel or Pt 20 mA, 1600 C wire gauze WE: 200 mg of 10% 0.5 M solution of Conversion: 100% Two-compartment simple Pd/Al₂O₃ powder on RVC acetic acid or Cirtiu et al. dynamic cell design with using Pd/Al_2O_3 with 2006 137 Cyclohexanone suspended in solution and phosphoric acid in catalyst powder circulated. acetic acid. circulated through the water. 20 mA for 160 min cell. WE: Ni, Cu, Co, graphite Conversion: 42% electrodeposited on 60 Aqueous (graphite) – 94% (Ni Dabo et al. Two-compartment H-cell mesh stainless steel at 4 F/mol and Cu at 1996.127 2-cyclohexen-1-one methanol with Nafion[®] 324. screen compared to 6 F/mol) fractal Ni and stainless steel

Table 1.1. Electrocatalytic reduction stude of various organic substrates (WE = working electrode, CE = counter electrode, RE = reference electrode, RaNi = Raney nickel, RVC = reticulated vitreous carbon, ACC = activated carbon cloth)

Cyclohexene, 2- cyclohexen-1-one, benzaldehyde, acetophenone, styrene, 1,3- cyclohexadiene, trans, trans-2,4-haxadien-1- ol, citral, linalool, Geraniol (olefins, aldehydes, ketones).	Aqueous, NaCl or NH ₄ Ac, NH ₄ Cl, NH ₃ + NH ₄ Cl with MeOH, EtOH, t- BuOH or acetonitrile co- solvent (4:1) with concentration of 0.1 M, 0.2 M, 0.35 M.	WE: Iron CE: Ni sacrificial Anode (Ni foam). RE: Ag/AgCl 3 M KCl	Undivided cell (N₂ was used to maintained inert atmosphere when NH₄AC was used as an electrolyte.)	Conversion: 2- cyclohexen-1-one (5.7–55 %) Current Efficiency: 9.5–100 %	Santana et al. 2004 ¹⁴³
Cyclohexen-1-one	3 mL methyl alcohol + 32 mL water +0.3088 g (NH_4^+) (CH ₃ COO) + 0.1% vol thiophene.	WE: WS ₂ on vitreous carbon RE: Ag/AgCl saturated	Glass batch reactor with glass frit in the middle used to separate anode and cathode	Current Efficiency: up to 77% at 2 nm	Holt et al. 2010. ²
Phenol	1M KH2PO4 + 1M NaOH (29ml) / 1M NaOH	WE: Pd/Al ₂ O ₃ , Pd/BaCO ₃ , and Pd/BaSO ₄ in RVC CE: Pt mesh RE: Standard Colomel Electrode (SCE)	Two-compartment jacketed glass H-cell with Nafion [®] 324 and a cooled condenser on top of the cathode compartment. 100 mA/dm ²	Conversion: 0% (RVC)-100% (Pd/Al ₂ O ₃) Current Efficiency = 0% (RVC, Pd/BaCO ₃ , Pd foil) - 26.3% (Pd/Al ₂ O ₃)	Laplante et al. 2003 ¹³⁹
Phenol	Neutral – 0.5 boric acid + 0.005- 0.05 M NaCl (initial pH= 4, final pH=6).	WE: RaNi (steel grid), Rh 3.5%/Ni, Ru 3.5%/Ni, Ru 2.3%/Ni, Ru 4.4%/Ni, Ru 5%/Ni, Ru 4.4%/Inox, platinized platinum. CE: glassy carbon plate or Pt grid cylinder.	Two-compartment jacketed glass H-cell with Nafion [®] 324 at 60 °C, 8.8E-3 M phenol, current density= 1mA/cm ² - 301mA/cm ²	Conversion: reported as unreacted phenol = 0-100% and mass balance = 92-100% Current Efficiency: 0-87 %.	Martel et al.1997. ¹²¹

Phenol	Aqueous buffers, unbuffered or ethanol-water + DDAB or CTAB	WE: RaNi at stainless steel CE: Pt perforated cylinder RE: Ag/AgCl saturated KCl	Two-compartment jacketed glass H-cell with Nafion [®] 417 at 30°C. Pre-electrolysis conducted at 100mA before phenol was added and then ran at current density of 1.5- 2 mA/cm ² and a theoretical charge of 6 F/mol.	Conversion: 25–79% Current Efficiency: <1% to 77% (with DDAB at pH=2 at 30°C)	llikti et al. 2002. ¹²²
Phenol	0.05 M H ₂ SO ₄	WE: highly dispersed Pt on Vulcan XC-7212 with Teflon as a binding material, platinized platinum, platinized carbon rod, Pt/C CE: platinized platinum screen	Two-compartment glass H- cell with Nafion [®] 324 membrane (cation exchange) and 470 mg of phenol. Conducted at galvanostatic conditions of 40 mA, 6 F/mol, 60 °C.	Current Efficiency: 0.5–85 %	Amouzegar et al. 1993 ^{123, 124, 138}
Phenol	0.5M acetic acid (pH5 with NaOH in water/methanol 4:1 v/v solution (29ml))	WE: 10% Pd/Al ₂ O ₃ (200mg) + RVC (powder dynamically circulated)	Two-compartment cell with Nafion [®] 117 Galvanostatic conditions of 20mA for 6h		Bannari et al. 2006, 2008. ^{119, 144}
Phenol	Acetic acid buffer adjusted to pH 5 with NaOH (10M)	WE: RVC + Pd nanoaggregates on SnO ₂ (solgel) CE: Pt wire	Dynamic cell with variable flow pump, with a flow rate of 1L/min, polarized by passing 50 C, 1 mL phenol (9.58x10 ⁻³ M).	100%	Tountian et al. 2009. ¹⁴⁵
2,6-dimethylphenol, 2-tert-butylphenol	Buffers pH=2 or pH=9 with non- micelle forming DDAB surfactant (diododecyldimet hylammonium)	WE: RaNi on stainless steel CE: Pt perforated cylinder RE: Ag/AgCl saturated KCl	Two-compartment glass H- cell with Nafion [®] 417 at 65 °C and a low current density of 1-7 mA/cm ² . Theoretical 6 F/mol charge passed.	Conversion: 7.5– 82% Current Efficiency: 0.13% to 70%	llikti et al. 2004 ¹⁴⁰

Guaiacol, phenol, syringol	Acidic – 0.2M HCl Neutral – 0.2M NaCl Basic – 0.2M NaOH	WE: Ruthenium on activated carbon (Ru/ACC) prepared using different impregnation methods and different loadings. CE: Pt wire	Two-compartment glass H- cell with Nafion [®] 117 placed in a water bath at controlled temperatures of 50 °C and 80 °C. performed under galvanostatic control (100mA) for 2h.	Conversion: 89% (phenol), 75% (guaiacol), 58% (syringol) Current efficiency: up to 31%	Li et al. 2012. ²³
Alkoxyphenols	0.1 M pH 8 potassium borate solution and CTAB	WE: RaNi on stainless steel mesh CE: cobalt phosphate	Two-compartment H-glass cell with Nafion [®] 117 at 75 °C and current of 50mA (8 mA/cm ²) for 6h		Lam et al. 2015. ¹⁵
Catechol	1M NaOH, phosphate buffer or acetate buffer	WE: 5% Rh-Al ₂ O ₃ on RVC electrode CE: platinum grid	Two-compartment glass H- cell with Nafion [®] 117 and current = 10 or 5 mA	100% conversion after 500 C of charge was passed	Brisach- Wittmeyer et al. 2006. ¹⁴¹
Acetophenone (AP)	96% ethanol/water (90/10) or 96% ethanol	WE: Pd ink on Toray paper RE: Ag/AgCl	Proton-exchange membrane electrochemical reactor Hydrogen flow rate 50ml/min	Conversion of 70% (ethanol/water), 35% (ethanol)	Saez et al. 2012. ⁴
Limonene, p- methene, and carvone	Hydroorganic – 0.2M NaCl + ethanol +water (85:15 v/v) Emulsified – 3.6 mmol limonene in aqueous buffer	WE: RaNi CE: graphite rod	Two-compartment glass H- cell with Nafion [®] 324	Conversion: 8–97% Current Efficiency: 0-30%	Chambrion et al. 1995. ¹⁴⁶

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	Micellar – 5.5 X 10-2M CTAB + 0.2M NaCl in water				
α and β unsaturated ketones, benzaldehydes and acetophenones	10ml solvent water/methanol (1:1) + supporting electrolyte NH4Cl (0.2 mmol)	WE: Nickle deposited on Fe, Ni, Cu, Fe/Ni CE: Ni sacrificial anode	One-compartment cell with Ni sacrificial anode Pre-electrolysis J = 350 mA/dm ² until 60 C of charge was passed 1 mmol substrate added and ran at 350 mA/dm ² current density	Conversion: product yield of up to 97% achieved Current Efficiency: up to 92% achieved	Vilar et al. 2010. ¹⁴⁷
Furfural to furfuryl alcohol and 2-methyl furan	4:1 water/methanol mixture + 0.2M ammonium chloride	WE: Ni deposited on Fe, 30855, Cu, Aland Ni CE: Ni sacrificial anode	One-chambered cell with Ni sacrificial anode 1254 coulombs (130% hydrogen equivalent) of charge passed 600 mA/dm ² current density and voltage varied from 1.6 v to 2.1 v	Conversion: 66 – 97% Current Efficiency: 18–56%	Li et al. 2012. ⁵
5 wt% furfural, 5 wt% furfuryl alcohol, 5%furfural sparged with 30SCCM hydrogen gas.		WE: Pt/C or Pd/C CE: pt-Ru/C RE: Ag/AgCl	Continuous electrocatalytic (flow 0.2 ml/min) membrane reactor with 20 min residence time.	Current Efficiency: 24–30%	Green et al. 2013. ¹²⁸
Furfural and 5 hydroxymethyl-2- furfural	500 mM H2SO4 + water/acetonitrile mixture	WE: Cu, Ni, Pt, C, Fe, Pb, Al RE: Ag/AgCl at KCl	Two-compartment H-cell with cation exchange membrane. Current 200 mA (10 mA/cm ²) and runtime of 2-4 h, kept in an ice bath at 8		Nilges et al. 2013. ¹²⁹

			°C. Nitrogen gas passed through the cathode compartment. Volatiles from cathode trapped using a reflux condenser through ACN.		
Furfural to furfuryl alcohol	H₂SO4, HCl, HClO₄ and NaOH	WE: Ni, Cu, Pb and Pt, Pt/ACF CE: Pt sheet RE: SCE	Two compartment glass H- cell with Nafion [®] 117 and oxygen removed by bubbling argon.	Conversion: 0% (blank ACF) – 90% (Pb) 82% (3%Pt/ACF) Current Efficiency: 0 (blank ACF) – 78% (3% Pt/ACF)	Zhao et al. 2014. ¹³⁰
5-Hyroxymethyl furfural to 2,5dihydroxymethyl furan (DHMF), 5methyl furfural, 2,5- dimethylfura, 2,5dimethyl-2,3- dihydrofuran studied in the presence or absence of glucose.	0.1M Na ₂ SO ₄	WE: Fe, Ni, Ag, Zn, Cd, In, Pd, Al, Bi, and Pb, Co, Au, Cu, Sn, Sb CE: large gold coil RE: RHE	Conventional single compartment three electrode glass cells. Oxygen removed by bubbling argon		Kwon et al. 2013. ¹⁴⁸
Levulinic acid	Neutral – K ₂ HPO ₄ + KH ₂ PO ₄ Acidic – 0.5M H ₂ SO ₄	WE: Pb or Cu CE: Pt foil RE: Ag/AgCl (3.5 M KCl)	Flow cell (single electrolytic flow cell), Batch half-cell (3 electrode cell), and Solid polymer electrolyte membrane cell	Yield: 90% valeric acid with 95% selectivity Current Efficiency: 85.6%	Xin et al. 2013. ⁶

Levulinic acid (LA) reduction and Formic acid (FA) oxidation	0.5 M H ₂ SO ₄	WE: Pb/Pt/C + Nafion [®] CE: Pt foil/Pd/C	Proton exchange membrane single electrocatalytic flow cell reactor (reduction of LA with FA)	High selectivity (90%) to valeric acid Current Efficiency: (>47%)	Qui et al. 2014. ¹³¹
Lactic acid	0.2M H ₂ SO ₄ , 0.1M HCl, 0.01 H ₂ SO ₄ , 0.01 HCl, 0.01 M HClO ₄	WE: 5% Ru/C powder on RVC connected by copper wire to circuit. CE: Pt wire RE: Ag/AgCl	Two-compartment glass cell with anode compartment separated by a glass frit. 1 mL of LA solution added (0.1wt%, 11.1 mmol in 75 mL volume). Current = 40 mA, 100 mA.	Conversion: reported as amount of LA remaining = 63-71%, with material balance = 59.9 to 97.1%. Current Efficiency: 7.48E-7 (0.01 H ₂ SO ₄) to 1.29E-5 (0.01 M HCIO ₄)	Dalavoy et al. 2006. ¹⁸
Benyl phenol ether, benzyl methyl ether, β -phenoxy ethyl benzene, α -phenoxy acetophenone.	NaCl (0.1M) in ethanol/water (75:25, v/v)	WE: RaNi/Ni prepared by pressing a mixture of Raney alloy powder and fractal nickel powder (80:20, v/v) and leaching out the aluminum. CE: glassy carbon plate	Two-compartment glass H- cell with a jacketed cathodic compartment with Nafion [®] 324 membrane	Conversion: 9-100% Current Efficiency: 42-124%,	Mahdavi et al. 1997. ¹⁷
Lignin Model Dimers Phenolic monoethers (with one β -O-4 linkage) phenolic diether (with two β -O-4 linkages) a non-phenolic monoether (with β -O- 4 linkage) 4-phenoxyphenol (4- O-5 linkage)	1 M NaOH Or 1 M NaOH in 1:1 ethanol-water	WE: Raney Ni and palladium-based electrodes	Two-compartment jacketed glass H-cell with Nafion [®] 324 membrane A constant current of 5 or 20 mA was applied.	Conversion: 31–95%	Cyr et al. 2000. ⁹²

Table 1.1 (cont'd)

4-Phenoxyphenol	1 M NaOH	WE: Ni, Ni ₂ B (crytaline and amorphous), RaNi, activated charcoal (C), 5% Rh/C, 5% Pt/C, 5% Ru/C, 5% Pd/C, 10% Pd/C, 5% Pd/Al ₂ O ₃ , 5% Rh/Al ₂ O ₃ , 5% Pd/BaSO ₄ , 5% Pd/Ni	Two-compartment glass H- cell with a jacketed cathodic compartment with Nafion [®] 324 membrane Current = 5 mA and temperature = 50 °C	Conversion: 0–100%	Dabo et al. 1999. ⁹¹
2-(2-fluoro-4- biphenyl) propanoic acid 2-Isopropyl-α- methylene-5-indan acetic acid	Ethanol containing 10% sulfuric acid	WE: Ni	Undivided cell kept under atmospheric nitrogen at 50 °C with a constant current density of 100 A/m ²	Current efficiency: 60–83%	Raju et al. 2001. ¹⁴⁹
Benzophenone	0.5 M solution of various acids (acetic acid, phosphoric acid) in aqueous ethanol and pH adjusted to 5 with 1 M NaOH	WE: 10% (w/w) Pd/Al ₂ O ₃ powder or finely divided Pd was suspended in solution and dynamically circulated on the RVC cathode	Two-compartment cell with Nafion [®] 117. ECH was performed under galvanostatic conditions of current = 20 mA	Conversion 100%	Cirtiu et al. 2007. ¹⁴²
Polycyclic aromatic compounds (phenanthrene, anthracene, naphthalene)		WE: RaNi CE: graphite rod or Pt grid or Pt plate RE: SCE	Two-compartment jacketed glass H-cell with Nafion [®] 324 membrane The cell voltage was varied between 20 and 40 V to provide current = 20 mA	Conversion: 0–82% Current Efficiency: 0–53 %	Robin et al 1990. ¹⁹
Water soluble bio-oil (WSBO)	WSBO in 0.2 M NaCl	3 wt% Ru on activated carbon cloth	Two compartment jacketed glass H-cell with Nafion [®] 117		Li et al. 2013. ²⁴
Edible oils			Packed-bed flow-through electrochemical reactor		An et al. 1998. ¹³⁵

Soybean oil		WE: finely divided RaNi powder CE: expanded titanium grid coated with IrO ₂			Yusem et al. 1992. ¹⁵⁰
Indigo	1 M NaOH	WE: Ti, NI, Cu, stainless steel and Pb CE: Pt/Ru RE: Ag/AgCl (3 M KCl)	Two-compartment H-cell with Nafion [®] 324 membrane performed at 50 °C		Roessler et al 2002. ¹³³
Vat dyes	1 M NaOH	WE: Pt black, Rh black, Pd black, RaNi, RaCo, Devarda Cu CE: Pt/Ru RE: Ag/AgCl (3 M KCl)	Two-compartment H-cell with Nafion [®] 324 membrane	Conversion: 1.4– 81.9% Current efficiency: 1.1–65.5%	Roessler et al 2002. ¹³⁴

Conclusion

Electrocatalytic hydrogenation of lignin-derived oxygenated intermediates offers a sustainable way to integrate renewable energy sources such as wind and solar with biomass conversion methods to produce valuable products. Using this process, abundant low-value lignin intermediates can be used to capture excess renewable electricity in the form of chemical bonds. Furthermore, this process offers the opportunity to avoid harsh conditions that are often associated with catalytic hydrogenation processes, further reducing energy inputs. In the subsequent chapters, the characterization of EA and Cu-AHP derived lignin streams will be addressed to inform pyrolysis protocols and identify the monomers that can be obtained from this process. Then, studies of ECH of lignin-derived monomers and dimers will be introduced and discussed to develop an advanced understanding of how the different monomer functionalities and linkages behave during ECH. Furthermore, conditions that improve faradaic efficiency are explored as they can minimize energy inputs into the ECH system and are vital for economical scale up of this process at centralized biorefineries to valorize lignin.

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Chapter 2 : Biomass Pretreatment, Lignin Extraction, and Characterization

Abstract

Pretreatment processes such as extractive ammonia (EA) process and copper catalyzed hydrogen peroxide (Cu-AHP) offer a way to extract lignin while the hemicellulose and cellulose are directed towards cellulosic ethanol production via fermentation. As lignin is a component of biomass comprising up to 30% of its mass and 40% of its energy, it offers great potential as a feedstock for conversion processes such as fast pyrolysis. Biomass fast pyrolysis (BFP), which uses heat (400–600 °C) in an oxygen free environment to convert biomass to bio-oil, biochar, and combustible gas, is an alternative way of producing liquid transportation fuels to displace to fossil fuel use and its impact on the environment. The major fraction, bio-oil, can be further upgraded to liquid hydrocarbon fuels and value-added products. As lignins derived from different biomass have complex structure and varying thermal degradation properties, characterization of these feed materials is needed. In this chapter, corn stover lignin extracted via EA and polar lignin extracted via Cu-AHP are characterized using elemental analysis, bomb calorimetry, thermogravimetric analysis, and pyrolysis gas chromatography mass spectrometry (py-GC/MS). The results offer some insight into the thermal degradation properties to inform pyrolysis trials and identify relevant monomers for further ECH upgrading.

