TOWARDS CONTINUOUS BIO-OIL UPGRADING USING ELECTROCATALYTIC HYDROGENATION

By

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A THESIS

Submitted to Michigan State University in partial fulfillment of the requirements for the degree of

Biosystems Engineering — Master of Science

ABSTRACT

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Electrocatalytic hydrogenation (ECH) offers a viable option for improving bio-oil's properties for use as a fuel product. Studies using ECH are typically performed in a batch reactor, owing to the convenience of the experimental procedures. However, batch studies offer limited rate information and low productivities. For this reason and since continuous systems are preferred in industrial applications, continuous studies are needed.

In the following study, a direct methanol fuel cell (DMFC) was modified to act as a proton exchange membrane (PEM) fuel cell that can continuously convert furfural into its hydrogenated products, furfuryl alcohol and tetrahydrofurfuryl alcohol, under constant current using a Ruthenium catalyst. The cell was designed with an increased geometric surface-area-to-volume ratio compared to current batch reactors to enable quicker conversion. The most significant factor affecting the faradaic efficiency was the current, while product yield was affected most by the initial concentration. Conversion of 5-hydroxymethylfurfural to 2,5-dihydroxymethyltetrahydrofuran was also observed in significant quantities, however, due to the unavailability of standards, results could not be properly quantified. When operating in a single pass, the reactor was able to achieve successful hydrogenation of furfural to tetrahydrofurfuryl alcohol for the first 4 hours but was deactivated due to either catalyst leaching or active site blocking.

ACKNOWLEDGMENTS

I would like to begin my thesis by thanking everyone who has helped in its completion. There were lots of barriers and struggles during it but through their support, guidance, and advice, this work was completed and would not have been possible without them.

First, I would like to thank my graduate advisor, Dr. Saffron, for all the support, advice, and encouragement he has provided throughout this project. I was able to learn so much from him. To the other members of my graduate committee, Dr. James Jackson, and Dr. Wei Liao. I would like to thank them for their patience and flexibility during this research along with their feedback and encouragement in its completion.

To the members of the research team, specifically Meheryar Kasad. I would like to thank him for everything he has helped with throughout the completion of this work. From his mentoring in the lab, patience, advice, and friendship, this project was completed and would have not been nearly the quality it is without him.

To my family and friends that have supported me along the way; this project has been filled with lots of ups and downs and I cannot thank them enough for any support they gave. No matter how small it may have seemed or how easily it was given; it was essential for the completion of this work.

As my time here comes to an end, there are so many things that I will miss from MSU and so many memories I will carry with me after I leave.

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I. Introduction

Climate change continues to be an issue in the world due to the increasing greenhouse gas (GHG) emissions, mainly carbon dioxide (CO₂). According to the National Aeronautics and Space Administration (NASA), 19 of the 20 warmest years on record have occurred since 2000 with the highest in 2016 and 2020 at 1.02° C above the 1951-1980 average. Recently, temperatures have stayed at their elevated levels and the last 6 years have been some of the warmest on record. This increase in global temperatures has resulted in environmental impacts such as the melting of the polar ice caps causing sea levels to rise. The increase in global temperatures can be directly related to the rise in carbon dioxide levels. In July 2021, the Mauna Loa Observatory recorded the CO₂ concentration at 417 parts per million (NASA, 2021).

The Environmental Protection Agency's (EPA) 2019 annual report of United States (U.S.) emissions by economic sector identified the highest emitting industry was transportation at 29%, equating to 1.902 billion tonnes of CO₂ equivalent per year. This is due to the use of fossil fuels and petroleum products such as gasoline or diesel that are combusted for energy(U.S. EPA, 2021). While these products are extremely useful for energy, the combustion of gasoline and diesel results in 8.9 kilograms (kg) per gallon (gal) and 10.17 kg per gallon of emitted CO₂, respectively; CO₂ emissions from fossil fuels are not captured at the same rate as they are emitted, thus leading to climate change according to the U.S. Energy Information Administration (EIA) (US EIA, 2014). CO₂ emissions when sustainably burning biofuels are photosynthetically balanced as part of the global carbon cycle.