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Introduction

Lignin is one of three major fractions of lignocellulosic biomass and is typically present at levels of 15–30 wt.%.¹ Lignin is a heterogeneous polymer consisting of three monolignols that undergo free-radical polymerization to form its complex aromatic structure. Approximately 45-60% of the bonds between aromatic moieties are β -O-4 linkages, followed by 5-5 (3–27%), α -O-4 (6–8%), 4-O-5(4–9%), β - β (2–12%), and β -5 (3–12%).^{2,3} To gain the most value from biomass, it is vital that lignin be upgraded to higher-value products.⁴ However, barriers exist to the extraction and depolymerization of lignin. Biomass pretreatments have long been used to overcome biomass' recalcitrance, primarily to hydrolysis, as the availability of sugars limits biological conversion.⁵ New biomass pretreatments are being developed that also fractionate biomass by removing lignin, thus leaving cellulose and hemicellulose behind for saccharification. Lignin removal, though possible, is difficult owing to its complex nature, which provides the plant with structural stability and protection from pathogens. It is because of this structure that lignin contributes to carbohydrate recalcitrance in the cell wall matrix.⁵ To make sugars available for subsequent bioconversion and extract lignin for further valorization, biomass pretreatment and lignin extraction processes are paramount.

Biomass pretreatment processes are essential steps in biomass conversion to fuels and chemicals. Pretreatment methods help to alter cellulose crystallinity, improve conversion efficiency, hydrolyze hemicellulose, and extract different biomass components such as lignin.⁶⁻⁹ Various techniques involving physical methods (size reduction),¹⁰ chemical methods (oxidation, organosolv, acid hydrolysis, and alkaline hydrolysis),^{6,11,12} biological methods (microbial degradation),^{6,7} and physicochemical methods (ammonia fiber explosion, CO₂ explosion, SO₂

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explosion, and steam explosion)¹³⁻¹⁵ have been investigated as pretreatments for biomass. Pretreatments that fractionate biomass into its major components offer direct routes for valorizing lignin.

Extractive ammonia (EA) processing is a pretreatment method that utilizes anhydrous ammonia to solubilize biomass components such as lignin and transform cellulose I to cellulose III.⁸ As lignin is the structural component of biomass that is resistant to enzymatic degradation and can cause enzyme inhibition, it is a barrier to cellulosic conversion efficiency.⁸ Processes such as EA can help in solubilizing and extracting lignin so that sugar conversion efficiency is improved and lignin can be made available for valorization. Alkaline hydrogen peroxide pretreatment (AHP) is another method that is often used in the paper industry for pulping and bleaching. This process can remove lignin while retaining cellulose and is therefore a pretreatment method at biorefinieries.^{16, 17} The process involves treatment of biomass with hydrogen peroxide in basic conditions (NaOH) to achieve delignification and improve enzymatic hydrolysis.¹⁵ Partial depolymerization of lignin makes cellulose more accessible to enzymatic hydrolysis, though hemicellulose is also degraded.¹⁸⁻²⁰ Recent studies show that introducing small amounts of copper 2,2'-bipyrydine (Cu(bpy)) further enhances enzymatic hydrolysis compared to the conventional AHP process.²¹⁻²³ Finally, Cu(bpy) AHP pretreatment improves cellulose hydrolysis and lignin recovery from woody biomass varieties, and is thus considered in this investigation.

These novel pretreatments extract lignin to enhance enzymatic hydrolysis efficiency and produce liquid fuels from carbohydrates and heat and power from lignin. However, heat and electricity are relatively low-value uses of lignin. As one of the few natural sources of aromatic hydrocarbons and accounting for 40% of the energy in biomass, lignin may be better suited for

making higher-value aromatic chemicals and transportation fuels. Further depolymerization and valorization of the complex, amorphous, cross-linked lignin polymer remains a challenge in lignocellulosic biomass conversion.²⁴ This investigation attempts to further valorize lignin fractions that are the byproducts of pretreatment processes via pyrolysis and electrocatalysis to produce liquid fuel and chemical intermediates. Pyrolysis, a thermochemical conversion method that employs heat (400–600 °C) in the absence of oxygen, deconstructs the complex lignin polymer to produce liquid (bio-oil), solid (biochar), and gas. Although bio-oil has potential as a liquid fuel intermediate, its instability, corrosive nature and high moisture and oxygen contents necessitate further upgrading and stabilization. Before subjecting lignin fractions to pyrolysis and electrocatalytic upgrading, assessing the chemical and thermochemical properties of these feedstocks is needed. EA⁸ and AHP²³ lignin fractions obtained from two research groups at Michigan State University (East Lansing, MI) were characterized to assess their fuel value and to determine the composition of the lignin pyrolysis products. Along with analytical-scale pyrolysis in tandem with GC/MS (py-GC/MS), elemental analysis (CHONS) and thermogravimetric analysis are included to predict higher heating value and the onset temperature of pyrolysis. Such information is important for identifying model compounds to be used in subsequent ECH studies.

Experimental Methods

The EA lignin extraction process, as described by da Costa Sousa et al., involves corn stover solubilization in 6:1 ammonia-to-biomass ratio at 120 °C and further extraction in water and ethanol (Figure 2.1).⁸ EA lignin fractions obtained from Dr. Bruce Dale's group at MSU included the recovered liquid after EA treatment (EA-FO), an ethanol-insoluble/water-insoluble fraction

(EA-F1), an ethanol-soluble/water-insoluble fraction (EA-F3), and a water insoluble solid fraction after enzymatic hydrolysis (EA-F5).



Figure 2.1. Extractive ammonia process lignin extraction scheme using 6:1 ammonia-to-biomass ratio and extraction using solvents. Percent lignin in each fraction and molecular weight data reported based on data from da Costa Sousa et al.⁸

Two different copper-catalyzed alkaline hydrogen peroxide (Cu-AHP) lignin streams prepared from hybrid poplar based on the methods outlined by Bhalla et al. were obtained from Dr. Eric Hegg and Dr. David Hodge at MSU (Figure 2.2).²³ Both fractions were alkaline preextracted Cu-AHP lignins but Cu-AHP-DI was washed with DI water after extraction to remove any residual sugars from the extraction process. These lignin fractions were further characterized using elemental analysis, bomb calorimetry, thermogravimetric analysis, and py-GC/MS.





Elemental Analysis and Bomb Calorimetry

Elemental analysis of all lignin fractions was performed at Atlantic Microlabs (Norcross, GA). Carbon, hydrogen, nitrogen and sulfur contents were reported, while oxygen content was determined by difference. Bomb calorimetry was used to determine the higher heating value (HHV) of the six different lignin streams using a Parr Plain Jacket Oxygen Bomb Calorimeter (Parr Instruments Co., Moline, IL). Samples of about 110 mg of each fraction were mixed with 10–14 mg of dodecane and combusted to determine the HHV.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) was conducted to study the thermal degradation properties of the different lignin fractions from both EA and AHP methods. TGA was performed using a Mettler Toledo Thermogravimetric Analyzer (Mettler Toledo, Columbus, OH). Two replicates of 8–10 mgs of each sample were introduced into the TGA using ceramic crucibles. The analysis was performed in an oxygen-free environment under nitrogen (20 ml/min). Initially the temperature was held at 30 °C for 10 mins and then increased from 30 °C to 104 °C at a rate of 10 K/min and held at 104 °C for 10 mins to remove moisture from the samples. Finally, the temperature was increased from 104 °C to 800 °C at 10 K/min and purged with nitrogen for 10 minutes at the end of each run.

Pyrolysis GC/MS

Pyrolysis GC/MS was performed to determine the products that can be expected from pyrolysis of the different lignin fractions. A CDS Pyroprobe 5250 (CDC Analytical Inc. Oxford, PA) coupled with a Shimadzu QP 5050A GC/MS (Shimadzu Corp. Columbia, MD) was used to pyrolyze about a milligram of each lignin sample. The pyroprobe temperature was set to 600 °C for 10 s,

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while the transfer line temperature and the GC port temperature were both set at 280 °C. The GC oven temperature was programmed to increase the oven temperature at a ramp rate of 8 °C/min from 40 °C to 270 °C. Peaks were identified based on the NIST (National Institutes of Standards and Technology) library and the relative abundance (individual peak relative to the total combined area of the major peaks) was reported to show significant peaks. Response factors for each compound were not computed in this analysis, thus the data are only qualitative.

Results and Discussion

Elemental Content and Higher Heating Values of EA and AHP Lignin Streams

Characterization of EA and AHP lignin streams proceeded with the aim of understanding key attributes of these unique feedstocks. High carbon atom and energy efficiencies are two of the twelve principles of green chemistry.²⁵ Elemental analysis measures carbon, hydrogen, oxygen and nitrogen contents, which are needed for closing carbon atom balances and for estimating heating value. Oxygen content, not directly measured by traditional elemental analysis, but typically calculated by difference, affects the higher heating value of each lignin stream. Oxygen from the original feed material is retained in the pyrolysis bio-oil and distributed in more than 200 bio-oil compounds. Oxygen contents from raw biomass bio-oils can be quite high, in the range of 35–60% by mass .²⁶⁻²⁹ The high oxygen content of bio-oil results in low heating value, high corrosiveness, and high reactivity during storage compared to conventional crude oils.²⁸ High oxygen content also contributes to increased polarity of bio-oil which affects its miscibility with non-polar petroleum fuels making fuel blending difficult.²⁸

The elemental analysis of the different lignin streams from EA and AHP processes revealed that the EA-F3 fraction has the highest carbon content (66 wt.%) and the lowest oxygen content

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(23 wt.%) among the EA and AHP lignins (Figure 2.3). It also had the lowest nitrogen content compared to the other EA fractions. When comparing the Cu-AHP and Cu-AHP-DI lignins, Cu-AHP-DI has higher carbon content (56 wt.%) and lower oxygen content (38 wt.%) than Cu-AHP (C=48 wt.%, O = 46 wt.%). Both AHP fractions do not have significant nitrogen contents when compared to the EA fractions. The EA fractions' nitrogen content might be residual from the ammonia in the system, corn stover protein degradation, or ammonolysis reactions in plant cell walls resulting in such compounds as acetamide.⁸ Ultimately the presence of nitrogen in these lignins is not desirable as it might contribute to NO_x formation during combustion.⁸ In this regard, the less than 1% nitrogen content of both AHP lignins is favorable and is more consistent with commercially produced lignins (Figure 2.3).⁸ Attributed to its low oxygen content, EA-F3 has the highest HHV (30 MJ/kg), while all other EA and AHP fractions are around 22 MJ/kg. Because of high carbon content, low oxygen content, and high HHV, the EA-F3 fraction has the most desirable fuel properties and should thus be selected for fuel production. Note, direct comparison of the EA and AHP lignins was not performed as the biomass sources are different for the two processes.8

Additionally, fluidized bed reactor trials were conducted using the EA-F5 fraction to make a viscous bio-oil/tar. Several fractions of the bio-oil were recovered from the reactor. The yield was about 48% and included a highly viscous, sticky tar mixed with a watery fraction. The two phases were completely separated and mixing by mechanical agitation was not successful. The tar was difficult to remove from the electrostatic precipitator (ESP), so methanol was refluxed using the ESP as a reverse condenser to form a bio-oil/methanol mixture. The higher heating value for the EA-F5-tar fraction was 21.32 MJ/kg, which is very close to the HHV of the feed material (EA-F5

lignin). HHV of the watery bio-oil could not be determined due difficulty in combusting it attributed to its highwater content. Elemental analysis of both the tar and the liquid bio-oil where conducted. Both the tar and the liquid fraction contained some nitrogen. The tar fraction was rich in carbon while the liquid fraction was rich in oxygen (possibly from the water). Similar findings have been reported for the pyrolysis of Kraft lignin, where the water soluble fraction of the bio-oil was 80% water, while the water-insoluble fraction was rich in aromatic carbons.^{30, 31} Further analysis of this bio-oil/bio-tar mixture is essential to determine the potential for larger scale pyrolysis of lignins. Future work in this area should compare the pyrolysis of different lignin streams and optimize the pyrolysis process for EA and AHP lignin streams. Further bench-trials of these bio-oil/tar fractions can help inform the large-scale potential lignin bio-oil ECH.



Figure 2.3. Elemental analysis and higher heating values of EA (F0, F1, F3 and F5), Cu-AHP and Cu-AHP-DI lignin fractions obtained from the Dale research group and the Hegg/Hodge research groups respectively and EA-F5 bio-oil and tar (arrows indicate the relatively high nitrogen content of the EA fractions compared to the AHP lignin streams, the boxes indicate the two best feed materials based on carbon and oxygen content and higher heating values).

Thermogravimetric Analysis of EA and AHP Lignin Streams

TGA for all lignin streams reveals the major thermal events (inflection points) that occur when the different samples are heated. However, direct application of these results for scaling pyrolysis is limited as the heating rates of TGA (10 °C/min) are much lower than those of a fast pyrolysis reactor, which can reach to 300–1,000 °C/min.³² Degradation products can also differ when compared to fast pyrolysis products. Even so, coupling TGA with GC/MS would provide useful information regarding the pyrolysis vapor composition;³³ this task is the subject of future research. In this study, TGA is still useful for identifying the major thermal events that occur during heat treatment, as different samples, or pretreatment streams, may behave differently when heated. The three major biomass components have different zones of thermal degradation. Cellulose and hemicellulose, which are polymers of simple sugars, tend to degrade at lower temperatures (220–315 °C and 315–400 °C respectively) than lignin, which is a more complex network of branched aromatic rings that degrade later and over a larger temperature range (200–600 °C).^{8, 34}

In this study, TGA revealed that significant mass loss (not related to moisture loss) for all the lignin streams occurred between 100–500 °C. For all streams (EA and AHP), 60–70% of the mass was lost by the time the temperature reached 600 °C with around 35% char remaining at 740 °C. (Figure 2.4). The onset temperature (initial decomposition temperature) of each sample, which can indicate the thermal stability of the lignin sample is reported in Table 2.1. Early onset temperature can mean that the sample is less resistant to thermal degradation. This could indicate the presence of carbohydrates that degrade at relatively lower temperatures and release volatiles such as CO, CO₂, and CH₄.³⁵

As seen in Table 2.1, the onset temperature for EA-F0 was 154 °C, compared to an average onset temperature of 280 °C for the other fractions (EA-F1, EA-F3 and EA-F5). Furthermore, this fraction had lost 14% of its mass by 100 °C compared to only about 6% for the other fractions. By the time it reached DTG_{max} (the maximum value on differential thermogravimetric curve) at around 287 °C, it had lost close to 50% of its mass compared to only about 20% mass loss for the other fractions. This indicates the thermal instability of the EA-F0 fraction compared to the other EA fractions. EA-F0 is the ammonia-soluble fraction of corn stover, which contains 44% of the lignin and is further fractionated into the F1-F4 fractions.⁸ NMR analysis of this fraction by da Costa et al. indicated the presence of polysaccharides and other compounds solubilized in ammonia that might have degraded around 188 °C and 291°C resulting in two major thermal events around these temperatures.⁸

Lignin Type	% Lignin	Onset (°C)	Endset (°C)	DTG _{max} Temperature (°C)	% Left at DTG _{max}	% Residue at 740 °C
Cu-AHP	-	238	418	242/367	81/58	35
Cu-AHP-DI	-	246	430	287/362	78/56	29
EA-F1	69	276	402	348	63	38
EA-F3	92	276	418	337	67	34
EA-F5	43	286	405	357	59	33
EA-F0	-	152	345	188/287	75/54	27

Table 2.1. TGA for EA and AHP lignin fractions indicating key thermal events upon anoxic heating. EA fraction % lignin values obtained from da Costa Sousa et al.⁸

The EA-F1, EA-F3, and EA-F5 fractions all had similar onset temperatures with EA-F5 showing slightly improved resistance to thermal degradation than the other two. EA-F3 had a slightly higher endset temperature than the other two possibly due to its high lignin content that
continues to degrade. EA-F1 and EA-F5, the high molecular weight fractions that contain some carbohydrates (as reported by da Costa Sousa et al.⁸), a narrower DTG curve peak that similar to what is reported in other studies for lignin containing carbohydrates is observed. ³² Due to its high (92%) lignin content, EA-F3 shows decomposition over a broad temperature range between 200 °C and 500 °C. Additionally, EA-F3 has a very small thermal event peak around 250 °C (Figure 2.5). Although mass loss in this region could be attributed to polysaccharide degradation, in this case, the very low amounts of sugars reported for EA-F3 by da Costa Sousa et al.⁸, make it unlikely. Alternatively, this thermal event could be indicative of successive cleavage of various lignin linkages. It is reported that α -O-4 and β -O-4, the weakest linkages in lignin, can be thermally cleaved at 200–250 °C while carbon-carbon linkages (β -1, β -5, and 5-5) are more resistant to thermal cracking and degrade at higher temperatures.³⁶⁻³⁸ According to the NMR results by da Costa Sousa et al.⁸, EA-F3 contains high amounts of intact β -o-4 linkages that could be degrading around 250 °C.

As observed in Figure 2.5, both Cu-AHP and Cu-AHP-DI have two major inflection points. The first inflection point occurred in the 220–315 °C range, likely revealing hemicellulose degradation (from the 2.5–3.5% xylan present in these lignins), while the second occurs around 315–400 °C, which probably results from cellulose degradation. Furthermore, mass loss above 350 °C corresponds to lignin degradation. Of the fractions analyzed, EA-F3 and the two Cu-AHP samples degrade over a wide range of temperatures which is indicative of lignin degradation.



Figure 2.4. Thermogravimetric (TGA) curves indicating the mass as function of sample temperature for EA and AHP lignin fractions.



Figure 2.5. The first derivative of the TGA curves (DTG) of EA and AHP lignins indicating mass loss as a function of sample temperature. These DTG curves shows the major thermal events (inflection points) where maximum mass loss occurred for each sample.

Pyrolysis GC/MS Analysis of EA and AHP Lignin Streams

All lignin samples were also subjected to py-GC/MS analysis to determine the various S, G, and H lignin-derived monomers present in each fraction based on methods found in the literature.^{5, 39} For the Cu-AHP samples, the lignin stream that was not washed with DI water had a furfural peak (Figure 2.6), which is a product of carbohydrate pyrolysis and indicates that the extra washing step probably enhances carbohydrate removal. The EA-F1 fraction had a large acetamide peak along with other nitrogen compounds such as pyrazine and pyrrole that are possibly remnants of the ammonia from the EA process (Figure 2.7). As confirmed by elemental analysis, the EA fractions all contained nitrogen that likely undergo thermal transformations and result in such products (acetamide, pyrrole and pyrazine) during pyrolysis.