When a biofuel such as ethanol is blended into gasoline, the octane levels increase allowing it to combust more completely (Minnesota Bio-fuels Association, 2016). The most common ethanol-gasoline blend, E10, contains about 10% ethanol by volume, emits about 8.6 kg

of CO_2 per gallon during combustion. While lower, there is not a significant difference between E10 and pure gasoline in terms of their CO_2 emissions. When evaluating diesel emissions, B20 is the most common biodiesel-petroleum diesel blend. When combusted, B20 emits about 9.19 kg of CO_2 per gallon which is closer to the emissions of pure biodiesel combustion at about 9.15 kg CO_2 per gallon. These blended products are still primarily petroleum-based fuels that are not able to recycle their emissions out of the atmosphere. Therefore, there is a greater need for greener fuels that recycle the CO_2 emissions produced during combustion(US EIA, 2014).

Recently, research began on a new alternative fuel additive and potential replacement; bio-oil. It is derived from fast pyrolysis and while it is more similar to gasoline than ethanol, it is very unstable, corrosive, contains a high amount of oxygen, and is very viscous; all properties that are unlike conventional petroleum fuels. Because of these issues, an upgrading step is required during bio-oil production.

Currently, techniques used for upgrading bio-oil include hydroprocessing and catalytic cracking which both operate at extreme pressures and temperatures. Therefore, alternative upgrading methods are being investigated. One alternative that operates at more mild operating conditions is electrocatalytic hydrogenation (ECH). ECH involves passing an electrical current through water to split the molecules into oxygen atoms (1/2O₂), hydrogen ions (H⁺), and electrons (e⁻). The oxygen atoms form an oxygen molecule (O₂) and leave the system while the H⁺ cross a membrane to combine with the oxygenated molecules like those present in bio-oil. Hydrogenating the individual molecules results in a stabilized bio-oil product that is less corrosive and more energy dense.

Even though upgraded bio-oil seems to be a promising alternative to petroleum-based fuels, economic constraints have made biofuel production problematic. When looking at the

economics of the process, the extra processing steps to upgrade bio-oil increases the manufacturing cost and therefore, the selling price. While using biofuels, including bio-oil, does reduce GHG emissions due to their ability to recycle CO₂ emissions, fossil fuels are much cheaper due to their higher energy density and optimized processing strategy.

One way to make biofuel production more economically favorable is to transition the technology from a batch system to a continuous processing system. Continuous upgrading using ECH could require less energy, lower catalyst inputs, and lower capital costs while being able to output a larger amount of stabilized product that can be processed into fuel. Because there is less downtime involved with a continuous system, more products can be produced which decreases the overall operating costs. Research on continuous systems is extremely limited, therefore this thesis attempts to help close the knowledge gap in the area using 2-furfuraldehyde (furfural) as the model compound and ruthenium (Ru) on activated carbon cloth as a catalyst.

II. Literature Review

1. Ethanol as a Biofuel

In 2019, the U.S. EIA reported that the U.S. consumed about 105.7 EJ of energy, 89% of which came from non-renewable sources. Most of these non-renewable sources are petroleum and natural gas, which are mainly used by the transportation and industrial sectors, respectively. As stated earlier, these non-renewable sources produce high levels of CO₂ and have been linked to climate change. Only 11% of the energy consumed came from renewable sources where biofuels account for 20% (US EIA, 2020).

Most biofuels being used today come from grains, starches, and vegetable oils and are considered first-generation. These contain high amounts of glucose that is fermented into ethanol. Ethanol production generally starts with milling the grains and starches to increase the surface area and provide the yeast with easier access to the glucose monomers. This is followed by fermentation where yeast produces ethanol from the exposed glucose. Finally, the mixture is distilled to purify the ethanol. The most common strain of yeast used in first-generation ethanol production is *Saccharomyces cerevisiae* (*S. cerevisiae*) which uses glycolysis for fermentation from glucose monomers. The utilization of more complex molecules from biomass is still being researched but currently, first-generation ethanol is the only renewable, biomass-derived fuel used in the transportation industry. It is commonly blended in a 10% ethanol-90% gasoline (E10) ratio to make gasoline burn more completely and cleanly while also helping the transportation industry reach federal renewable fuel standards (Naik et al., 2010).

Although ethanol has been an environmentally friendly addition to gasoline, problems begin to arise when considering the amount of energy provided. Ethanol has a very low energy density, 26.8 MJ/kg LHV, which is about 67% of the energy density of gasoline, 46 MJ/kg LHV.

Thus, a gallon of E10 contains about 96% of the energy in a pure gallon of gasoline (Hore-Lacy, 2007). This low energy density makes a complete switch to ethanol as a fuel for transportation unlikely.

Another reason why ethanol production is concerning from an industry standpoint is the low theoretical yield of fermentation. This occurs for a variety of reasons. First, in the chemistry associated with fermentation, yeast releases about a third of the feedstock's carbon as CO₂, based on the stoichiometric relationship of the reaction, creating a maximum theoretical carbon yield of only 67%. On a mass basis, this translates to about 0.511 grams (g) of ethanol produced per gram of glucose metabolized. The sensitivity of glycolysis and fermentation to the reaction conditions can also impact ethanol yield. Conditions like ATP deprivation, byproduct production, inhibition from ethanol accumulation, and environmental stresses, usually decrease the yield to 60-62% (0.46-0.475 g ethanol produced per 1 g glucose metabolized) (Bai et al., 2008).

First-generation ethanol production is also considered in the food vs. fuel debate. Ethanol is commonly produced from corn grain but can also be used as animal feed for chickens, cows, and pigs. Given its importance, the food industry can commit more resources to secure its supply thereby decreasing the amount available for ethanol production. This problem raises the importance of second-generation biofuels that are derived from lignocellulosic feedstocks like corn stover and wheat straw or grasses like switchgrass that are not used in the food industry. These biofuels offer significant economic and environmental advantages but are not in the production stages yet. The process differs by requiring a hydrolysis step before fermentation to further break the biomass fractions of cellulose, hemicellulose, and lignin into their respective sugar monomers. During this process, lignin, which represents about 10-25% of a plant's biomass (Wang et al., 2017), is often disregarded because it is unable to be fermented into

ethanol due to its varying structure of *p*-hydroxyphenyl, guaiacyl, and syringyl units. Because it is very difficult to utilize without a deconstruction process, currently, almost all lignin is burned as a low-grade fuel for process heat resulting in decreased yields of ethanol per unit biomass (Garedew et al., 2020a).

2. Whole Biomass Utilization

Lignin utilization presents a major but necessary challenge for biomass-derived fuel production for several reasons. First, lignin's volume in plants provides an abundant feedstock source for fuel production. Based on the Billion-Ton Report released in 2016, the amount of fossil carbon in petroleum utilized by the U.S. exceeds the amount of carbon projected for the 2030 production of non-food biomass (Langholtz et al., 2016). The U.S. cellulosic ethanol industry produces about 60 million tons of lignin per year, a surplus compared to what is combusted for process heat. Therefore, whole biomass utilization, including lignin, is needed for significant biofuel production. Second, lignin contains the highest energy per unit mass in biomass (22.2–28.5 MJ/kg), compared to cellulose (17.5 MJ/kg), due to its higher carbon to oxygen ratio (2:1 in lignin vs. 1:1 in cellulose). To produce a suitable biofuel replacement for petroleum, lignin utilization is critical.