The distribution of different monomers found in the pyrolysis products of these lignin streams and their relative abundances are displayed in Figure 2.8. Phenol, guaiacol, syringol, 4ethylguaiacol, creosol, methoxyeugenol, 4-vinylguaiacol, and isoeugenol are lignin degradation products for all the lignin fractions, while *p*-cresol, 4-vinylphenol and 3-ethylphenol were only products from the EA lignin fractions. Vanillin and syringaldehyde only appear as a product of Cu-AHP pretreated poplar. This is consistent with the pyrolysis of hardwoods reported by Saiz-Jimenez et al. where guaiacyl and syringyl derivatives such as coniferyl alcohol and sinapyl alcohols were observed.⁴⁰ For corn stover pyrolysis, similar to what is observed in the EA fractions, 4-vinylphenol, syringol, and 4-vinylguaiacol were the major products with yields ranging between 1-4%, while phenol, guaiacol, creosol, 4-ethylguaiacol were also observed.³³ The py-GC/MS data is informative of what kind of monomers can be expected from the degradation of lignin. This information was used to formulate a list of monomers for further upgrading using electrocatalytic hydrogenation (ECH).



Figure 2.6. Major products of py-GC/MS of Cu-A HP and Cu-AHP-DI lignins at 600 °C for 10 s with major peaks confirmed using NIST library.



Figure 2.7. Major products of py-GC/MS of Cu-A HP and Cu-AHP-DI lignins at 600 °C for 10 s with major peaks confirmed using NIST library.



Figure 2.8. Relative abundance of relevant monomer products of pyrolysis of EA and AHP lignins plotted by peak area (response factors were not considered).

Conclusion

In this study six lignin streams extracted from EA and Cu-AHP process were characterized to understand their potential as feed material for pyrolysis and electrocatalytic upgrading. Based on elemental analysis it was found that the EA-F3 fraction had the highest carbon content, lowest oxygen content and the highest higher heating value of the EA and the Cu-AHP lignins. The EA lignins all exhibited significant levels of nitrogen, which will require abatement to avoid NOx formation during combustion. For TGA analysis, it was observed that all fractions degrade over a large temperature range (100–600 °C) as is expected for lignins. Close to 60% of the mass for these samples was lost by 500–600 °C while some char was recovered. Finally, analytical pyrolysis provided the list of monomers that are products from these lignin streams, which are candidates for electrocatalytic upgrading. REFERENCES

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Chapter 3 : Electrocatalytic Hydrogenation and Deoxygenation of Model Monomers Derived from Pyrolysis of Lignin Extracted from Pretreated Biomass

Abstract

Pretreatment enhances the effectiveness of enzymatic hydrolysis of carbohydrate fractions of plant biomass and remove lignin which often contributed to biomass recalcitrance. Extractive ammonia (EA) pretreatment and alkaline hydrogen peroxide process (AHP) offer a way to extract this lignin for further valorization. One approach to valorizing these EA and AHP lignin streams is via fast pyrolysis to create a lignin-derived bio-oil that is rich in phenolics. Fast pyrolysis involves rapid heating (400–600 °C) of the feedstock without oxygen to produce bio-oil, biochar and combustible gas. Electrocatalytic hydrogenation (ECH), preferably using electricity from wind and solar sources can be employed to upgrade lignin-derived bio-oil. In this study, model compounds that represent lignin pyrolysis products were subjected to ECH under mild conditions using ruthenium on activated carbon as a catalytic cathode. To date, several such compounds have been successfully reduced to more stable forms. For example, phenol, alkyl-substituted phenols, guaiacol, alkyl-substituted guaiacols, syringol, vanillin and syringaldehyde have been hydrogenated and deoxygenated. By integrating biomass pretreatment with thermochemical depolymerization and electrochemical upgrading, lignin (a major biorefinery byproduct) can be valorized to fuels and valuable chemical products.

Introduction

To address concerns of climate change caused by human fossil fuel consumption, several strategies have been proposed and implemented for the production of both bioenergy and biobased chemicals from biomass.¹ On the energy front, although there have been advancements in the deconstruction of biomass to produce liquid fuels from polysaccharides and triglycerides (e.g. ethanol and biodiesel), production of transportation fuel intermediates from lignin-derived sources is not well advanced, owing, in part, to challenges in lignin depolymerization.² As lignin is one of the major components of biomass (up to 30 wt.%) and is the only large source of renewable aromatic compounds, valorizing lignin is an essential component of displacing fossil fuels with renewable fuels.² While recent pretreatment methods are adept at fractionating biomass to isolate lignin, the polymeric nature of this product requires further deconstruction. Thermochemical conversion processes such as pyrolysis provide a way of effectively depolymerizing biomass, including lignin, to produce bio-oil (liquid), biochar(solid) and combustible gas.^{3, 4} Though bio-oil is a potential liquid fuel intermediate, in its raw form it is corrosive, highly oxygenated, and reactively unstable during storage, all of which are major barriers to the adoption of pyrolysis systems.⁵ Catalytic upgrading via hydrogenation and deoxygenation is needed to stabilize bio-oil components and produce fuel intermediates and valuable chemicals.6

Catalytic hydroprocessing to upgrade pyrolysis products has been studied extensively and is used for the hydrogenation and hydrodeoxygenation of lignin-derived model compounds and pyrolysis oils.⁷ Catalytic studies have been performed on lignin-derived compounds such as phenol,⁸⁻¹¹ guaiacol,^{12, 13} cresols,¹³⁻¹⁵ pyrolysis oil¹⁶⁻¹⁸ and many others. The main challenges of

catalytic hydroprocessing include the need for high temperatures, the need for pressurized hydrogen, and the formation of coke which encapsulates and deactivates catalysts.^{19, 20} Attempts to reduce the operating severity during hydroprocessing are met with lower observed catalyst activity.²¹ These challenges can increase capital costs, operating costs, and energy demands. In contrast, electrocatalytic hydrogenation and deoxygenation (ECH) of organic substrates can be performed at mild conditions, e.g. room temperature and atmospheric pressure. ECH works by producing the hydrogen ions needed for hydrogenation *in situ*, which helps avoid hydrogen gas solubility and mass transfer issues in aqueous systems.²² The low temperatures needed for ECH avoid catalyst deactivation by coke formation, potentially reducing the costs associated with catalyst purchase and recycle.^{22, 23} Furthermore, the applied voltage is a much more sensitive parameter than is temperature for controlling catalyst activity, reaction rate, and product selectivity.²⁴ Controlling product formation by adjusting the voltage expands the range of possible product slates, without the undesirable side reactions associated with hydroprocessing.

To date, ECH has been explored as a hydrogenation and deoxygenation method for a variety of organic substrates using different electrocatalysts. Some examples include, phenol,²⁵⁻²⁹ guaiacol,^{28,29} syringol,²⁸ furanic compounds,³⁰⁻³⁴ polycyclic aromatic compounds,³⁵ model dimers^{22,36,37} and bio-oil.³⁸ One drawback of ECH is the low faradaic efficiency for reducing organic substrates as a result of unwanted hydrogen gas production on the catalytic cathode surface. Although molecular hydrogen has some value, this reaction competes with the substrate reduction reaction. Hydrogen formed directly on the catalyst surface hydrogenates the adsorbed organic species, which then desorbs into the electrolyte solution.³⁹ The hydrogen gas produced via Tafel or Heyrovsky reactions usually does not react with the organic substrate and is instead

evolved from the cathode.^{22, 36, 40, 41} To counteract undesirable hydrogen evolution, catalysts that are effective at hydrogenating organic molecules but are not as effective at hydrogen production should be examined as electrocatalysts, an approach in contrast with desirable catalysts for fuels cells. Ruthenium is one such catalyst that is known to be suited for the selective hydrogenation of both aromatic rings and carbonyl groups in the vicinity of conjugated or isolated double bonds.⁴² It is also reported to be amongst the least active metals for hydrogen evolution.⁴³ Furthermore, ruthenium dispersed on carbon can capably reduce aromatic compounds as seen from previous ECH experiments.^{28,43} Li et al. demonstrated the effectiveness of ruthenium loaded on activated carbon cloth (Ru/ACC) to transform model lignin monomers from pyrolysis such as phenol, guaiacol, and syringol to cyclohexanol.²⁸ Additionally, they examined how differing ruthenium salt precursors, ruthenium loadings, temperatures, and current densities affected guaiacol conversion and faradaic efficiency. However, these studies were performed on a limited subset of lignin-derived monomers while only using one starting concentration, which fails to capture the impact of substrate concentration on faradaic efficiency. What is needed is a comprehensive investigation of model compounds that represent products in lignin-derived biooils. This can further help in evaluating the variety of lignin monomers that can be reduced and the extent to which they can be upgraded. Furthermore, a better understanding of how different functional groups and their positions affect the formation of products can be useful in understanding how these products can behave during electrocatalytic upgrading of real bio-oil mixtures. Such studies could additionally bridge the knowledge gap that exists from not having adequate mass, energy, and performance data to complete technoeconomic models.

This investigation expands on the work by Li et al. to advance an understanding of how lignin is valorized by a sequence of pyrolysis and ECH as a means of conversion and upgrading. To this end, lignin extracted from two different biomass feedstocks is subjected to bench scale pyrolysis to identify bio-oil components that require upgrading. Eighteen model aromatic compounds were selected based on this identification for subsequent ECH to understand and optimize how each compound is transformed. To close the knowledge gaps that hinder technology adoption, several features of lignin monomer ECH were studied, including the effects of varying functional group positions and sizes. Functional group types, bulkiness and position, can potentially impact product conversion and selectivity upon ECH. The effect of substrate concentration on faradaic efficiency is also included to improve modest cell efficiency and inform energy balances and future economic analysis. Finally, the last section of this study includes the investigation of an electrochemical method to deposit ruthenium on activated carbon along with catalyst reusability studies. This is done with an aim of bypassing the high temperature and pressure catalyst reduction process. Success of this process will result in decreasing energy inputs into the catalyst preparation process and the ECH process as a whole.

Experimental Methods

Bench Scale Pyrolysis of Lignin Fractions

Lignins from two different feedstocks, corn stover and poplar, were isolated using two different fractionation methods. Extractive ammonia processing (EA) was used to obtain corn stover lignin as described by da Costa Sousa et al. in Prof Bruce Dale's lab.⁴⁴ Briefly, corn stover was solubilized in 6:1 ammonia-to-biomass ratio at 120 °C and further extracted by solubilizing it in water and ethanol, resulting in four different lignin fractions. These include a mixture of corn

stover and liquid ammonia (EA-F0), an ethanol-insoluble/water-insoluble fraction (EA-F1), an ethanol-soluble/water-insoluble fraction (EA-F3), and a water insoluble solid fraction (EA-F5). Poplar lignin was obtained using copper-catalyzed alkaline hydrogen peroxide (Cu-AHP) fractionation. This lignin was prepared in Prof. Eric Hegg's lab using the methods outlined by Bhalla et al.⁴⁵ at Michigan State University. Accordingly, the poplar was pre-extracted in sodium hydroxide and pretreated with copper sulfate and bipyridine and the lignin-rich liquor extracted. After extraction, this lignin was then washed with deionized water at room temperature, to remove any residual sugars that would lead to furans and anhydrosugars upon pyrolysis.

Pyrolysis gas chromatography mass spectrometry (py-GC/MS) was performed to determine the products that can be expected upon the heat treatment of the different lignin fractions. A CDS pyroprobe 5250 (CDC Analytical Inc. Oxford, PA) coupled with a Shimadzu QP 5050A GC/MS (Shimadzu Corp. Columbia, MD) was used to pyrolyze about a milligram of each lignin sample. A Restek RTX-1701 column (Restek, Bellefonte, PA) of 60 m length, 0.25 mm diameter and 0.25 µm thickness was used in the GC. Temperature in the pyroprobe was set at 600 °C for 10 seconds, while the transfer line temperature and the GC port temperature were both set at 280 °C. The GC oven temperature was programed to increase from 40 °C to 270 °C at a ramp rate of 8 °C/min. Eluting analytes were identified using the NIST library and the relative abundances (individual peak relative to the total combined area of the major peaks) were reported to show significant peaks.

Catalyst Preparation: High Temperature and Pressure Parr Reactor Reduced Catalyst (Ru/ACC)

Zorflex[®] activated carbon cloth (ACC) (Zorflex[®] ACC FM100) obtained from Calgon Carbon Corporation (Pittsburgh, PA) was used to support hexaammineruthenium(III)chloride

(Ru(NH₃)₆Cl₃) which was obtained from Alfa Aesar (Tewksbury, MA). As described by Li et al.,²⁸ ACC was cut into 1.5 x 3.0 cm pieces, agitated overnight in deionized water, oven dried at 150 °C and soaked in a ruthenium salt solution (Ru(NH₃)₆Cl₃ (1.01 g), dissolved in ammonium hydroxide (1.96 ml) and water (13.02 ml).) to saturate the pores and Kimwipes[®] were then used to remove excess ruthenium solution from the cloth . The Ru/ACC catalyst was then dried overnight at room temperature, further dried under vacuum for 24 h, then reduced with molecular hydrogen at 310 °C and 500 psi for 12 h in a Parr Reactor (model 452HC, Parr Instrument Company, Moline, IL).

Catalyst Preparation: Electrochemically Deposited Catalyst (EC-Ru/ACC)

Similar to the Ru/ACC described in the previous section, Zorflex[®] activated carbon ACC was cut into 1.5 x 3.0 cm pieces, agitated overnight in deionized water, oven dried at 150 °C and prepared using incipient wetness (IW) method described by Li et al. ²⁸ by soaking in a ruthenium salt solution to saturate the pores and then removing excess ruthenium solution using Kimwipes[®]. The Ru/ACC catalyst was then dried overnight at room temperature, further dried under vacuum for 24 h. Based on the methods described by Bhatia et al.⁴⁶, it was then reduced in the electrochemical cell described in the next section at 150 mA for 1 h before being used for the ECH of the model compound.

Alternatively, three different ruthenium loadings (0.025 g, 0.05 g and 0.1 g) were also investigated and compared to the incipient wetness soaking method described in the previous paragraph. The washed and dried activated carbon cloth pieces were soaked and allowed to stand in the ruthenium solution for 4 h and then dried overnight under nitrogen to evaporate the liquid while leaving the ruthenium on the carbon cloth. This was followed by electrochemical reduction at 150 mA for 1 h before use for the ECH of the model compound.

Electrocatalysis Setup

Model compounds catechol, anisole, phenol, guaiacol, 3-methoxyphenol, 4-methoxyphenol, syringol, 1,3-dimethoxybenzene, p-cresol, o-cresol, m-cresol, creosol, vanillin, syringaldehyde and eugenol were obtained from Sigma Aldrich (St Louis, MO). 4-ethylphenol and 4-propylphenol were obtained from TCI America (Portland, OR) while 4-ethylguaiacol and 4-propylguaiacol were obtained from Alfa Aesar (Haverhill, MA). A two-chambered electrochemical glass H-cell (fabricated by the Department of Chemistry Glassblowing Facility at Michigan State University (East Lansing, MI) was used for conducting the experiments. The chambers were separated using a Nafion[®] 117 membrane obtained from Dupont (Wilmington, DE). 30 ml of 0.2 M HCl solution was used as cathode chamber electrolyte and 30 ml of 0.2 M phosphate buffer was used as the anode electrolyte. Ru/ACC was used as the cathode and platinum wire obtained from Alfa Aesar was used as the anode (Figure 3.1). An Instek GPR-11H30D (Instek America Corp., Montclair, CA) power supply provided constant electrical current. To maintain constant temperature of 80 °C the entire cell was placed in a heated water bath for all experiments. After the cell setup was completed, a 10-min pre-electrolysis step was performed on the catalyst at 80 mA before adding the substrate.

After pre-electrolysis, depending on the experiment, 20 mM of the desired substrate (dissolved in 1 ml isopropyl alcohol to increase solubility of organic substrates) was added to the cathode chamber and each experiment was run at 100 mA. For the mixture study, 20 mM solution of both guaiacol and *p*-cresol in isopropanol was prepared and used in the ECH reaction. For the substrate concentration studies, 5, 10, 20, 40, and 60 mM solutions of guaiacol were used. For testing the performance of the electrochemically reduced catalyst, 20 mM guaiacol

solution was added to the cathode after the 1 h, 150 mA, catalyst deposition step. Reaction duration was determined based on the number of electrons needed for a complete conversion of each substrate assuming 20% faradaic efficiency. The current density based on the geometric surface area was calculated to be approximately 22.22 mA/cm². Samples were collected at the beginning and the end of each experiment for further analysis.



Figure 3.1. Electrocatalytic Hydrogenation of two-chambered H-cell depicting the flow of protons and the reduction of guaiacol on ruthenium on activated carbon as a cathode and platinum wire as the anode.

Catalyst Reusability and Desorption

High Temperature and Pressure Parr Reactor Reduced Catalyst (Ru/ACC)

Repeated studies with guaiacol as a substrate were used to assess catalyst reusability using the ECH system. After the first experiment, the catalyst was stirred in 30 ml methanol dichloromethane (DCM) and a 1 ml sample of the stirred methanol or DCM was obtained for analysis. The cloth was then placed in a 20 ml vial and dried under vacuum for 24 h. This methanol and DCM washing procedure was evaluated for eight consecutive trials. The difference between the two solvents used for washing the catalyst was compared.

Electrochemically Deposited Catalyst (EC-Ru/ACC)

Repeated studies with guaiacol as a substrate were used to assess catalyst reusability using the ECH system. After the first experiment, the catalyst was stirred in 5 ml DCM and a 1 ml sample of the DCM solution was obtained for analysis. The cloth was then placed in a 20 ml vial and dried under nitrogen for 24 h and used for two consecutive trials.

Catalyst Characterization

JEOL 6400LV (tungsten hairpin emitter) scanning electron microscope (JOEL Ltd., Tokyo, Japan) was used to image the surface morphology of ruthenium particles on the carbon fiber support.²⁸ Each sample was vacuum dried overnight and mounted on the stage using carbon tape and analyzed using secondary electron and back scattered imaging. Energy dispersive X-Ray spectroscopy (EDX) was performed to characterize surface elemental content using an Oxford Instrument Aztec system software version 3.1 (Oxford Instruments, High Wycomb, Bucks, England) with a 20 mm² Silicone Drift Detector (JEOL 6400LV SEM) and an ultra-thin window.

Catalyst ruthenium content, and ruthenium leaching into the electrolyte solution was measured using a Varian 710-ES inductively coupled plasma optical emission spectrometer (ICP-OES) according to the methods by described by Li et. al.²⁸ The catalyst samples were prepared by digestion in aqua regia for 4 h in a water bath at 100 °C, filtration, and dilution with DI water. To measure ruthenium leaching, the electrolyte solution was dried under nitrogen, the residue was digested in 4% aqua regia for 4 h and filtered. The ruthenium content in the samples was measured at a wavelength of 245.554 nm and quantified using RuCl₃ standards prepared in 4% aqua regia, with concentrations of 0.08 ppm, 0.4 ppm, 2 ppm, 10 ppm, and 50 ppm.