In nature, lignin exists as a polymer interwoven between the cellulose and hemicellulose fractions of a plant. To utilize lignin, it must be broken down into its three main functional units, or monomers: *p*-coumaryl, coniferyl, and sinapyl alcohols, which are converted into their base phenolic hydroxyl, guaiacyl, and syringyl units, respectively. The exact percentages of these monomers vary depending on the type of plant. In softwoods, coniferyl alcohol makes up about 90-95% of the lignin compared to grasses, which are more evenly distributed. Linkages between monomers are made up of carbon-carbon bonds and ether linkages. The most common linkage is

the β -aryl ether (β -O-4), which makes up around 50-60% of the total depending on the plant species. These bonds must be cleaved to separate monomers for conversion to the base units and can occur through many different platforms (Wijaya, Smith, et al., 2020a). This can be done in a pretreatment step that degrades polymers, separates biomass fractions, and potentially causes chemical transformations. Some common pretreatment steps are Kraft, Steam Explosion, AFEX, and pyrolysis. The most common pretreatment in the paper industry is the Kraft lignin process, which uses high pH's, high amounts of aqueous sodium hydroxide, and high temperatures with residence times of about 2 hours (hrs) to deconstruct lignin. After this pretreatment step, Zakzeski et al. discuss the production of higher-value chemicals and fuels in a biorefinery through different treatment methods. The use of catalysis in the petroleum industry can also perform transform lignin from a low-quality, low-value waste by-product to value-added renewable, aromatic compounds. This offers the potential for integration of a biorefinery with the petroleum industry infrastructure to would reduce the capital costs (Zakzeski et al., 2010).

Another significant portion of biomass available to be utilized is the hemicellulose fraction. Generally, hemicellulose makes up 15-30% of a plant's mass but can be as high as 35% in bioenergy crops such as switchgrass. Its structure consists mainly of hexoses, such as glucose and galactose, and pentoses, such as xylose and arabinose. The amount of these varies significantly based on the type of plant. Hardwoods and grasses generally have significantly more pentose sugars, specifically xylose, and softwoods usually have more hexoses. The different types of long sugar chains contained in hemicellulose have significantly different properties based on their composition. For example, in hardwoods, the most abundant polysaccharide is glucuronoxylan, O-acetyl-4-O-methylglucuronoxylan, which has a degree of polymerization of about 200 compared to the most abundant polymer in softwood hemicellulose,

galactoglucomannan, which has a degree of polymerization between 40-100. This means that chains of molecules in hardwoods can be much longer than in softwoods (Wang et al., 2017). In ethanol production, hemicellulose is often disregarded due to its heterogeneous structure and inability to produce ethanol in significant yields. Because of this, it is often separated using a pretreatment step. To utilize hemicellulose and optimize the yield of ethanol per unit biomass, biotechnological advances are being developed, such as genetic recombination of *S. cerevisiae* or other microorganisms to better convert hemicellulose to ethanol and be less sensitive to the reaction conditions (Gírio et al., 2010).

Many of the biomass conversion platforms fall under three categories: biological, chemical, and thermochemical. Biological platforms utilize bacteria and enzymes to break down lignin similar in function to the rumen in animals such as cows. They offer a very eco-friendly solution and can be genetically engineered for high selectivity of specific chemical production. However, they generally have low efficiency and require a long culture period before production. These platforms are currently used to produce a great variety of products used in different industries. Chemical platforms like acid- and base-catalyzed depolymerization operate at temperatures between 100-350 °C and require a catalyst for operation. Acid- and base-catalyzed processes are a low cost and effective solution for biomass conversion yet, they often pose environmental concerns and are prone to polymerization. Thermochemical platforms, which include pyrolysis and gasification, break down biomass at temperatures greater than 400 °C to produce products such as non-condensed gas, bio-oil, or biochar. Pyrolysis operates quickly and easily but offers low product selectivity in production with byproduct formation (Garedew et al., 2020a) (Chio et al., 2019).

3. Bio-oil Production and Upgrading

Fast pyrolysis is considered the most effective way to produce bio-oil for energy generation. It involves heating biomass to about 500 °C for about 1 second in the absence of oxygen which produces biochar, non-condensable gasses, and organic vapors containing molecules with high oxygen content such as aldehydes, phenolics, and furans. This process often follows drying and grinding to maximize heat transfer, mass transfer, phase transition, and chemical reaction kinetics. After pyrolysis, vapors are condensed into bio-oil at yields of around 75%.

One of the most common fast pyrolysis reactor types is the fluidized bed reactor that uses recycled gas and biochar to heat the reactor. There are two types of fluidized bed reactors: bubbling and circulating fluid beds. Bubbling fluid bed reactors are understood and offer advantages such as simple construction, operation, and efficient heat transfer. These reactors stream hot gas at high speeds through the dried biomass particles causing it to behave like a fluid. During this, biomass is pyrolyzed and the heated biochar-vapor mixture is ejected into cyclones to collect the char and avoid undesired char-catalyzed vapor cracking of the bio-oil. Circulating fluid bed reactors heat incoming biomass similarly, however, the hot sand exits the reactor with the pyrolysis vapor and is recovered after char combustion in the associated furnace. This corresponds to a higher char production which can be burned to heat the sand for the reactor. Both reactor types have a high bio-oil yield of 70-75% and are established in the bio-oil industry (Bridgwater, 2012).

BTG Bioliquids is a commercial bio-oil manufacturer that uses multiple rotating cone fast pyrolysis reactors each capable of producing 2,000 kg of bio-oil per hr. In this configuration, hot sand, heated char, and biomass are fed into the bottom and driven up a rotating cone while they

are heated; the organic vapors exit the reactor and are condensed after being separated from sand and biochar. These reactors usually produce bio-oil yields of 60-70% (Bridgwater, 2012; BTG Bioliquids, n.d.)(BTG Bioliquids, n.d.).

Kelkar et al. studied pyrolysis in a screw-conveyor reactor. In this type of reactor, biomass is fed into a hopper that constantly feeds the reactor's screw, which conveys biomass through the different heating zones along the reactor barrel. After the mixture exits the reactor, biochar is collected, the organic vapors are condensed into bio-oil, and the non-condensable gases (NCG) are released or combusted to heat the reactor. Using this reactor design, Kelkar et al. evaluated the effects of temperature and residence time on bio-oil yield produced from spent coffee grounds were evaluated. From their data, a statistically developed response surface model was used to find the optimum conditions for maximizing bio-oil yields. In doing this, they were able to find that the bio-oil yield increased with decreasing residence time and increasing temperature up to 505 °C with a maximum yield of 61.7% (Kelkar, Saffron, Chai, et al., 2015). Using this data would encourage the establishment of an industrial bio-oil system from spent coffee grounds.

While fast pyrolysis is a promising way to convert whole biomass into a fuel, barriers to its commercialization include a high operating cost, undesirable properties, and low product selectivity. Heterogeneous catalysis using zeolites has improved pyrolysis yields and selectivity toward aromatic compounds (Kelkar, Saffron, Andreassi, et al., 2015). These zeolite catalysts provide high activity and break down larger molecules to facilitate mass transport into catalyst pores. However, such catalysts are prone to coke formation which blocks catalytic active sites. Kelkar et al. created a catalyst using crystallized and calcinated polymers containing both nitrogen and silicon for structure directing. Results from poplar catalytic fast pyrolysis found

increased pyrolysis vapor yield and product selectivity toward larger aromatics due to mesopore size while also reducing char and coke formation. These results improved further when their catalyst was loaded with gallium (Kelkar et al., 2014).

When produced, bio-oil's properties can be problematic for fuel usage in four ways. First, fresh bio-oil has a very high viscosity and contains between 15-30% water along with many small organic molecules that are not economically condensable. Second, the higher heating value (HHV) of bio-oil, 16-19 MJ/kg, is significantly lower than gasoline, 46.5 MJ/kg. Third, once the bio-oil is condensed, one of the most abundant molecules present is acetic acid which gives bio-oil a very corrosive pH of about 2.5. This can be verified using the Total Acid Number (TAN), as measured using ASTM D664 and ASTM D3339 methods presented by Oasmaa et al. (Oasmaa et al., 2010). Finally, this high acidity and abundance of small molecules make raw bio-oil extremely vulnerable to polymerization during storage. Due to these properties, a low-cost upgrading method is necessary to transform it into a potential fuel (Lam et al., 2020) (Basu, 2018).