Sample Extraction and Analysis

The samples collected at the beginning and end of each experiment were saturated with NaCl, acidified to pH 1.0 with concentrated HCl, and extracted in DCM. The catalyst was sonicated in 5 ml DCM to collect the organic products adsorbed to the cloth. All samples were analyzed using a Shimadzu QP-5050A GC/MS (Shimadzu Corp, Columbia, MD). Standards in DCM were used for identifying products by retention time and to construct a four-point calibration curve. This curve was used to determine product yields and calculate faradaic efficiency.

Relevant Calculations

Yield _A = (Moles of A) / (Initial moles of reactant)

Selectivity $_{A}$ = (Moles of A) / (Moles of total products)

Conversion = (Moles of reactant consumed) / (Initial moles of reactants)

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

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

Results and Discussion

Pyrolysis of Lignin Fractions

Lignin and lignin streams obtained from EA processing of corn stover and Cu-AHP extraction of poplar were subjected to analytical pyrolysis (py-GC/MS). The resulting py-GC/MS data identified the monomers that were formed upon the degradation of lignin from herbaceous and woody biomass sources. All lignin samples (EA-F0, EA-F1, EA-F3, EA-F5, Cu-AHP, and Cu-AHP-DI) were subjected to py-GC/MS analysis using established methods,^{47, 48} and the major product peak areas are displayed as relative abundances in Figure 3.2. Phenol, guaiacol, syringol, 4ethylguaiacol, creosol, methoxyeugenol, 4-vinylguaiacol, and isoeugenol are lignin degradation products for all the lignin fractions, while *p*-cresol, 4-vinylphenol and 3-ethylphenol were only products from the EA lignin fractions. Vanillin and syringaldehyde only appear as a product of Cu-AHP pretreated poplar. This is consistent with the literature for lignin pyrolysis. During pyrolysis of hardwoods, similar to the Cu-AHP lignins, Saiz-Jimenez et al. reported that guaiacyl and syringyl derivatives such as coniferyl alcohol and sinapyl alcohols were observed.⁴⁹ For corn stover pyrolysis, similar to what is observed in the EA fractions, 4-vinylphenol, syringol, and 4vinylguaiacol were the major products with yields ranging between 1–4%, while phenol, guaiacol, creosol, 4-ethylguaiacol were also observed.⁵⁰ Based on these results, lignin pyrolysis monomers from two extraction methods and two biomass sources were investigated for quantification of ECH performance.

Based on results obtained from py-GC/MS data of the EA and Cu-AHP lignins studied, the selected monomers were subjected to ECH using Ru/ACC. Monomers included are: phenol, guaiacol, *p*-cresol, creosol, 4-ethylguaiacol, 4-propylphenol, 4-propylguaiacol, eugenol, syringol, vanillin, syringaldehyde. 4-Vinylphenol and 4-vinylguaiacol, though abundant pyrolysis products, are expensive and were not included in this study. Instead, eugenol was used as a surrogate to study the ECH of allyl-substituted guaiacols. Though not observed in the py-GC/MS data, anisole, catechol, 3-methoxyanisole and 4-proplylanisole were also investigated to understand the effect of the functionalities present in these compounds on conversion. Overall, these compounds represent a range of lignin pyrolysis products with varying functional groups at varying positions.



Figure 3.2. Relative abundances of pyrolysis products from EA and AHP lignins; no response factor correction was used to quantify individual peaks.

Study of Different Functional Groups

Monomers obtained from pyrolysis of lignin often exhibit varying oxygenated functional groups such as hydroxyl, methoxy, and carbonyl groups, in addition to alkyl and allyl functionalities. These groups can often be located at varying positions on the aromatic ring. In previous studies it has been reported that different parameters such as catalyst type, substrate type, pH, and reaction conditions can affect the conversion and selectivity of phenolic model compounds.⁵¹ The effect of temperature, electrolyte type and current density on ECH of guaiacol using Ru/ACC is already reported.²⁸ However, type, number, and bulkiness of substituents, and presence of hydroxyl groups can also affect ECH of aromatic compounds.⁵¹ To understand how these functionalities behave during ECH using Ru/ACC, compounds with hydroxyl groups (phenol and catechol), methoxy groups (anisole and 3-methoxyanisole), methoxy and hydroxyl groups (guaiacol and syringol), alkyl and hydroxyl groups (p-cresol, 4-ethylphenol, 4-propylphenol), alkyl

or allyl and methoxy groups (4-methylguaiacol, 4-ethylguaiacol, 4-propylguaiacol and eugenol), and finally benzaldehydes (vanillin and syringaldehyde) were all examined.

Ruthenium catalysts have been shown to be capable of hydrogenation of aromatic rings.⁴² Therefore, regardless of the functional groups attached to the aromatic ring, hydrogenation products from ring saturation were observed for all substrates with the exception of syringaldehyde. Additionally, for the methoxy-substituted rings (guaiacol, 3-methoxyanisole, 4-propylanisole, eugenol, alkyl guaiacols, and vanillin) both hydrogenation products (resulting from ring saturation) and demethoxylation products were observed, with the exception of anisole for which no demethoxylation products (benzene or cyclohexane) were recovered (Figure 3.3).

For the compounds with only methoxy groups attached to the aromatic ring, anisole and 3methoxyanisole were investigated. Anisole was mainly converted to methoxycyclohexane with very trace amounts of cyclohexanol (<1%). In this case, it appears that anisole ring saturation dominates with some demethylation and hydrogenation to cyclohexanol observed instead of demethoxylation (Figure 3.3). Similarly, for 3-methoxyanisole, demethylation and hydrogenation to form traces of cyclohexanol (~1%) and ring saturation to form 1,3-dimethoxycyclohexanol was observed (Figure 3.3). Additionally, although complete demethoxylation to cyclohexane was not detected, the cleavage of one of the two methoxy groups and ring saturation formed methoxycyclohexane (Figure 3.3).



Figure 3.3. Reactions conditions and observed products for the ECH of model compounds with varying functional groups. (NQ = catechol conversion was not quantified due to the difficulty in obtaining quantifiable peak area after extraction in DCM).

Curiously, 4-propylanisole was demethoxylated and hydrogenated to form significant amounts of both 1-methoxy-4-propylcyclohexane, 4-propylcyclohexane and traces of 4propylcyclohexanol (Figure 3.4). This indicated that 4-propylanisole undergoes ring saturation similar to anisole and 3-methoxyanisole, but the presence of the propyl chain appears to aid in the demethoxylation as well. It is possible that anisole and 3-methoxyanisole are similarly undergoing complete demethoxylation, but the cyclohexane is not being recovered due to its low boiling point (80.74 °C); the reaction temperature used is around 80 °C. The study of methoxylated aromatic rings in the absence of a hydroxyl group also indicates that when using Ru/ACC, the phenolic hydroxyl group is not necessarily needed to achieve demethoxylation of these substrates. This is contrary to the results of Lam et al. who observed demethoxylation only in the presence hydroxyl groups when using Raney nickel. ²⁹ Furthermore, as observed from 4propylanisole, complete demethoxylation and removal of oxygenated functionalities is possible, which is essential in upgrading bio-oil model compounds to hydrocarbon fuels.



Figure 3.4. Reactions conditions and observed products for the ECH of 4-propylanisole.

When comparing phenol and anisole, anisole is more completely converted >99% vs. 91% as shown in Table 3.1. The same trend, although more pronounced, was observed for 3-methoxyanisole vs. syringol (92% vs. 52%). The presence of the hydroxyl group appears to negatively affect conversion, most likely due to the increased steric hindrance it exerts.⁵¹ After 2 hours, conversion of syringol and 3-methoxyanisole (both compounds with two methoxy groups) was 52% and 92%, respectively, compared to 91% and 99% for guaiacol and anisole (only one methoxy group). As expected, for syringol and 3-methoxyanisole the presence of two methoxy groups reduces their conversion as an extra pair of electrons is needed compared to the ECH of anisole or guaiacol and the increased π system's electron density with increased number of methoxy groups.²⁸ However the syringol conversion is considerably lower than that of the 3-methoxyanisole. Similar to what is observed for anisole vs. phenol, where the presence of the hydroxyl group in phenol reduces its conversion, syringol also likely experiences the hindrance effect imposed by the hydroxyl group while 3-methoxyanisole does not.

Table 3.1. Conversion of different aromatic compounds classified by functional groups and subjected to ECH at 80 °C, 100mA in 0.2 M HCl solution

Functional Group	Substrate	Time (h)	Conversion (mole %)	
Mathawa	Anisole	2	>99	
Methoxy	3-Methoxyanisole	Ζ	92	
Lludrovul	Phenol	2	91	
nyaroxyi	Catechol		-	
Methoxy and	Guaiacol	2	90	
hydroxyl	Syringol	2	52	
Methoxy and alkyl	4-Propylanisole	6	100	
Alkyl and hydroxyl	<i>p</i> -Cresol		87	
	4-Ethylphenol	2	88	
	4-Propylphenol		81	
	Creosol		72	
Alkyl/allyl, hydroxyl and methoxy	4-Ethylguaiacol		59	
	4-Propylguaiacol	2	60	
	Eugenol		100	
Hydroxyl, methoxy	Vanillin	9	81	
and carbonyl	Syringaldehyde	galdehyde 10	85	

The reaction route for 3-methoxyanisole occurs either by the complete hydrogenation of the ring followed by demethoxylation of the one methoxy group or by demethoxylation followed by the ring saturation. From the experiment conducted it is not clear which route is taken but it is possible that the symmetrical nature of 3-methoxyanisole promotes its co-planar interaction with the catalyst surface, which promotes ring saturation to form 1,3-dimethoxycyclohexane. While the second route could be responsible for the formation of methoxycyclohexane via cleavage of one methoxy group to form anisole and its subsequent hydrogenation or demethylation.

From the two-hour and nine-hour experiments of syringol, the observed major products included 2-methoxycyclohexanol, what is believed to be 2,6-dimethoxycyclohexanol, and cyclohexanol (Figure 3.5). Syringol conversion likely follows either the direct hydrogenation route which could then result further in the cleavage of the methoxy group to form 2methoxycyclohexanol and eventually is demethoxylated to cyclohexanol (Route 1). In contrast, the second route can start by formation of guaiacol and either proceeds via the formation of 2methoxycyclohexanol (Route 2a) or the formation of phenol which could further be converted to cyclohexanol (Route 2b). Although no guaiacol, phenol cyclohexanone, or 2methoxycyclohexanone were recovered, it has previously been demonstrated by Li et al. using Ru/ACC prepared by cation exchange method that syringol hydrogenation forms these compounds.²⁸ Furthermore, a control experiment on 2-methoxycyclohexanol did not show any conversion to cyclohexanol, so it is possible that two different routes are being followed. One route forms cyclohexanol via the formation of guaiacol which either forms 2-methoxy cyclohexanol or and phenol (with high conversion rates to cyclohexanol), and another that forms 2,6-dimethoxycyclohexanol and 2-methoxycyclohexanol.

Voltage data collected for anisole, guaiacol and syringol indicates that after the first hour the voltage stabilizes and remains relatively constant (Figure 3.6). Upon further investigation, the recorded pH values from these experiments indicate that while the pH remained less than 3 for the first hour of the experiment, after 360 coulombs of charge was passed through the system the cathodic pH increases to around 12 possibly due to the production of OH⁻ ions.



Figure 3.5. Possible reaction pathways for syringol conversion to cyclohexanol (blue = confirmed compounds, black = observed, grey = not observed).



Figure 3.6. Voltage and pH data for ECH of anisole, guaiacol and syringol in 0.2 M HCl, at 100 mA and 80 $^{\circ}$ C.

With respect to benzaldehydes, vanillin ECH forms vanillyl alcohol (32%) and creosol (6%) (Figure 3.7) after 9 hours of ECH. Very low levels of cyclohexanol, 4-methylcyclohexnaol (*cis* and *trans*) have also been recovered from the catalyst cloth and identified. Catalytic hydrogenation of vanillin has been investigated previously using both homogeneous and heterogeneous ruthenium catalysts and showed similar reaction pathways of conversion to vanillyl alcohol and creosol.⁵²⁻⁵⁴ Syringaldehyde conversion after 10 hours was 85% but interestingly, the only

significant identifiable product peak was 2,6-dimethoxy-4-methylphenol, mostly recovered from the catalyst cloth. Other peaks, although present are difficult to identify as they are dwarfed by the 2,6-dimethoxy-4-methylphenol peak. Similar to what is observed during ECH of guaiacol vs. syringol, it is expected that the extra methoxy group present in syringaldehyde will significantly impede the conversation rate, and after 10 hours, complete hydrogenation and deoxygenation is rather slow in this system compared to vanillin. The observed hydrodeoxygenation, hydrogenation and C-C bond cracking (observed in catalytic hydrogenation processes), however, is a promising result for bio-oil upgrading.





ECH of Alkyl-substituted Phenols and Alkyl- and Allyl-substituted Guaiacols

Catalytic hydrogenation of alkyl-substituted phenols has been investigated by other groups.^{51, 55-58} ECH of alkyl-substituted phenols has been studied using Raney Ni as the catalytic cathode in the presence and absence of surfactants.⁵⁹ It is widely recognized that alkylphenol hydrogenation generally forms a mixture of *cis* and *trans* alkylcyclohexanol and follows one of two routes (Figure 3.8), one via the formation of alkylcyclohexanone and the other by direct hydrogenation to alkylcyclohexanol. Several factors such as catalyst type, substrate structure, and reaction conditions affect the orientation and adsorption of the aromatic substrate to the catalyst surface,

thus altering the reaction pathway for the selective production of one compound versus the other.⁵¹ Neri et al. have suggested that adsorption of the aromatic ring parallel to the catalyst surface facilitates aromatic ring hydrogenation while non-planar adsorption facilitates the formation of a ketone intermediate. ^{59, 60}



Figure 3.8. Reaction pathway for ECH of alkyl-substituted phenols to form alkylcyclohexanols.

In the current study, phenol and alkyl-substituted phenols (*p*-cresol, 4-ethylphenol, and 4propylphenol) were examined to understand the effect of alkyl group size on ECH transformation pathways, conversion, selectivity, and faradaic efficiency. As shown in Figure 3.9a, phenol is directly converted to cyclohexanol, while the alkylphenols proceeded to form alkylcyclohexanols as major products with traces of alkylcyclohexanes (for ethyl- and propyl-substituted phenols). To determine whether the alkylcyclohexane was formed by the hydrogenolysis of the alkylcyclohexanol, ECH of 4-ethylcyclohexanol was conducted. After 2 hours, only traces of 4ethylcyclohexanone (an oxidation product) was formed while most of the 4-ethylcyclohexanol was recovered. It is likely that the oxidized product was formed by direct catalysis in the presence of strong acid (0.2 M HCl electrolyte). This result combined with the observation of trace amounts of toluene during *p*-cresol ECH, suggests that the formation of alkylcyclohexane most likely occurs via the formation of alkyl benzene first followed by ring saturation. Similar hydrogenolysis products (cyclohexane and benzene) have been detected during catalytic hydrogenation of phenols over Ni catalyst.⁵¹

Initially, the alkylphenol experiments were conducted for a duration of 6 hours, and although complete conversion of each substrate was achieved, the alkylcyclohexanol recovery and the mass balance decreased with increasing alkyl chain length (Figure 3.9b). It is suspected that decrease in alkylcyclohexanol yield is related to the increased selectivity towards the formation of alkylcyclohexanes with increasing alkyl chain length. Several attempts to capture these volatile products and improve the mass balance was unsuccessful. Since the faradaic efficiency is calculated based on moles of product recovered, we see a significant decrease in its value as the product recovery decreased with increasing alkyl chain length. Additionally, for a 6-hour experiment, as the substrate concentration in the bulk solution decreases over time, surface coverage of the catalyst active sites decreases. This in turn results in chemisorbed hydrogen reacting to form hydrogen gas via the Tafel and Heyrovsky reactions thus resulting in modest faradaic efficiency.



Figure 3.9. ECH of phenol and alkyl-substituted phenols with varying alkyl group lengths: a). reaction conditions and observed products b). Conversion (mole %), product recovered (mole %), and faradaic efficiency.

To get a better understanding of the effect of alkyl chain length on conversion and faradaic efficiency, the experiments were repeated, this time for a duration of 2 hours. After 2 hours, it was observed that the phenol conversion was only slightly (3-4%) better than the 4-methylphenol and 4-ethylphenol, but about 10% better than that of 4-propylphenol (Table 3.2). Organic chemical hydrophobicity increases with increased length/bulkiness, number of alkyl substituents, and number of hydroxyl groups.^{51, 59} This in turn leads to more difficult and slower conversion rates of substituted phenols compared to phenols.⁵¹ It has previously been demonstrated during ECH of substituted phenols that the presence of bulky groups such as *tert*-butyl or two methyl groups results in decreased conversion and efficiency of the substituted phenols when compared to phenol.⁵⁹ Similarly, in the current study, the results support that the presence of a propyl group results in decreased conversion rate and slightly improved selectivity towards the hydrogenolysis product (propylcyclohexane) compared to the phenol and 4-methylphenol. In regard to the faradaic efficiency, improved efficiency was observed after two hours, confirming the initial claim

that when ran for 6 hours, the depletion of the substrate reduces surface coverage and impacts

the faradaic efficiency.

R	Conversion (mole %)		R		R		Faradaic Efficiency (%)	
	2 h	6h	2 h	6 h	2 h	6h	2h	6h
R = H	91	100	100	100	0	0	49	20
R = Methyl	87	100	100	100	0	0	39	9
R = Ethyl	88	98	98	100	2	-	43	8
R = Propyl	81	100	97	93	3	7	43	6

Table 3.2. Conversion (mole %), product selectivity (mole %) and faradaic efficiency (%) for ECH of 20 mM alkyl-substituted phenols at 80 °C, 100 mA in 0.2 M HCl

For guaiacol and the alkyl- and allyl-substituted guaiacols (creosol, 4-ethylguaiacol, 4propylguaiacol and eugenol), ECH proceeds via hydrogenation of the aromatic ring to form 2methoxycyclohexanol or alkyl-substituted 2-methoxycyclohexanols and via ether cleavage to form cyclohexanol or alkylcyclohexanol (Figure 3.10a). These results are consistent with previous studies of guaiacol.²⁸ Similar to what is observed for alkylphenols, after 7 hours, complete conversion of each starting material was observed but product (alkylcyclohexanol) recovery generally decreased with increasing alkyl group length for the same amount of charge supplied (Figure 3.10b). This results from the shift in selectivity to form the alkyl-substituted 2methoxycyclohexanol. As seen in Table 3.3, after 7 hours, selectivity to cyclohexanol is 57% (for guaiacol but with the addition of a propyl chain on the aromatic ring, the selectivity shifts to favor ring saturation to form 2-methoxy-4-propylcyclohexanol (66%) over the methoxy group cleavage product (34%). For the 2-hour experiments, conversion decreases significantly when comparing guaiacol to the alkyl-substituted guaiacols, indicating that the presence of alkyl group, and to a certain extent its length, has an effect on conversion rate (Table 3.3). Similar to what was observed in the alkylphenol studies, formation of 4-propylcyclohexane was observed during ECH of 4propylguaiacol, although at a much lower yield (less than 1%). The oxygen content of bio-oil contributes to its undesirable properties, so if indeed hydrogenolysis of the hydroxyl group is occurring as observed from alkylphenol and alkylguaiacol ECH, this will be beneficial in bio-oil upgrading and reducing oxygen content of these compounds and parameters that enhance this reaction pathway should be explored further.