Another barrier to bio-oil production is the production of biochar which can impact the yield of fast pyrolysis. As stated earlier, biochar is a byproduct of pyrolysis which is often burned for heat or sold externally and can amount to 15% of the yield depending on the biomass type. Patwardhan et al. studied the effects of inorganic salts contained in biomass on biochar yields using switchgrass hemicellulose at a variety of temperatures. In their study, they found that inorganic salts increase biochar, CO₂, and furfural yields while decreasing yields of lower molecular weight compounds like formic acid and acetol. Fast pyrolysis temperatures also affected char yields where an increase in temperatures resulted in a decrease in char yield. Higher molecular weight compounds had the highest yields at relatively low temperatures

between 350-450 °C. Based on the results of their study, Patwardhan et al. were also able to conclude that hemicellulose undergoes a reaction pathway like cellulose with multiple competing pathways that yield a wide variety of products (Patwardhan et al., 2011).

One major benefit of using pyrolysis is that it works independently of the type of biomass feed and has been validated on different types such as agricultural waste products and forestry waste. Pyrolysis from lignocellulosic biomass often produces various products from the cellulose, hemicellulose, and lignin fractions. When focusing on the pyrolysis of hemicellulose, certain characteristics set it apart from cellulose and lignin. First, it is far less thermally stable and therefore requires lower activation energy and temperature for deconstruction due to its amorphous, branched structure and low degree of polymerization. Second, during pyrolysis, hemicellulose often produces more char and significant amounts of acetic acid, which negatively affects the bio-oil yield and stability. In addition, its specific thermal behavior and product distribution are difficult to determine due to the wide range of products produced from the pyrolysis of lignocellulosic biomass (Zhou et al., 2017).

In Räisänen et al.'s study on the pyrolysis of hemicellulose, different products are formed based on the number of carbons in the molecule being pyrolyzed. Since hemicellulose contains both 5 and 6 carbon (C5 and C6) sugars along with sugar alcohols (arabinitols), there will be different major products for each. Of the C5 sugars, furfural was the most common product. The main product of the sugar alcohols, mainly D-arabinitol, changed with an increase in temperature. Another major product, 5-hydroxymethylfurfural (5-HMF), a C6 furan, was only found in the pyrolysis products of D-mannose, a C6 sugar (Räisänen et al., 2003). These were confirmed by Wang et al. finding that furfural was the major product of xylose degradation and 5-HMF was the major product of the pyrolysis of mannose and galactose. In doing a thermodynamic analysis of the pyrolysis reaction pathway for the sugars, it was found that 5-HMF formation was more favorable than furfural due to the stability provided by the hydroxymethyl group in C6 sugars (Wang et al., 2013). In general, pyrolysis of whole biomass will produce a liquid bio-oil product containing many compounds, however, this report will only focus on the upgrading of pyrolysis products of hemicellulose, specifically furfural and 5-HMF.

Furfural and its derivatives are very important molecules in the world today as they are set in a wide range of industries. Furfural is currently used in a wide range of applications such as an extractant, a fungicide, and a solvent. Furfuryl alcohol (FA) is a key derivative of furfural and forms when 2 hydrogen atoms are added to the aldehyde group turning it into an alcohol group. Currently, it is used as a bioplastic in polymer concretes, flavorings, fragrances, foams, and wood adhesives, and has the potential to produce fuels upon furan-ring opening. Upon further hydrogen addition to the furan ring, tetrahydrofurfuryl alcohol (THFA) forms which is a key intermediate in the pharmaceutical industry. Furoic acid forms when furfural undergoes an oxidation reaction and adds another oxygen to the carbon bonded to the aldehyde group. It is an excellent bactericidal and fungicidal agent that can be used in pasteurization and sterilization. Its ring-hydrogenated product, tetrahydrofuroic acid, is also a key intermediate in the pharmaceutical industry. Methylfuran (MF) is another furfural derivative that occurs after the hydrogenolysis of the hydroxyl group and is currently used in the synthesis of pesticides, perfume intermediates, and has potential use as a biofuel (Iroegbu et al., 2020). Furfural is also readily available in amounts of about 250,000 tons/year through the hydrolysis and dehydration of agricultural byproducts or by cyclodehydration of xylose. As of 2008, China was the biggest producer at over 200,000 tons per year with the most common uses to produce furfuryl alcohol

or a resin with the majority being the former (Mamman et al., 2008). Furfural is a very important molecule in the world today because of its value-added products.

A techno-economic analysis performed by Li et al. evaluates the economic feasibility of different types of biorefineries for fuel production. The authors first considered whether the biorefinery would be a stand-alone refinery. Since much of the upgrading equipment used in biooil production can be found in petroleum refineries, integrating these biorefineries with an existing petroleum refinery would be a good way to alleviate the costs of production. The integrated biorefineries would utilize the hydroprocessing units for upgrading via hydrotreating, hydrocracking, and fluid catalytic hydrocracking, thereby reducing the capital costs. The other condition that was evaluated was whether a mixed alcohol by-product would be collected and sold. One of the fractions of bio-oil is the light bio-oil stage fraction, SF5, which could be used for either hydrogen generation through steam-methane reforming or to produce a mixed alcohol by-product through ketonization. Hydrogen generation would displace the need for natural gas which would improve the biorefinery's environmental impact, but alcohols have a higher economic value and could offer more profits. This resulted in four different bio-refinery scenarios: 1) a stand-alone biorefinery producing only hydrocarbon fuels (SH), 2) an integrated biorefinery producing only hydrocarbon fuels (IH), 3) a stand-alone biorefinery producing both hydrocarbon fuels and a mixed-alcohol by-product (SHA), and 4) an integrated biorefinery producing both hydrocarbon fuels and a mixed-alcohol byproduct (IHA).

All biorefineries were set at a feed rate capacity of 2,667 metric tons per day using red oak as the feedstock at 25% moisture content, a 30-year plant life, and a 10% internal rate of return. The base case for the study was the SH biorefinery that would produce about 279 metric tons per day of gasoline, 245 metric tons per day of diesel, and 1,315 metric tons per day of

waste that is anticipated to mainly come from hydrogen reforming at 605 metric tons of waste per day.

The total project investment of the SH biorefinery summed to \$432.5 million with direct costs equating to 65% of the total, indirect costs at 20%, and working capital at 15%. When comparing this to the SHA refinery, it is cheaper as the SHA refinery requires a significantly larger stabilization cost to collect the alcohol product. When specifically looking at the direct costs, usually the equipment costs represent most of it. The highest equipment cost for all refineries were the pretreatment and pyrolysis steps at \$119.71 million combined. However, due to the integration into the pre-existing petroleum industry, the IH and IHA refineries were significantly cheaper as the hydrogen generation equipment was not needed.

The operating costs or minimum fuel selling price (MFSP) of each biorefinery were also calculated. Overall, the IH and IHA had lower operating costs due to a lower capital depreciation from a lower capital cost. Alcohol credits that were given at \$0.14/gal also played a role in lowering the operating costs of the SHA and IHA. The main contributor to the operating costs was the dry biomass feedstock costs at \$0.94/gal for each refinery. The integrated refineries also had a lower average return on investment and fixed costs which significantly dropped their operating costs. At \$2.25/gal, the IHA refinery had the lowest operating costs while the SH had the highest at \$2.85/gal. The table below summarizes the total costs of each refinery as well as the operating costs (Table 1).

Refinery	Total Project Investment	Total Equipment Costs	Annual Operating Costs or
	(\$Million)	(\$Million)	MFSP (\$/gal)
SH	432.5	277	2.85
IH	-	163	2.33
SHA	454.5	289.7	2.77
IHA	_	174.6	2.25

Table 1: Cost summary of each refinery (Li et al., 2017).