Figure 3.10. ECH of guaiacol, methyl, ethyl and propyl-substituted guaiacols and eugenol with a). reaction conditions and observed products b). Conversion (mole %) and product recovery (mole %) (*4-methyl-2-methoxycylohexanol and 4-ethyl-2-methoxycylohexanol recovery was not reported due to difficulty in obtaining pure compounds for quantification using standard curve)

For eugenol its complete conversion to 4-propylguaicol with high selectivity (77%) was observed after 2 hours, indicating that the hydrogenation of the allyl chain double bond is relatively easy (Table 3.4). When allowed to run for 9 h, further reduction of 4-propylguaicol to 2-methoxy-4-propylcyclohexanol and 4-proplycyclohexanol is observed, with selectivity shifted

towards the formation of the former.

Table 3.3. Conversion (mole %), product selectivity (mole %) and faradaic efficiency (%) for ECH of 20 mM alkyl-substituted guaiacols at 80 °C, 100mA in 0.2 M HCl. (dashes represent product selectivity that was not determined due to difficulty obtaining pure compounds for quantification using standard curve)

R	Conversion (mole %)		R		R OH		Faradaic Efficiency (%)	
	2 h	7h	2 h	7h	2 h	7h	2h	7h
R = H	90	100	62	57	38	43	33	20
R = Methyl	72	98	-	-	-	-	-	-
R = Ethyl	59	100	-	-	-	-	-	-
R = Proply*	60	100	36	34	63	66	29	8

Table 3.4. Conversion, product selectivity and faradaic efficiency for ECH of 20 mM Eugenol at 80 °C, 100mA in 0.2 M HCl for 2 and 10 h. 100% conversion to the corresponding products was observed for all experiments.

Starting Material	Pro	Faradaic		
ОН	ОН	ОН	ОН	Efficiency (%)
2 h	77	12	11	3
9 h	0	73	24	16

Effect of Methyl and Methoxy Group Positions

As substituted phenols with alkyl and alkoxy groups on different positions on the aromatic ring are observed in lignin pyrolysis products, a better understanding of how alkyl and alkoxy group position affects ECH is needed. To study the effect of alkyl group positions, ECH was performed on *p*-cresol, *m*-cresol, and *o*-cresol. Each substrate was hydrogenated to its corresponding methylcyclohexanol. As can be seen from Figure 3.11b, no drastic differences in the conversion of these substrates are observed, though *o*-cresol conversion appears to be
slightly improved compared to the *m*-cresol and *p*-cresol. This could be attributed the adsorption properties of these compounds on activated carbon cloth. It is reported in the literature that *o*-cresol shows improved adsorption followed by, *m*-cresol then *p*-cresol. ⁶¹ To study the effect of methoxy group position guaiacol, 3-methoxyphenol and 4-methoxyphenol were subjected to ECH. The conversion and cyclohexanol yield were found to be higher for 2-methoxyphenol compared to the 3 and 4 positions (Figure 3.12b). Similar observations were reported by Lam et al. where the demethoxylation was favored by the proximity of the methoxy group to the hydroxyl group.²⁹



Figure 3.11. ECH of *o*-cresol, *m*-cresol and *p*-cresol with a). reaction conditions and observed products b). conversion (mole %)

ECH of Mixture of Guaiacol and *p*-Cresol

Bio-oil is a mixture of many oxygenated compounds, so understanding how these compounds interact during ECH is important. When in a mixture, guaiacol and *p*-cresol conversions are decreased compared to when they are subjected to ECH separately. After 2 hours of run time, conversion of *p*-cresol and guaiacol are 87% and 90%, respectively, but in the mixture after 4 hours conversion is decreased to 84% and 76%, respectively (Figure 3.13). This could be due to the competitive adsorption of the substrates on the catalyst surface. This experiment was conducted as a preliminary test and further investigation is needed to fully understand the mixture interaction of various model compounds.



Figure 3.12. ECH of 2-methoxyphenol, 3-methoxyphenol, and 4-methoxyphenol with a). reaction conditions and observed products b). conversion (mole %) and cyclohexanol yield (mole %)



Figure 3.13. Conversion and product yield upon ECH of 20 mM guaiacol and 20 mM *p*-cresol separately versus in a mixture. The mixture contained 20 mM *p*-cresol and 20 mM guaiacol in the cathode solution (conversion and product recovery are reported as *p*-Cresol (mix) and guaiacol (mix)).

Substrate Concentration Effect

It has been demonstrated that ruthenium is capable of hydrogenating and to some extent deoxygenating lignin-derived monomers, however, it is apparent that the current efficiency of such transformations is modest.²⁸ This implies that most of the current being used is going

towards producing hydrogen gas. Though a valuable commodity if stored and utilized, decreasing the hydrogen evolution reaction could be beneficial in ensuring that electrical energy is being used efficiently to produce desired products. It is well known that substrate adsorption to the catalyst surface directly impacts ECH efficiency and is the rate limiting step.⁶² Higher substrate concentration means increased surface coverage of the catalyst by the substrate species, which results in increased hydrogenation. In this study, when increasing substrate concentration from 5 mM to 20 mM, there is an increase in the faradaic efficiency. Increasing concentration from 20 mM to 60 mM maintains similar faradaic efficiency this could be a result of saturation of the catalyst surface with substrate species (Figure 3.14).



Figure 3.14. Conversion, product selectivity and faradaic efficiency of ECH of guaiacol using different substrate concentrations (5, 10, 20, 40, and 60 mM) in 0.2 M HCl at 100 mA and 80 °C.

Comparison of Parr Reactor Reduced and Electrochemically Reduced Catalyst for Guaiacol ECH

For the electrodeposition method, to study the effect of different ruthenium loading on conversion, yield, faradaic efficiency and selectivity, ECH was conducted using ACC soaked in 0.025 g, 0.05 g, and 0.1 g ruthenium salt solution and dried under nitrogen. Additionally, activated carbon cloth soaked using incipient wetness method (in a similar manner as the Parr reactor reduced catalyst) was dried under vacuum and investigated. For the electrochemical deposition step, all 4 ruthenium soaked ACC were dipped in the 0.2 M HCl solution and the deposition was achieved at 150 mA for 1 hour without any organic substrate, using the methods reported by Bhatia et al.⁴⁶ Initially when the soaked cloth is dipped in the solution, significant leaching is observed visually (Figure 3.15a). However, after the first five minutes, the color changes to light yellow. After 15 minutes another color change to dark blue is observed (Figure 3.15b) which eventually clears during the 1-hour electrodeposition step. These color changes are likely due to ruthenium's several oxidation states as it gets reduced from its 3⁺ state. After this step, there is a distinct silvery deposition of ruthenium on the carbon cloth surface (Figure 3.16b).



Figure 3.15. Ruthenium leaching during the electrodeposition stage at 150 mA. The first image shows initial leaching of ruthenium immediately after immersing the ruthenium-soaked cloth in the electrolyte solution. The second image shows ruthenium at a different oxidation state 10 minutes into the electrodeposition stage.



Figure 3.16. Ruthenium deposition on catalyst surface before and after a 1-hour electrochemical deposition step.

To better observe the surface morphology of the deposition, SEM analysis was conducted. The secondary electron image (SEI) depicted in Figure 3.17a and 3.17b show the clean carbon cloth and the soaked carbon cloth soaked with ruthenium (using incipient wetness) respectively. The ruthenium particles appear as small specks on the carbon fibers randomly distributed over the surface of the carbon cloth. After the deposition step of the IW soaked cloth, the ruthenium is completely coating the carbon fibers and more uniformly distributed with only some areas of the carbon fibers slightly exposed (Figure 3.18a and 3.18b). EDX analysis also shows the presence of both ruthenium and chlorine at less than 10 wt.%, each, with carbon accounting for 68 wt.% before the electrodeposition step. The carbon content decreases to 23 wt.% while ruthenium increases to 54 wt.% after electrodeposition. A comparison of image of the 0.1 g loaded catalyst prepared by soaking and drying the cloth in a salt solution (Figure 3.19a and 3.19b) shows that at higher loading the ruthenium coating appears to peel off the carbon fibers, which is similar to the lower loading catalyst prepared by our conventional soaking method.



Figure 3.17. a). SEI of clean ACC (75X magnification) b). SEI of ACC soaked with ruthenium salt using the incipient wetness soaking procedure (75X magnification).



Figure 3.18. a). SEI of ACC soaked with ruthenium salt using the incipient wetness soaking procedure after 1-hour electrochemical deposition step (75X magnification) b). same image at 750X magnification.



Figure 3.19. a). SEI of ACC soaked with 0.1 g ruthenium salt and reduced catalyst after 1-hour electrochemical deposition step (75X magnification) b). same image at 750X magnification. Plated ruthenium appears to peel off from the carbon fibers.

Based on ICP analysis, the ruthenium loading for each catalyst is reported in Table 3.5. The IW method exhibited ruthenium loading of 2.45 wt. % which was closest to the Ru/ACC (3.76 wt. %) compared to the catalysts prepared by the alternate soaking method. It appears that the alternate soaking method results in much lower ruthenium loading of less than ~2% (even for the 0.1g loaded catalyst). All the EC-Ru/ACC samples had some ruthenium leaching into the electrolyte solution with the IW soaked catalyst showing the least ruthenium leaching (0.0183 mg) and the EC-Ru/ACC (0.1 g) showing the most leaching (0.0744 mg).

Catalyst	Ruthenium loading (wt. %)	Ruthenium Leaching (mg)
Ru/ACC	3.76	-
EC-Ru/ACC (IW)	2.45	0.0183
EC-Ru/ACC (0.025 g)	0.90	0.0361
EC-Ru/ACC (0.05 g)	2.09	0.0713
EC-Ru/ACC (0.1 g)	1.94	0.0744

Table 3.5. Ruthenium loading and leaching for Ru/ACC and EC-Ru/ACC catalysts (IW stands for incipient wetness soaking procedure)

After the 1-hour deposition step, the substrate (guaiacol) was added and ECH was performed at 100 mA for 6 hours. The four different loadings were compared to each other and to the regular Ru/ACC based on conversion, product yield, product selectivity and faradaic efficiency. Ru/ACC and EC-Ru/ACC with IW soaking showed comparable results with 100% conversion, similar yields, faradaic efficiency (Figure 3.20), and selectivity towards cyclohexanol (Figure 3.21). However, the catalyst prepared by the alternate soaking method all show decreased conversion, yield, and faradaic efficiency while selectivity towards cyclohexanol was slightly lowered. As was seen from the SEM images in Figure 3.19a and b, the catalysts soaked in this manner exhibited some peeling of the ruthenium coating and ICP showed increased leaching for ruthenium in to the solution for these three catalysts compared to IW soaked EC-Ru/ACC catalyst; which could all be contributing to the decreased conversion. Additionally, the lower loadings 0.05 g and 0.025 g exhibited lower conversion compared to the 0.01 g EC-Ru/ACC.

In addition to the electrodeposition method, one other way of reducing capital cost for this system is by replacing the expensive anode material (Pt) with a cheaper alternative. In this case preliminary experiment was conducted using ACC as the anode material. This experiment showed comparable conversion to our conventional Ru/ACC method with Pt anode with increased selectivity towards cyclohexanol, as shown in Figures 3.20 and 3.21. This result is promising for future application and should be explored further.



Figure 3.20. Comparison of conversion, product yield and faradaic efficiency of catalyst prepared by high temperature/pressure reduction vs. electrochemical deposition. Comparison to ACC anode is also included. (Ru/ACC is the Parr reactor reduced catalyst, EC-Ru/ACC is electrochemically reduced catalyst, and IW stands for incipient wetness soaking).



Figure 3.21. Comparison of product selectivity of catalyst prepared by high temperature/pressure reduction vs. electrochemical deposition. Comparison to ACC anode is also included.

Catalyst Reusability Study for Parr Reactor Reduced and Electrochemically Reduced Catalyst

In addition to testing the ECH of different monomers, a reusability test of the Ru/ACC and EC-Ru/ACC catalysts was conducted. The catalyst was used to reduce guaiacol using the same catalyst for several runs. Both methanol and DCM were used to wash the catalyst by stirring, but not sonication to avoid disruption of the catalyst fibers. The catalyst was then dried under vacuum to ensure that all the products and washing solvent were removed from the cloth. Early trials indicated that solvents, if not removed, can block active sites on the catalyst deactivation can be avoided by using the vacuum drying method after each run. The cloth washed in DCM showed some deactivation after four uses possibly due to residual DCM adsorbed to the cloth while the cloth washed in methanol did not show any significant deactivation after eight uses (Figure 3.22 and 3.23).



Figure 3.22. Conversion and product yield of ECH of 20 mM guaiacol at 80 °C, 100 mA, for 6 h in 0.2 M HCl using the same catalyst for eight consecutive runs by wash with DCM.



Figure 3.23. Conversion and product yield of ECH of 20 mM guaiacol at 80 °C, 100 mA, for 6 h in 0.2 M HCl using the same catalyst for eight consecutive runs by wash with Methanol.

For the electrochemically reduced catalyst, three consecutive runs were conducted, by washing with DCM there appears to be a slight decrease in conversion after each run (Figure 3.24). This could be caused by leaching and loss of ruthenium from the catalyst surface or by deactivation from washing in DCM. Leaching studies and use of other solvents such as methanol should be explored in the future to determine the cause of and avoid deactivation.



Figure 3.24. Comparison of conversion and product yield and faradaic efficiency of ECH of 20 mM guaiacol at 80 °C, 100 mA for 6 h in 0.2 M HCl solution using the same EC-Ru/ACC catalyst for three consecutive runs by washing with DCM (Parr reactor reduced Ru/ACC conversion, product yield and faradaic efficiency values included for comparison).

The mass balance for these experiments, however, could not be closed as the total product yields were around 45%, even if the conversion of the substrate was 100%. To study why this was happening, activated carbon cloth pieces were soaked in 0.2M HCl solution, without any current, at 80 °C for 6 hours with guaiacol, phenol and cyclohexanol. Each compound was recovered using

methanol and DCM and the recovery percentage was recorded (Figure 3.25). This study indicated that even if methanol is better at extracting products such as cyclohexanol from the cloth, compared to DCM, only about 70% of the cyclohexanol was recovered, the remaining cyclohexanol was likely lost due to adsorption on the cloth. Additionally, to avoid disruption of the catalyst fibers, mechanical agitation using sonication to recover products was not used for these trials, which may result in decreased product recovery. Multiple washing methods and solvents need to be explored in the future to maximize substrate and product extraction efficiencies and improve the mass balance.





Conclusion

ECH of model compounds derived from pyrolysis of lignins extracted from EA and AHP processes was demonstrated to be effective. The model compounds phenol, *p*-cresol, 4-ethylphenol, and 4-propylphenol were successfully converted to their corresponding alkylcyclohexanols at high conversion rates. Alkyl chain length was demonstrated to have an

effect on conversion, increasing alkyl chain length resulted in decreased conversion after 2 hours. Similarly, guaiacol, alkyl and allyl guaiacols (creosol, 4-ethylguaiacol, 4-propylguaiacol and eugenol) were all hydrogenated and partially deoxygenated to their respective alkylcyclohexanols and alkyl-substituted 2-methoxycyclohexanols. Alkyl chain length also affected both the conversion and selectivity of alkylguaiacols, conversion decreased with increasing alky chain length while a shift in selectivity to produce more alkyl-substituted 2methoxycyclohexanol was observed with increasing the alky chain length. For both the alkylphenol and alkylguaiacol studies, increased formation of alkylcyclohexane was observed with increasing alkyl chain length. Other model monomers, namely vanillin and syringaldehyde, were also hydrogenated and deoxygenated, while C-C bond cracking was also observed. Methyl group position showed only a minor effect, where the proximity of the alkyl group to the hydroxyl group resulted in a slightly better conversion. Similarly, the proximity of the methoxy group to the hydroxyl group also showed improved conversion and cyclohexanol yield. Increasing substrate concentration was demonstrated to improve faradaic efficiency. Finally, the use of an electrodeposition method for reducing ruthenium on activated carbon was successfully tested and showed comparable results as Parr reactor reduced catalyst for the ECH of guaiacol. This study demonstrated that a sequence of pyrolysis and ECH provides a strategy to depolymerize lignin and further upgrade it to valuable products.

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Chapter 4 : Electrocatalytic Cleavage of Lignin Model Dimers Using Ruthenium Supported on Activated Carbon Cloth

Abstract

Lignin, a component of biomass and one of the largest natural sources of renewable aromatic compounds is an ideal candidate for the production of higher-value products. Lignin valorization however is challenging due lignin's complex structure that is naturally resistant to biological degradation. Because of its amorphous crosslinked structure consisting of ether bonds, effective lignin depolymerization requires the cleavage of aryl ethers bonds. High temperature cracking of lignin is possible via pyrolysis, but linkages such as 4-O-5 bonds are reported to be resistant to thermal degradation. Electrochemical upgrading offers an alternative whereby mild conditions (low temperature and atmospheric pressure) can be used to achieve ether bond cleavage and aromatic ring hydrogenation to produce valuable products. To investigate the effectiveness of ruthenium on activated carbon cloth on the cleavage of 4-O-5 bonds, model compounds 3-phenoxyphenol, 4-phenoxyphenol, 3-phenoxyanisole and 3-phenoxytoluene were investigated. The effect of different electrolytes, substrate concentrations, and current density on conversion and current efficiency reported in this chapter.

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Introduction

In response to the increasing environmental concerns surrounding the use of fossil fuel, research and development efforts in renewable energy systems is of growing interest. The development of renewable energy production methods that are efficient, environmentally friendly, and economically sound is essential. As plants store energy from the sun via photosynthesis in the form of chemical bonds between carbon, hydrogen, and oxygen, biomass has great potential to make carbonaceous fuels for supplying renewable energy.¹ Although cellulose and hemicellulose, polymers of simple sugars, have been well studied in terms of conversion to fuel ethanol, lignin valorization is a more nascent technology. Lignin, a complex racemic mixture of aromatic polymers produced from the oxidative coupling of three major 4-hydroxyphenylpropanoid monolignols, is the only significant source of natural aromatic compounds.²⁻⁴ It is an attractive feed for the production of hydrocarbon fuels due to its lower O:C ratio compared to cellulose and hemicellulose. But because of its complex structure, lignin has been one of the more difficult components to deconstruct and use as fuel.⁵

Lignin's three dimensional structure is very rigid and resistant to deconstruction as it is intended to protect the cell wall polysaccharides from biological degradation.³ Lignin is also resistant to acid hydrolysis but can readily be oxidized and condensed with phenol and thiols and is soluble in alkaline and bisulfite solutions.⁶ Because lignin is an amorphous polymer of carbon and oxygen that is bonded at the α and β positions of its phenyl ring, the depolymerization of lignin is dependent upon the successful cleavage of lignin-specific linkages (e.g. β -O-4, β - β , β -5, 5-5, and 4-O-5).⁷ Unraveling this complex polymer and being able to produce valuable monomeric phenols is a challenge to be addressed.⁸ To this end, lignin valorization require its

separation from biomass carbohydrates, cleavage of α -aryl and β -aryl ether linkages, and conversion to liquid fuel and value-added products. Lignin depolymerization has previously been conducted using methods such as pyrolysis,⁹ oxidative cleavage,¹⁰ reductive catalytic hydrogenation,¹¹ and electrocatalytic reduction.¹²⁻¹⁵ These methods can have limitations however; for example, during thermal degradation some linkages could be resistant to thermal cracking. Oxidative degradation can create radicals that lead to lignin polymerization instead of cleavage.⁷ Catalytic reduction can occur either via hydrogenolysis of C-O bonds or hydrogenation of aromatic rings by addition of chemisorbed hydrogen at elevated temperatures and pressure. However, if hydrogenation of the aromatic ring occurs before hydrogenolysis of the ether bond, lignin degradation can be limited. Additionally, catalytic reduction can suffer from lack of selectivity.⁷ Electrocatalytic upgrading offers an alternative whereby mild conditions (low temperature and atmospheric pressure) can be used to achieve hydrogenation and deoxygenation.¹⁶ This method offers certain advantages over catalytic hydrogenation and hydrogenolysis; in electrocatalytic hydrogenation/hydrogenolysis (ECH), the kinetic barrier related to hydrogen dissociation is avoided as the hydrogen needed for reduction is produced in situ.¹⁷ Additionally, mass transport limitations of hydrogen gas in aqueous solutions is also avoided in ECH.¹⁷ Even catalyst poisoning due to coke formation is prevented due to the cathodic potential that can prevent the adsorption of anionic poisons.¹⁷ Furthermore, ECH provides the means to selectively produce specific desired products by controlling cell potential.^{18, 19}

Electrocatalytic hydrogenation proceeds via a multistep process whereby the electroreduction of water occurs on the catalyst surface in the cathode compartment producing chemisorbed hydrogen. The organic substrate is co-adsorbed on surface forming a metal

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substrate complex ([R=R]M). The metal/hydrogen ([H]M) complex that is formed on the catalyst then interacts with the neighboring substrate/metal ([R=R]M) complex causing reduction of the organic substrate. Hydrogenation products then desorb from the catalyst and migrate into the electrolyte. In parallel reactions, hydrogen evolution also occurs when hydrogen desorbs from the catalyst surface. ^{12, 14, 18-20} Hydrogen evolution reactions compete with organic hydrogenation reactions lowering the cell's faradaic efficiency, which is defined as the fraction of charge passed that will be allocated to produce the desired products.¹⁷ The rates of both hydrogenation and hydrogen evolution 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 (related to substrate concentration and functionalities present),¹⁸ strength of bonding of hydrogen to the catalyst surface,¹⁷ and current density.²¹ Investigating the effects of these factors on cell performance for lignin cleavage is needed to evaluate lignin valorization using ECH.

As a bulk polymer, lignin's chemical structure and physical properties limits the efficacy of ECH. Molecular size can inhibit adsorption as lignin's functional groups can sterically block catalyst active sites and limit subsequent hydrogenation.^{12, 18, 22} Though soluble under alkaline conditions, lignin's solubility in certain electrolyte solutions, especially at lower pH, poses transport limitations. Solution pH can also affect substrate adsorption to the catalyst surface. For example, many lignin-derived phenolic compounds, with pKa > 10, will deprotonate in basic conditions to form anions at high pH. These anions will tend to remain in polar solutions instead of adsorbing to catalytic cathode surfaces, themselves negatively charged.²³ Radical formation during lignin ECH can lead to polymerization similar to what is seen during lignin biosynthesis, hindering mass transfer to the catalytic cathode, thus limiting conversion.⁷ As it pertains to

bonding, although C-O bonds like β-O-4 linkages might be relatively easy to cleave,⁷ others such β-β, β-5, and 4-O-5 could be challenging due to their bond strength.²⁴ Even for C-O bonds, the ease of hydrogenolysis depends on the structures participating in the ether linkage, as benzyl-O-phenyl is easier to cleave than benzyl-O-alkyl, which itself is easier than cleaving alkyl-O-alkyl.⁷ Electrochemically, the amount of charge passed for ECH is determined by the number of electrons needed for cleaving each ether bond. However, in ECH of lignin, determining the needed charge is difficult due to lignin's size and varied structure. As the structure is not well defined, analysis and quantification of products becomes difficult. *In lieu* of using complex lignin polymers, simpler model compound studies can address these limitations to develop an advanced understanding of lignin ECH. In this regard, previous ECH studies of model dimers, with lignin-specific linkages, have been very beneficial in understanding the effectiveness of ECH for lignin degradation.¹²⁻¹⁴

As lignin is a byproduct of other industries, utilizing it as a feedstock for biofuels and bioproducts is worthy of consideration. What is needed to de-risk lignin ECH is an understanding of how lignin-specific linkages are cleaved under varying conditions. In this study, first the effectiveness of thermal cracking on lignin linked dimers is investigated qualitatively. Then the effectiveness of ECH for the cleavage of thermally resistant dimers is tested. As ECH's performance towards dimer hydrogenation is impacted by current density, electrolyte type, and nature of the substrates (functional groups and position), variations in these factors are included in this study. The effect of varying solution pH, current density, functional group type and their position is needed to determine whether ECH can be used to valorize lignin-based substrates.

Experimental Methods

Model Compounds

First, to investigate the effect of pyrolysis on lignin dimers, dimers exhibiting lignin linkages were obtained from several sources. Two β -O-4 dimers were obtained from Dr. John Ralph's laboratory and from Dr. Shannon Stahl's laboratory both at the University of Wisconsin (Madison, WI). 4-O-5, β - β , β -5, and 5-5 dimers were synthesized in Dr. Ned Jackson's laboratory at Michigan state university. All these dimers were subjected to analytical pyrolysis. Electrocatalytic cleavage of lignin-specific linkages and overall conversion was studied using the model compounds shown in Figure 4.1. 4-Phenoxyphenol, 3-phenoxyphenol, 3-phenoxytoluene and 3-phenoxyanisole were investigated to represent the 4-O-5 type linkage, and 4-biphenylmethanol a 5-5 bonded dimer was also investigated. All of these compounds obtained from Alfa Aesar (Ward Hill, MA).



Figure 4.1. Dimers a) 4-phenoxyphenol b) 3-phenoxyphenol c) 3-phenoxyanisole d) 3-phenoxytoluene e) biphenyl methanol

Analytical Pyrolysis of Dimers

Pyrolysis gas chromatography mass spectrometry (py-GC/MS) was performed to observe the effect of pyrolysis on lignin dimers. A CDS pyroprobe 5250 (CDC Analytical Inc. Oxford, PA) coupled with a Shimadzu QP 5050A GC/MS (Shimadzu Corp. Columbia, MD) was used to pyrolyze about a milligram of each lignin dimer sample. Temperature in the pyroprobe was set at 650 °C

for 20 seconds, while the transfer line temperature and the GC port temperature were both set at 280 °C. The GC oven temperature was programed to increase from 40 °C to 270 °C at a ramp rate of 8 °C/min. Eluting analytes were identified using the NIST library.

Catalyst Preparation

Zorflex[®] activated carbon cloth (ACC) (Zorflex[®] ACC FM100) obtained from Calgon Carbon Corporation (Pittsburgh, PA) was used to support hexaammineruthenium(III) chloride (Ru(NH₃)₆Cl₃) which was obtained from Alfa Aesar. As described by Li et al.,²⁵ ACC was cut into 1.5 x 3.0 cm pieces, agitated overnight in deionized (DI) water, oven dried at 150 °C and soaked in a ruthenium salt solution (Ru(NH3)6Cl3 (1.01 g), dissolved in ammonium hydroxide (1.96 ml) and water (13.02 ml).) to saturate the pores. The ruthenium on activated carbon cloth (Ru/ACC) catalyst was then dried overnight at room temperature, further dried under vacuum for 24 h, then reduced with molecular hydrogen at 310 °C and 500 psi for 12 h in a Parr Reactor model 452HC (Parr Instrument Company, Moline, IL).

ECH Setup and Experimental Design

A two-chambered electrochemical glass H-cell fabricated by the Department of Chemistry Glassblowing facility at Michigan State University (East Lansing, MI) was used for conducting the experiments. The chambers were separated using a Nafion[®] 117 membrane obtained from Dupont (Wilmington, DE). Ru/ACC was used as the cathode and platinum wire obtained from Alfa Aesar was used as the anode (Figure 4.3). An Instek GPR-11H30D (Instek America Corp., Montclair, CA) power supply provided constant electrical current. To maintain constant temperature of 80 °C the entire cell was placed in a heated water bath for all experiments. After the cell setup was completed, a 10-min pre-electrolysis step was performed on the catalyst at 80

mA before adding the substrate. After pre-electrolysis, depending on the experiment, the desired amount of substrate was added, and each experiment was run at the desired current density for the desired duration. Three separate studies were conducted to investigate different conditions and substrates; substrate study, electrolyte effect study, and current density study.



Figure 4.2. Two chambered H-cell setup showing reduction of lignin model compound guaiacol to cyclohexanol using Ru/ACC as a cathode and platinum wire as an anode.

Sample Extraction and Analysis

During the experiments electrolyte samples were taken, saturated with NaCl, acidified to pH 1.0 with concentrated HCl, and extracted in dichloromethane (DCM). At the end of the experiment the catalyst was placed in 30 mL DCM, and sonicated for 10 min, and filtered prior to analysis by gas chromatography mass spectrometry (GC-MS). Samples of the solution were analyzed using a Shimadzu QP-5050A GC/MS (Shimadzu Corp, Columbia, MD). Standards in DCM were used for identifying products by retention time and to construct a four-point calibration curve. This curve was used to determine product yields and calculate current efficiency.

Calculations

Yield A = (Moles of A) / (Initial moles of reactant)
Selectivity A = (Moles of A) / (Moles of total products)
Conversion = (Moles of reactant consumed) / (Initial moles of reactants)
Current efficiency = (Charge used generate to products) / (Total charge passed)
Current Density = (Current)/ (Unit area of catalyst used)

Results and Discussion

Pyrolysis GC/MS of Lignin Model Dimers

To determine the effectiveness of pyrolysis in the cleavage of lignin specific dimers, py-GC/MS was conducted at 650 °C for 20 seconds on several lignin linked model dimers obtained from different sources. The pyrolysis of β -5 dimer indicates that the dimer is easily pyrolyzed with guaiacol and creosol as the major product while other alkyl guaiacols and vanillin were also observed (Figure 4.3). β - β dimer is also cleavable upon pyrolysis, syringol is the major product with some methylation reaction products observed (Figure 4.4). 5-5 dimer is also cleaved to form guaiacol, creosol and propylguaiacol (Figure 4.5). The β -O-4 dimers were cleaved to yield various products including guaiacol, 4-vinylguaiacol, eugenol and other. Diphenyl ether dimers such as 4-O-5 bonded compounds, known to be abundant in Kraft lignins, are reported to resistant even to thermal cracking due to their much higher bond dissociation energy (314 kJ mol ⁻¹) compared to β -O-4 linkages (289 kJ mol ⁻¹).²⁶⁻²⁸ To confirm that 4-O-5 bonded dimers would not get cleaved by pyrolysis, a model dimer (2-phenoxyphenol) was subjected to analytical pyrolysis at 650 °C and was found to be completely unaffected (Figure 4.7). Lignin depolymerization and upgrading

however, is contingent upon cleaving of such bonds. As part of the study to valorize lignin-derived pyrolysis products, the ECH of 4-O-5 bonded dimers is investigated here.



Figure 4.3. Pyrolysis GC/MS products of β -5 dimer at 650 °C and residence time of 20 s (products identified using similarity to NIST library)



Figure 4.4. Pyrolysis GC/MS products of β - β dimer at 650 °C and residence time of 20 s (products identified using similarity to NIST library)



Figure 4.5. Pyrolysis GC/MS products of 5-5 dimer at 650 °C and residence time of 20 s (products identified using similarity to NIST library)



Figure 4.6. Pyrolysis GC/MS products of β -O-4 dimer at 650 °C and residence time of 20 s (products identified using similarity to NIST library)



Figure 4.7. Pyrolysis GC/MS products of 4-O-5 dimer at 650 °C and residence time of 20 s (products identified using similarity to NIST library)

ECH of Lignin Model Dimers using Ru/ACC

ECH has been investigated and demonstrated to be successful in the conversion of 4phenoxyphenol to phenol with high conversion using various catalyst materials such as palladium on alumina, palladium on carbon and Raney nickel. ^{14, 24} The effectiveness of Ru/ACC has also been reported previously by our group.²⁹ As an expansion of this study, ECH of 3-phenoxyphenol and 4-phenoxyphenol are investigated here to understand how the position of hydroxyl group affects conversion, product selectivity and faradaic efficiency. Electrolyte pH and current density were also investigated. ECH of both 3- and 4-phenoxphenol is suggested here to follow two pathways, one via ether bond cleavage to form phenol followed by hydrogenation of phenol to cyclohexanol. The other via hydrogenation of the aromatic ring then C-O bond cleavage (Figure 4.8). However, if the second route is followed and the hydrogenation of the ring occurs before hydrogenolysis, the C-O bond cleavage will be limited. This is due to the fact that compared to bezyl-O-phenyl, benzyl-O-akyl and alkyl-O-alkyl are much harder to cleave.⁷ This has implications in lignin depolymerization because if the ring hydrogenation occurs first, lignin degradation will be limited.



Figure 4.8. Suggested reaction routes for the ECH of 3-phenoxyphenol and 4-phenoxyphenol. Route 1 proceeds via ether bond cleavage to form phenol followed by ring saturation to form cyclohexanol. Route 2 proceeds by direct ring saturation followed by cleavage of the dimer.

Effect of Varying Electrolyte pH on ECH of 3-Phenoxyphenol and 4-Phenoxyphenol

To optimize the ether cleavage of 3- and 4-phenoxyphenol and maximize the cyclohexanol yield, different electrolytes (0.2 M HCl, 0.2 M NaCl, and 1 M NaOH) were investigated. Results from these experiments indicate that after 9 hours, complete conversion of both 3-phenoxyphenol (Figure 4.9) and 4-phenoxyphenol (Figure 4.10) was achieved in all electrolytes. The conversion products for all conditions and substrates include cyclohexanol and the saturated dimer cyclohexyloxycyclohexanol (not quantified). For both dimers, the cyclohexanol yield was maximum when using the 1 M NaOH electrolyte which favored the formation of the

hydrogenolysis product cyclohexanol over the hydrogenation dimer product (Figure 4.9). As lignin is soluble in basic electrolyte this this result is promising for lignin depolymerization. Additionally, when comparing the two dimers, it was observed that the position of the hydroxyl group has an effect on the cyclohexanol yield. The selectivity towards cyclohexanol is favored by the hydroxyl group proximity to the ether bond. This is similar to what was observed during the ECH of guaiacol, 3-methoxyphenol and 4-methoxyphenol where guaiacol shows improved conversion to cyclohexanol compared to 3-methoxyphenol and 4-methoxyphenol both on Ru/ACC and Raney Ni catalysts. ³⁰



Figure 4.9. a) Reaction conditions and observed products for the ECH of 3-phenoxphenol (square brackets indicate observed product that was only identified using mass spec matching with NIST library and not by injection of pure compound) b) conversion, cyclohexanol yield and faradaic efficiency for ECH of 20 mM 3-phenoxyphenol using different electrolytes (1 M NaOH, 0.2 M HCl, 0.2 M NaCl) at 80 °C, 100 mA, for 9 h. Faradaic efficiency calculated using only moles of cyclohexanol.



Figure 4.10. a) Reaction conditions and observed products for the ECH of 4-phenoxphenol (square brackets indicate observed product that was only identified using mass spec matching with NIST library and not by injection of pure compound) b) conversion, cyclohexanol yield and faradaic efficiency for ECH of 20 mM 4-phenoxyphenol using different electrolytes (1 M NaOH, 0.2 M HCl, 0.2 M NaCl) at 80 °C, 100 mA, for 9 h. Faradaic efficiency calculated using only moles of cyclohexanol.

Effect of Substrate Concentration on ECH of 3-Phenoxyphenol

One way of improving the faradaic efficiency is by increasing the rate of hydrogenation of the substrate by increasing the coverage of the catalyst sites with the substrate species. If more active sites are occupied by the substrate species then the likelihood of the chemisorbed hydrogens interacting with these species is increased while the likelihood of chemisorbed hydrogens combining to form hydrogen gas via Tafel and Heyrovsky reactions suppressed³¹ To investigate the effect of substrates concentration on the faradaic efficiency, three different concentrations were investigated. As can be seen from Figure 4.6, increasing the substrate

concentration from 10mM to 20 mM increases that faradaic efficiency from 8% to 16% and a further increase of concentration to 40 mM increased the efficiency to 25% (Figure 4.11). However, the faradaic efficiency is still modest so in the next section we explore the effect of current density to improve the efficiency of the system.





Effect of Current Density on ECH of 3-Phenoxyphenol

As can be seen from the results in the previous section, the faradaic efficiency at a maximum only reached 25% for conversion to cyclohexanol when using 40 mM substrate concentration. This means that close to 75% of the current could be going to HER. Several parameters can be controlled to suppress HER. In this case, the effect of current density on the conversion and faradaic efficiency of ECH of 3-phenoxyphenol was investigated. It was observed that decreasing the current from 100mA to 50mA (because measuring the effective surface area of the catalyst was difficult, the current density based on the geometric surface area was calculated to be approximately 22.22 mA/cm² to 11.11 mA/cm²) increased the faradaic efficiency from 16% to

34% further decreasing the current to 20 mA (4.44 mA/cm²) resulted in greatly enhanced faradaic efficiency of 96% (Figure 4.12). At lower current density, the HER is likely highly suppressed resulting in improved efficiency. After 9 hours, complete conversion was also achieved for all trials, while the cyclohexanol yield was slightly improved by the decrease in current density. This could be due to selective formation of phenol over the hydrogenated dimer at lower current density which would further result in higher cyclohexanol yields.





Study of Different Functional Groups

3-Phenoxyanisole and 3-phenoxytoluene were also investigated. Unlike 3-phenolxyphenol and 4-phenoxyphenol, the solubility of 3-phenoxytoluene and 3-phenoxyanisole was highly limited in the NaOH electrolyte so the conversions were much lower than those observed for 3phenoxyphenol and 4-phenoxyphenol (Table 4.1). For 3-phenoxyanisloe 23% cyclohexanol was observed. This could be through the cleavage of the ether bond and the formation of phenol and anisole which could further undergo hydrogenation and demethylation (in the case of anisole) to form cyclohexanol (Figure 4.13). No anisole was recovered from this experiment, however from ECH of anisole in the previous chapter, we know that it undergoes complete conversion in two hours to cyclohexanol and methoxycyclohexane so it could be completely converted in this study after 9 hours. Other products were observed for 3-phenoxyanisole but could not be accurately quantified. For 3-phenoxytoluene, cleavage of the ether bond appears to happen from two sides of the ether bond to form cyclohexanol and 3-methylcyclohxanol. For this it was observed that though ECH is effective at cleaving ether bonds in 4-O-5 type dimers, the functional groups present could have an impact on the conversion and selectivity of the reaction. The presence of the OH group in 3- and 4-phenoxyphenol, probably facilitates the adsorption of these substrates on to the catalyst surface however the 3-phenoxyanisole and 3-phenoxytoluen do not have this advantage additionally both are limited by their solubility resulting in their decreased conversion. Further studies can explore the combined effect of these different functional groups as lignin dimers tend to exhibit combinations of these varying groups. Finally, the ECH of 5-5 bonded dimer 4-biphenylmethanol was also investigated but cleavage of the C-C bond was not observed.



Figure 4.13. Reactions conditions and observed products for the ECH of 3-phenoxphenol, 4-phenoxyphenol, 3-phenoxyanisole and 3-phenoxytoluene (square brackets indicate observed product that was only identified using mass spec matching with NIST library and not by injection of pure compound).

Table 4.1. Conversion (mole%) and cyclohexanol yield (mole%) for 4-O-5 dimers with different functional group types and positions in 1 M NaOH at 100mA for 9 h.

Substrate	Current (mA)	Electrolyte (Cathode)	Conversion (mole %)	Cyclohexanol (mole %)
4-phenoxyphenol	100	1M NaOH	100	70
3-phenoxyphenol	100	1M NaOH	100	83
3-phenoxyanisole	100	1M NaOH	69	23
3-phenoxytoluene	100	1M NaOH	57	3

Conclusion

Analytical pyrolysis of lignin dimers was conducted to identify their resistance to thermal degradation. All lignin dimers, except the 4-O-5 linked dimer, were found to undergo cleavage at 650 °C. Consequently, ECH of the 4-O-5 linked dimers 4-phenoxyphenol and 3-phenoxyphenol was investigated in acidic, basic and neutral electrolyte. Both dimers were cleaved and further hydrogenated to cyclohexanol with 100% conversion. 3-phenoxyphenol in basic electrolyte showed the highest cyclohexanol yield and faradaic efficiency. To improve the modest faradaic efficiency, increased substrate concentration and decreased current density were investigated. Though increased substrate concentration resulted in modest improvement in faradaic efficiency, a decrease in current density to 20 mA increased the faradaic efficiency to 96% while 100% conversion and an 87% cyclohexanol yield was also achieved. ECH of 3-phenoxyanisole and 3-phenoxytoluene resulted in ether cleavage, but the limited solubility of these substrates resulted in lower conversion and formation of lower levels of cyclohexanol.
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Chapter 5 : Transition to Bioenergy in the Great Lakes Region - a Sociotechnical Imaginary that Became a Wicked Problem

Fossil fuel derived resources have sustained human activities since the industrial revolution. Whether by providing raw materials to produce chemicals or by serving as a source of transportation fuels and energy in the form of heat and power, the seemingly abundant amounts of coal, petroleum and natural gas have been and continue to be the primary sources of energy that sustain human existence on this planet. But in recent years, the non-renewable nature of fossil fuels combined with their clear contribution to the rising levels of greenhouse gas (GHG) emissions (which the Intergovernmental Panel on Climate Change (IPCC) has attributed to human fossil fuel use and activities) has prompted an increased interest in deriving fuels and raw materials from renewable sources.¹ Additionally, fossil fuel use also contributes to global energy dependence that further leads to economic and political conflicts. For example, according to the Energy Information Administration (EIA) about 24% of the petroleum consumed by the US in 2015 was imported, making the U.S. dependent on foreign nations to fulfill energy needs.² To this end, energy transitions from fossil-based fuels to renewable sources has become increasingly relevant. However, transitions to renewable sources of energy, bioenergy in particular, has encountered significant barriers. In this chapter, bioenergy is discussed using three theoretical frameworks (sociotechnical imaginary, wicked problem and political ecology frameworks) in an effort to understand the social aspects and the barriers associated with the transition to bioenergy.

Definition of terms

<u>Renewable sources of energy</u> are defined in this chapter as sources of energy that can derive their energy from existing and ongoing natural processes such as wind, solar, etc. and be replenished in a time scale that is relevant to human consumption.³

<u>Bioenergy</u> is a type of renewable source of energy that is derived from biological sources such as plants and organic waste.³

<u>Biofuels</u> are mostly liquid and transportation fuels derived from biomass. This term will be used interchangeably with bioenergy in this chapter.

First generation biofuels are biofuels produced from plant-derived sugars and oils usually using food crops such as corn, sugarcane or soybean as a feedstock.⁴ Examples of first generation biofuels are ethanol, biodiesel and biogas.⁵

<u>Second generation biofuels</u> are advanced biofuels that can be produced from a range of different "non-food biomass" sources.⁴

<u>Land use change</u> is defined by Plassmann as "a change in the use or management of land by humans. The Intergovernmental Panel on Climate Change (IPCC) distinguishes six broad land use categories: forestland, cropland, grassland, wetlands, settlements, and other land (e.g. bare soil, rock and ice), where the conversion from one land use category to another is called LUC."⁶

<u>Direct land use change</u> refers to emissions due to designated agricultural land that was used to produce a certain crop now being used to produce a different crop.

<u>Indirect land use change (ILUC)</u> refers to carbon emission due to pristine land being cleared for farming to compensate for agricultural land being used for biofuel crop production.⁷ Diverting

land use in one part of the world (e.g. diverting land to produce corn for ethanol in the U.S.) may result in pristine land (e.g rainforests and grasslands) in another part of the world being cleared in order to satisfy global food demand and compensate for the edible corn that was diverted for ethanol production. ^{6, 8}

<u>Sociotechnical imaginary</u> was first defined by Jasanoff and Kim in 2009 as "collectively imagined forms of social life and social order reflected in the design and fulfillment of nation-specific scientific and/or technological projects." ⁹

"Imaginaries, in this sense, at once describe attainable futures and prescribe futures that states believe ought to be attained. In the 2008 US presidential campaign, for example, Barack Obama repeatedly referred to the Apollo mission—shorthand for the claimed US capacity to plan and execute superhuman technological feats—as the inspiration for a massive program to achieve energy self-sufficiency in ten years. Such visions, and the policies built upon them, have the power to influence technological design, channel public expenditures, and justify the inclusion or exclusion of citizens with respect to the benefits of technological progress." ⁹

<u>Tame or benign problems</u> are defined by Rittel and Webber as problems that are "clear, definable, separable from other problems and have straight forward and findable (attainable) solutions."^{10, 11} An example of a tame problem includes a solvable mathematical equation.

<u>Wicked problems</u> are defined as problems that are "ill-defined, interconnected to other problems. They have no clear (agreed upon), true solutions and most of the time the solutions tend to create more problems."^{10, 11} According to the definition by Rittel and Webber, wicked does not equate with evil, but is used to describe the "tricky nature" of the problem.¹⁰ An example of a wicked problem is climate change.

<u>Political ecology framework</u> is defined by Van Der Horst and Evans as "a field of enquiry concerned primarily with the power structures that determine who has access to environmental assets and who does not." ¹² Similarly, Watts defines it as a framework that "seeks to understand the complex relations of nature and society through careful analysis of what one might call the forms of access and control over resources and their implications for environmental health and sustainable livelihoods."¹³

Sociotechnical Imaginary of Bioenergy Production (A Win-Win Scenario)

As the environmental repercussions from fossil fuel use have become more apparent, many nations have begun seeking ways to transition to renewable energy. Plant biomass—in the form of agricultural residues, energy crops, and wastes—is currently the only form of renewable carbon that serves as the backbone of hydrocarbon fuels.¹⁴ Using energy from the sun, plants capture CO₂ and offset the environmental impacts of CO₂ emissions from combustion.¹⁵ Additionally, the production of biofuels has potential to reduce dependence on foreign crude oil and lead to investment in creating jobs and reviving rural economies in the U.S.⁵ (Figure 5.1).

To transition to bioenergy, there has been an increased push from national actors (such as government entities) to legitimize the transition towards a "better future" or a "win-win scenario". In this scenario, nations can be less dependent on other nations for their energy supply, the environmental impact of fossil fuel use could be reduced and biofuel production could contribute to reviving rural economies (Figure 5.1).^{16, 17} As discussed by Eaton et al., "biomass-derived energy could be framed as a sociotechnical imaginary in which technological efforts such as those relating to development and implementation of bioenergy technologies are invested upon by national actors in hopes of building a better future and addressing social problems." ¹⁸

This treatise describes some ways national actors and policies in the U.S. have attempted to make

the biofuel sociotechnical imaginary a reality.



Figure 5.1. Biofuels: a win-win scenario to offset CO₂ emissions, produce energy and revive rural economies (adapted from University of Iowa, Energy and the Evironment¹⁹).

Although numerous policies were in place to address the issue of energy dependence for the U.S., it wasn't until the passing of 2005 Energy Policy Act (EPAct 2005) that a \$14 billion project of modernizing both traditional and renewable energy production systems was initiated.²⁰ To displace fossil fuels with renewable sources, the 2007 Energy Independence and Security Act mandated the introduction of 36 billion gallons per year of renewable fuels with 21 billion gallons being so called "advanced biofuels" by 2022.²¹ In response to this mandate, bio-based chemicals and bioenergy production from biomass has accelerated in the past few decades.²² Per the U.S. Energy Information Administration, more than 95% of the fuel consumed in motor vehicles in the U.S. in 2015 was 10% ethanol blended.²³

The 2013 International Energy Outlook predicts a 56% increase in total energy use by 2040.²⁴ With such growth in energy consumption, increased production of both fossil-based and renewable energy will be needed. However, such significant changes to energy production and

consumption will impact environmental, economic, societal, and political aspects of everyday life. With the aim of fulfilling the 2007 EISA mandates, several issues arise that make this transition to biomass-based fuels difficult. Towards analyzing this transition, two major sociotechnical frameworks are adopted. First, barriers that impede bioenergy system adoption cause "wicked problems," as such, frameworks that recognize and manage this complexity are utilized. After framing the wicked problem, the transition to bioenergy will be viewed from a political ecology perspective to understand how the powers embedded in the bioenergy system will influence and drive this transition. Both the wicked problem and political ecology frameworks will be geographically focused on the Great Lakes region.

Energy Transition Viewed Through Wicked Problem Framework

In contrast to tame problems that are relatively straightforward to define and solve, wicked problems are "dynamic, interconnected, and nonlinear".¹¹ Wicked problems are often influenced by social and political factors that are symptoms of other problems.²⁵ Multiple stakeholders view wicked problems differently, often with no one view being universally accepted.²⁵ Fast and McCormick argue that biofuels have moved from a "win-win" solution for other wicked problems to a new "contested position."^{11, 26} This means the transition to biofuel production and use has moved from solving wicked problems, such as climate change, to itself becoming a wicked problem.

Normal Science and Wicked Problems

Ideally, biofuels would solve many energy and environmental problems, and therefore the transition to increase their utilization might have followed a more linear trajectory without many barriers (Figure 5.2). Under the umbrella of "normal science," the biofuel adoption should

proceed from bench-scale research, to pilot-scale development, demonstration-scale field implementation, and finally to full-scale production. As with any normal science, there are assumptions that progress in science can lead to progress in society, but the opposite has been true for biofuels.²⁷ Batie described biofuels adoption as a wicked problem because it is challenged by society and there is doubt that science will adequately inform policy and decision-making.²⁵ This doubt can be attributed to four main reasons: first, a deeper understanding of sustainability issues raises concerns that normal science cannot control the risks it produces and that it introduces more risks and problems.²⁵ This is true for biofuels as their implementation has produced environmental risks such as land use change and negative impacts on water quality. Second, assumptions made by normal science to tackle wicked problems might not be realistic as they could be too linear and simplifying.²⁵ Third, perception of what constitutes "valid knowledge" is shifting to include not only normal scientific knowledge but "knowledge of practitioners" and "alternative knowledge;" the latter is becoming more relevant in decisionmaking.²⁵ Fourth, challenges to science are shared across stakeholders much more easily with the advancement of communication technologies.²⁵ Public perception and awareness of controversial issues such as biofuels is impacted by media portrayal, further affecting public participation in public policy and decision-making.²⁸ The next section draws on the literature by Batie and Fast and McCormick and highlights some of the ways energy transition to bioenergy is a wicked problem, especially describing the barriers to transition by using six of the ten characteristics that define wicked problems as outlined by Ritter and Weber.¹⁰ These characteristics frame the biofuel transition problem as a complex problem with wicked components. Characteristics that are described in detail include problem definition and

symptoms of other problems, ambiguous solutions, the stopping rule, consequences of imperfect solutions, and judging actions.



Figure 5.2. Linear trajectory of "normal science" form research to large scale implication. <u>Problem Definition and Symptoms of Other Problems</u>

Wicked problems are characterized by not having a clear formulation of the problem. Initially biofuels were promoted as a sociotechnical imaginary under the assumption that their implementation would provide a solution that can help mitigate climate change (itself a wicked problem), improve energy security and revive rural economies.¹¹ But eventually as biofuels have become more contested and stakeholder views have changed, there has not been a definitive way of distinguishing between "symptom and cause" of the problem.¹¹ Due to the constantly changing perceptions of stakeholders and the connection of biofuels to a range of different problems, there is no clear definition of the problem itself and no clear strategy for approaching the solution.¹¹ The solution depends on which aspect of the problem is prioritized by specific stakeholders.¹¹

Ambiguous Solutions

Wicked problems often don't have a definitive solution. The solutions are mostly viewed as "good or bad," "better or worse" or just "good enough."²⁵ There are no best solutions, just different options.¹¹ For example, one problem of biofuel production could be the issue of GHG emissions from land use change. The solution to this problem could be the implementation of policy that requires reduced GHG emissions, but what is the right amount of GHG emission reduction? For example, the US mandates a 20% reduction while Europe requires a 35% reduction.¹¹ There is also debate on whether there should be penalties for carbon debt or not.¹¹ A similar question could be posed such as: Will displacement of forest land for bioenergy crop production, to avoid competition with food, better or worse? In most of these cases both sides could be argued depending on who the stakeholders are and their values, further making the solution to the problem very ambiguous.

The Stopping Rule

As described by Fast and McCormick, "There is no final solution to wicked problems, planners and policy makers stop trying to address the problem not because the problem is solved but because the resources (time, money and patience) are depleted.^{"11} A good example of this, as outlined by Fast and McCormick, is the mandate made by the U.S. Congress for the U.S. EPA to include GHG emissions from indirect land use in rulemaking. However, after the completion of the second renewable fuel standard (RFS2), the EPA concluded that the solution to indirect land use change was incomplete and advancements in knowledge and assessment criteria in this area will continue to evolve, making it difficult to say definitively that a final solution was reached.¹¹

Consequences of Imperfect Solutions

Solutions change the problem and possibly introduce more problems, thus requiring new "problem formulation" and the issue is never settled.¹¹ As climate change becomes more tangible and the effects are felt across the world, the interaction of energy use, water use, land use, food production and how these all relate to climate change is relevant to what makes this whole system wicked. The issues of land use change, impacts on water quality and quantity, and the food vs. fuel debate (among a few others) are all barriers to the implementation of biofuels. These are examples of consequential problems that can fall under this category of wicked problem characteristics.

Impact of Biofuel Production on Land Use Change

Biofuels are inherently different from other renewable sources of energy due to land use change. The most immediate impacts of biofuel production on the environment and society are facilitated by direct or indirect land use change.²⁹ Land use directly affects society via use of farms, forests and ecosystems, and it impacts soil, water resources, and ecosystem functions.³⁰ The land is where people live and derive their food and water, and it provides recreation. Land is an integral part of human life, so anything that threatens the land threatens the livelihood of the people. Consequently, the notion that cellulosic biofuels can offset GHG emissions from fossil fuels is dependent upon the transition to biofuels meeting certain criteria regarding land use change. This includes avoiding the displacement of agricultural production, making sure that uncultivated natural lands are maintained to provide biodiversity and related ecosystem benefits and keeping carbon debt low when cultivating energy crops.³⁰ The issue with land use change is one of the most significant barriers posed to biofuels and is also a case study of how solutions

(displacement of fossil fuels by biofuels) to one wicked problem (climate change) could be imperfect and produce further problems (indirect land use change). Land use change in the Great Lakes is briefly addressed in the next section.

Land Use Change from Biofuel Production in The Great Lakes

According to a study by Mladenoff, 836,000 ha (37%) of non-agricultural land was converted to agricultural use in the Great Lakes States between 2008 and 2013, mostly for the cultivation of corn and soybean crops.³⁰ In the Midwest region, the biofuel industry was portrayed as a way of utilizing agricultural production to provide local employment and help reverse rural outmigration.³¹ But Mladenoff argues that available open land for cellulosic biomass cultivation in the Great Lakes region has peaked already in 2009 and the window of opportunity for establishing a "sustainable cellulosic feedstock economy" is closing rapidly due to the "reduction of open land availability for biomass production" and could incur a large GHG emission debt and negative effects as a result of indirect land use change.³⁰

Impact on Water Quality and Quantity

While bioenergy impact on land is one of the main concerns, bioenergy production also has considerable impact on water quality and quantity.³² This problem refers to how the hydrosocial cycle can be reshaped by the consumption of water due to increased land use for biofuel production, water contamination by nutrient leaching and GHG emissions related to water extraction. Unfortunately, the high demand for biofuels implies a high demand for biomass feedstock supply, which puts pressure on biomass production and supply in the form of agricultural sources to help meet this demand.²² In turn, this high demand for biomass supply will put even greater pressure on available water resources. Additionally, pumping fresh water from

ground or surface sources itself requires energy and could be GHG-intensive.³³ These issues will further add to the already existing problem of climate change and environmental issues.³⁴ In a cyclical way, climate change may impact water availability by altering water temperatures and duration of rainfall.³⁵ In addition to the GHG emission issue related to pumping freshwater and the water consumption to cultivate the biofuel crops, water is also needed for the fermentation process to make ethanol. According to Magdoff, it takes about five gallons of "new water" for one gallon of ethanol production from grain fermentation. This implies that a fully functioning ethanol plant that produced millions of gallons of ethanol per year could consume as much water as a town of five thousand people.³⁶ As for water quality, intensified biofuel crop production could increase nitrate and phosphate leaching into water sources.³⁷ As has been reported by Magdoff, cultivation of corn has led to leaching of nitrates into groundwater and surface water causing contamination of drinking water in communities in the Midwest. ³⁶ Additionally, the use of pesticides and other chemicals leads to further leaching of these chemicals and their derivatives into groundwater supplies.³⁶ So again, ultimately the production of biofuels, which is introduced as a solution to the wicked problem of climate change, further creates a problem loop related to water quality and quantity.

Water and Energy in the Great Lakes Region

This issue of water consumption and quality, though relevant anywhere in the world, becomes even more relevant in the Great Lakes region which holds 20% of the world's fresh surface water supply and 95% of the U.S. surface freshwater supply.³⁸ With such abundant water resources, the Great Lakes are attractive for water-intensive energy production systems and energy in turn is needed to ensure a clean water supply. Considering two Great Lakes

states,Wisconsin and Ohio, are among the top ten producers of biofuels in the nation, the issue of management of water withdrawal from surface and ground sources is a critical problem for this region.³⁹ But in the Great Lakes, water planning and energy planning are separate from each other, making it more difficult to effectively evaluate their impact on one another.⁴⁰ As the energy sector is the largest water user in the Great Lakes, most of it going towards hydroelectric power generation, thermoelectric power cooling, petroleum refining, and conversion of corn to ethanol, the wicked problem of water consumption and withdrawal is an issue that will need to be addressed.⁴¹ The challenge is the proper integration of energy and water management systems and monitoring of water quality and quantity "in real time" as it relates to energy production.

Concerns About Food vs. Fuel

This issue is another example of consequences of imperfect solutions. Biofuel production could affect food prices by replacing food crops with fuel crops.⁴² Growing corn and soybean as energy crops competing with food supply is a problem that can possibly be solved by clearing land that is not designated for farming to grow designated energy crops. But this "solution" could introduce another problem, indirect land use change, which results in additional GHG emissions from clearing land not designated for agriculture such as rainforest or grasslands elsewhere to sustain the global food crop demands.

Other Problems

Recently the biofuel industry has also faced competition from dropping oil prices. In addition, there are concerns regarding palm oil use for biodiesel production affecting forest biodiversity.¹¹ Biofuels can also affect biodiversity by direct or indirect conversion of forest and

other types of land.³⁷ More importantly, there is concern that some of the second generation biofuel crops could pose a threat to the environment as invasive species.³⁷

Judging Actions

"Consequences of actions 'matter' to the public and are judged by citizens and powerful stakeholder groups." ¹¹ In contrast to tame problems, failures by wicked problems are not treated as learning experiences to avoid future problems. Additionally, more actors outside of the problem solvers are involved in judging these failures, ¹¹ and the failures are judged more critically by stakeholders. This poses a challenge for the implementation of biofuels in terms of finding solutions for the barriers to implementation.

Biofuels Viewed through Political Ecology Framework

As a wicked problem the transition to biofuels is influenced by social and political factors with different stakeholders influencing the decision-making process.²⁵ The political ecology framework deals with how the distribution of power determines the use of natural resources as the physical environment is not separate from political and economic factors.¹² When looking at regional (Great Lakes) impacts of biofuel production, ecological, societal and economic issues need to be considered to identify and address issues and barriers.⁴³ In the Great Lakes, demand for energy is generally driven by economics, social, and political factors, while energy production has impacts on the environment, economics, social structures, and human wellbeing.⁴⁴⁻⁴⁶ Because the costs and benefits associated with environmental change are unevenly and disproportionately distributed among humans, investigating where the power of decision resides is very crucial for implementation of biofuels. As it relates to biofuel transitions, the political ecology framework can help in examining the interactions between powerful actors and how

decision-making is influenced by these interactions. The question of who holds power, who influences and implements policies, who benefits from these policies and who gets to enjoy the incentives are all very important questions that can help frame the issue with transitions to biofuels. For a bioenergy system, there are potentially several actors at play that could leverage power. These actors could include land owners, inventors (including academics), corporations (e.g. energy companies), consumers, regional government, and the federal government.

To use the political ecology framework to analyze biofuels in the Great Lakes region, the energy consumption of the region must be understood. This section shows how two states, Michigan and Wisconsin, serve as proxies for the region and therefore reveal important energy drivers relevant to this region. Then, the political ecology framework is used to explore (or examine, or assess) how some of the aforementioned actors interact in order to measure their influence on bioenergy systems in the Great Lakes.

Energy Demand, Production and Consumption in the Great Lakes

Michigan is among the top ten states in population and energy consumption.⁴⁷ Residential consumption is the largest user of energy with most of the energy going towards heating homes (due to the relatively cold weather), followed by the industrial and manufacturing sectors.⁴⁷ Michigan used coal the most (37.1%) for its electricity production in 2015, with natural gas (26.9%), nuclear energy (28.4%) and renewable sources (6.2%) also being used.⁴⁷ Out of that 6.2% contribution of renewable sources in 2015, biomass accounts for 35% of the electricity production, exceeded only by wind energy.⁴⁷

Currently Michigan's five operational ethanol production plants have the capacity to produce 270 million gallons of ethanol per year using corn as the major feed, making Michigan the 12th

largest ethanol producer in the nation.⁴⁷ Additionally its three biodiesel refineries produce 10 million gallons of biodiesel per year. ⁴⁷ In part due to the Clean and Renewable Energy Act of 2008 (Public Act 295), which mandates that "electricity suppliers obtain 10% of the electricity they sell from renewable sources", renewable energy has become an important aspect of Michigan's energy production and consumption, contributing to about 8% of Michigan's electricity genereation.⁴⁷ To achieve the requirements of this mandate, Michigan "offers tax incentives in Renewable Energy Renaissance Zones (RERZs)".⁴⁷ These zones are specifically designated areas to be conducive for the advancement of renewable energy technologies.⁴⁷

In Wisconsin, the industrial sector accounts for 32% of the state's energy use, and residential consumption per home in the state exceeds the national average by 15%.³⁹ Electricity is generated mainly from coal (53%), followed by natural gas (25.6%), nuclear energy (14.4%) and renewables (6.7%). Biomass primarily from animal waste accounts for one third of the renewable energy production. Additionally, due to its rich agricultural resources, Wisconsin produces over 500 million gallons of ethanol per year, making it one of the top 10 ethanol-producing states in the nation.³⁹ Through the establishment of the Energy Office in 2003 and the Office of Energy Independence in 2007, Wisconsin aims to achieve the goal of producing all of its electricity from renewable energy.³⁹ Furthermore, legislation established in 2006 mandates that 10% of energy sales come from a renewable source.³⁹

Looking at similar energy profiles of other Great Lakes states reported by the U.S. Energy Information Administration, it is clear that the Great Lakes region is a hub for energy production, with states like Indiana "capable of producing more than 1.2 billion gallons of ethanol per year", and Ohio being one of the seven largest ethanol-producing states in the nation -producing 530 million gallons of ethanol per year.⁴⁸ Yet another example is Illinois, a major corn and soybean producer with the third largest production capacity for both ethanol and biodiesel.⁴⁸ Clearly, Great Lakes states can have varied energy consumption needs for various sectors that are satisfied using both renewable and non-renewable sources of energy. Furthermore, the Great Lakes region is a major contributor to biofuels production in the U.S. Consequently, understanding the social and political drivers of the bioenergy system in the Great Lakes is important. To this end, an exploration of how different actors such as energy consumers, land owners, and other regional entities exercise their power in promoting or resisting the transition to a bioenergy system follows.

The Consumers and Land Owners

In the transition to biofuels, several types of actors may be involved, including public energy consumers, private non-corporate land owners and farmers. These actors have political power in terms of electing public officials, being willing or unwilling to supply land for biofuel crop production, being willing or unwilling to provide privately owned forest lands for advanced biofuel, and supporting or not supporting biofuel production facility sitings. Although there is some public support for transitioning away from conventional fossil-based fuels to renewable fuels, often when it comes to the actual siting of the renewable energy facilities the public can have a "not in my back yard" (NIMBY) attitude which poses a significant barrier for transition.¹⁸ Farmers and private (non-corporate) land owners could also prove to be resistant to biofuel crop production. In Wisconsin and Michigan, private land owners are unlikely to rent land for bioenergy crops. Even the land they are willing to supply is often covered with forest or crops, which means growing biofuel crops on this land could result in direct or indirect land use

change.⁴⁹ According to Swinton et al., while 55% of rural land in the northern part of the Great Lakes is covered by forest, land owners are "reluctant to replace forest with bioenergy crops" even at 2-5 times the regular rental rate for crop land.⁴⁹ "Less than 30% of landowners are willing to rent land for bioenergy crops" and even less (<10%) are "willing to rent land for corn and switchgrass".⁴⁹ In terms of cropland (which accounts for 28% of land use), only "28% of landowners showed willingness to rent land for corn" cultivation for biofuel production at double the rental rate.⁴⁹ For "farmable non-crop marginal land" (11% of the land area), only 23% of landowners would rent it for five times the normal rate.⁴⁹ Additionally, landowners also have the power to dictate the types of crops that can be planted on their land.

Regional Entities

Regional entities are typically governing bodies at the regional level. In the Great Lakes region, the Great Lakes Commission is one such governing body, described on its website as:

"...an interstate compact agency that promotes the orderly, integrated and comprehensive development, use and conservation of the water and related natural resources of the Great Lakes basin and St. Lawrence River. Its members include the eight Great Lakes states with associate member status for the Canadian provinces of Ontario and Québec." ⁵⁰

The Great Lakes Commission through the Great Lakes Compact is also authorized to conduct studies and implement plans regarding energy, the economy, and the environment.⁴⁰ The Great Lakes Commission's mission indicates a commitment to the promotion of clean energy to curb GHG emissions and to ensure energy security in the Great Lakes region.

"Energy production and use have an impact on the Great Lakes and St. Lawrence River economy and environment, including water resources. The current national energy mix, which relies primarily on fossil fuels, is an important contributor of greenhouse gas emissions. The Great Lakes states and provinces have joined two different regional forums to address this issue: the Regional Greenhouse Gas Initiative (New York, Québec and Pennsylvania) and the Midwest Governors' Association's Energy Security and Climate Stewardship Platform (Illinois, Indiana, Michigan, Minnesota, Ohio, Wisconsin). Still, there is no forum to address energy issues for the Great Lakes region as a whole. With our stateprovincial membership and mandate, the Commission is uniquely positioned to bring Great Lakes states, provinces and other stakeholders together to advance clean energy with a focus on how energy issues affect the water and other natural resources of the Great Lakes Basin." ⁵¹

As it pertains to clean energy, the Great Lakes Commission provides consultations with the state to help in evaluating and making recommendations concerning water use for energy. This is done to align with the objectives of the Great Lakes-St Lawrence river basin Sustainable Water Resource Compact.⁴⁰ To achieve this, the Great Lakes Commission aims at bringing together "federal agencies including U.S. EPA, Department of Interior (USGS), The U.S. Department of Energy, Environment Canada and Fisheries and Oceans Canada to collaborate with" states and provinces on matters of water and energy in the region.⁴⁰ The major goal is to promote the "region as a global leader for clean water, renewable energy and energy efficient technologies".⁴⁰ Powerful local actors such as the Great Lakes Commission, among others, have the ability to shape perceptions regarding the impact of bioenergy.⁵²

Other Actors

Other actors that have invested interest in bioenergy transitions include scientists and academics that have the power of scientific knowledge, research and tools to influence decision making and policy. In the Great Lakes region, The Great Lakes Bioenergy Research Center, funded by the U.S. Department of Energy and led by the University of Wisconsin-Madison and Michigan State University, has been conducting biofuel research for the past decade and is making advancements in biofuels. Its mission is "to perform the basic research that generates technology to convert cellulosic biomass to ethanol and other advanced biofuels."⁵³ Institutions such as this have power due to the scientific knowledge they possess which can impact public perception and decision-making backed by scientific data.

Other stakeholders with a vested interest include corporations (e.g. energy companies) and the federal government. The federal government has the power to implement policies and create incentives and subsidies, while the biofuel production companies and corporations could stand to benefit from these government subsidies and tax benefits, such as the federal renewable energy production tax credit (PTC). PTC "provides tax credit for the first 10 years of renewable energy facility operation".⁴⁰ Such alliances between corporations and the state could have the power to influence land ownership and livelihoods of rural communities.⁵⁴

Further analysis in this area can be done by asking questions such as, what are some of the partnerships in place for specific regions? How do partnerships, for example between both national and local governments and corporations, determine who gets the benefits? ⁵⁴ What are the implications of these partnerships? If there is lack of regulation, who will be responsible for the social and environmental impacts?⁵⁴ Who in the society loses or gains economic benefits if

the transition to biofuels is successful?⁵⁴ What is the impact on the environment?⁵⁴ Who may be disproportionally affected by the side effects of the environmental impacts?

The Path Forward

To fully understand the barriers to biofuel transitions through the wicked problem and political ecology frameworks, it is important to think about how to move forward to address some of these issues. Batie argues that normal science is inadequate to address wicked problems and that the combination of science and social science could better address the complexities of wicked problems.²⁵ Because of both the "biophysical complexity" and "multiple stakeholder perception," the solution to wicked problems is not just a scientific and technological endeavor but also a social and political one.⁵⁵ Social acceptability of biofuels can be affected by societal values shared by members of the society.¹⁶ Those values could be related to different aspects of the technology because different things are important to different stakeholders with different values. For example, there is resistance to offshore wind parks in Germany even if generally the public is very supportive of renewable energy efforts.¹⁶ Similarly, communities from ethanol producing regions in the U.S. understand and support ethanol production to help tackle energy security issues; however, they do not have high satisfaction with the economic benefits, they express concerns about water and air quality, and they are uneasy about the risk of a decline in the bioenergy industry in the future.^{56, 57} Therefore, to overcome public resistance to biofuels transitions, the technological design and the institution need to take these values into account.¹⁶ Künneke et al. argue that as moral and social values largely feed into societal acceptability of certain technologies and institutions, these values need to be incorporated in the design of the technology or the institution.¹⁶ A more integrative approach needs to be taken and concerns

from the community should be addressed.¹⁶ Rather than only focusing on laws and incentives to promote biofuel production, policymakers need to focus on social influences, i.e. building trust and social capital to facilitate "internalization" of benefits of biofuels is necessary.¹⁶ Public participation in decision making and formulation of social criteria and indicators is essential for the future success of bioenergy.^{58, 59} The science behind biofuels already supports its commercialization, but there is an intricate social network within the bioenergy systems that is often overlooked. A successful path forward would be a more integrated system that brings science and people together to help policy makers internalize the social dimension of biofuels.⁵⁸

Conclusion

This treatise has described some of the issues facing the transition from fossil fuels to biofuels by looking at the resistance to transition as a wicked problem and by looking at the social actors that influence this transition. Different participants in the system will often have different perceptions of the problems, and the outcome of the solution should be a combined effort between the scientific, political, and social sectors. This may require closing the gap between science and society. "Knowledge and action" (science and policy) need to be combined in order to address the challenges of biofuels acceptance.²⁵ Biofuels, if managed in a truly sustainable manner, can help solve various environmental, social and economic problems by providing access to high quality energy to promote "human prosperity and well-being,"⁶⁰ energy security, improved water and soil quality, emission reduction, job creation and food security. ⁶⁰

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Chapter 6 : Conclusions and Future Recommendation

Conclusions

Six lignin streams extracted from EA and Cu-AHP processes were characterized using elemental analysis, bomb calorimetry, TGA, and py-GC/MS to understand their thermal degradation properties and products. EA-F3 fraction had the highest carbon content, lowest oxygen content and the highest higher heating value of the EA and the Cu-AHP lignins. The EA lignins all exhibited significant levels of nitrogen. TGA analysis showed that that all fractions degrade over a large temperature range (100–600 °C) as is expected for lignins. Close to 60% of the mass for these samples was lost by 500–600 °C while some char was recovered. Analytical pyrolysis was primarily used to observe the product distributions of the six lignin fraction. EA lignins, derived from herbaceous biomass, exhibited pyrolysis products such as *p*-cresol, 4-vinylphenol and 3-ethylphenol while vanillin and syringaldehyde were only observed for poplar lignins.

Based on the list of model compounds obtained from py-GC/MS analysis, model compounds phenol, *p*-cresol, 4-ethylphenol, and 4-propylphenol creosol, guaiacol, 4-ethylguaiacol, 4propylguaiacol and eugenol were successfully subjected to ECH and successfully hydrogenated and deoxygenated at high conversion rates. Alkyl chain length was demonstrated to have an effect on conversion of both alkylphenols and alkylguaiacols; in both studies, formation of alkyl cyclohexane was observed with increasing alkyl chain length. In the case of alkylguaiacols, selectivity towards the formation of the alkyl-substitute 2-methoxycyclohexanol increased with increased alkyl chain length. Model monomers, vanillin and syringaldehyde, were also hydrogenated and deoxygenated. Though to a lesser extent than the phenols and guaiacols. Methyl and methoxy group positions on the aromatic ring were observed have an effect on conversion where the proximity of the methyl and methoxy groups resulted in higher conversion rates. To improve the modest faradaic efficiency, the effect of increased substrate concentration was studied and found to have a positive effect. Finally, in an effort to develop a one pot process that can be used to upgrade lignin intermediates and avoid the high temperature/pressure catalyst reduction step, an electrodeposition of ruthenium catalyst *in-situ* was tested and was found to be comparable to the regular Ru/ACC. Additionally, catalyst recycling, which is an important aspect of making this process greener, was tested for both Ru/ACC and EC-Ru/ACC and was demonstrated to be successful.

Based on dimer pyrolysis results that indicated the resistance of 4-O-5 linkages to thermal cracking at 650 °C, model dimers 3-phenoxyphenol, 4-phenoxyphenol, 3-phenoxyanisole and 3-phenoxytoluene were investigated. Though conversion of 3-phenoxyphenol and 4-phenoxyphenol to cyclohexanol was high, 3-phenoxyanisole and 3-phenoxytoluene showed significantly lower conversion rates and yields. For 3-phenoxyphenol, increased substrate concentration was found to increase faradaic efficiency modestly while 96% faradaic efficiency was achieved at lower current density (20 mA). This has promising implications for the energy efficient depolymerization of lignins using electrocatalysis.

In addition to technological and scientific advances that make bioenergy use more viable, social factors also influence the adaptation of biofuels and bioenergy. Briefly, the barriers to bioenergy adaptation by society are examined from a social science perspective using the wicked problem framework.

Future Recommendations

- 1. Quantify the yields of EA and AHP lignin pyrolysis products both using analytical scale and bench scale pyrolysis to determine the carbon and mass balances.
- Develop a fundamental understanding of the kinetics of the ECH system for different lignin derived functionalities to determine rate limiting steps to further improve the efficiency and minimize energy inputs.
- 3. To further understand the interactions of bio-oil components during ECH, mixture trials should be expanded and studied in a comprehensive manner.
- Following mixture studies, lignin derived raw bio-oil studies should be run to test the how knowledge from model compound studies can inform real bio-oil ECH.
- 5. Test electrodeposited methods for conversion of various other lignin derived model compounds and dimers and further explore the use of cheap anode materials.