When determining the most impactful category for the MSFP, a sensitivity analysis was performed and showed that the feedstock price would be the most influential. At a base case of \$75/dry ton using the SH refinery, the feedstock price was varied from -25% to +50% which resulted in an MSFP change from \$2.85/gal to \$2.61/gal and \$3.32/gal. Other important factors analyzed, listed in order of impact, were the fixed capital investment, hydrotreating catalyst life, and gasoline and diesel yield.

A Life-cycle assessment (LCA) was also performed on each of the stand-alone biorefineries (SH and SHA) using a chosen impact category of global warming potential. Both scenarios were evaluated based on their GHG emissions and compared to gasoline production from a petroleum refinery. Key assumptions made by Li et al. were that biochar and NCG produced from pyrolysis were used for steam and heat generation while bio-oil was upgraded into gasoline and diesel, and that carbon sequestration of biomass would completely cancel out all GHG's formed from combustion. The SH and SHA refineries reduce total GHG emissions from gasoline production by 66% and 63%, respectively. The main contributor is the hydrogen gas (H₂) production from natural gas for use during stabilization at 17.86 grams of CO₂ per mega joule (gCO₂e/MJ) for the SH refinery and 24.07 gCO₂e/MJ for the SHA refinery. More natural gas is used in the SHA scheme to produce the H₂ for the alcohol byproduct. Overall, the SH will emit slightly less GHG than the SHA production, 31.8 gCO₂e/MJ and 34.4 gCO₂e/MJ, respectively.

While the SH system had a better environmental impact, it also had a higher MFSP than the SHA refinery due to the production of the alcohol byproduct. The study also showed that integrating the biorefinery with existing petroleum refineries would further reduce the MFSP to a competitive price. The MFSP in all cases would be reduced further if the feedstock price is decreased, catalyst life is increased, or the product yield is increased (Li et al., 2017). These findings seem to be consistent with a design case presented by Jones et al. who evaluated the production of fuels from biomass using fast pyrolysis for bio-oil production and hydrotreating for upgrading. This design case was done in 2007 and all dollar amounts have been corrected to 2017 for comparison with Li et al. In 2007, they found that a standalone plant designed to produce 76 million gallons/yr would cost \$357 million and would have a minimum selling price of \$2.42/ gallon. If integrated with an existing petroleum refinery to utilize the pre-existing hydroprocessing units, this capital investment could drop to \$221 million with a selling price of \$2.06/gallon(Jones et al., 2009).

Two main forms of upgrading bio-oil are hydroprocessing (HP) and catalytic cracking. HP combines a hydrogen feed with the bio-oil stream to remove oxygen through dehydration reactions producing water. This process operates at temperatures and pressures around 400 °C and 20 MPa. For years, HP has been the most effective upgrading method and is already used in the petroleum refinery process. However, due to its extreme operating conditions, HP faces numerous challenges like catalyst coking which can lead to catalyst deactivation, methane formulation, and bio-oil polymerization due to its high temperature. Catalyst cracking is another common form of upgrading that is typically performed using a zeolite catalyst which causes

deoxygenation through simultaneous dehydration–decarboxylation. In this reaction, oxygen is displaced as CO₂ and CO and produces mainly aromatic compounds at operating temperatures of around 450 °C. These aromatics are valuable to both the fuel industry as a gasoline additive and as a key intermediate to the chemical industry. While these represent the most common upgrading techniques, others techniques used are mild cracking over base catalysts of cellulose- and hemicellulose- derived products to decrease gas and coke formation, esterification, and steam reforming on the water-soluble bio-oil fraction (Bridgwater, 2013).

4. Electrocatalytic Hydrogenation as an Upgrading Technique

While HP and catalytic cracking require extremely high temperatures and pressures for bio-oil upgrading, ECH can operate at room temperature and atmospheric pressure. Reactions are generally carried out in a two-chambered, H-type cell with the two sides, anode and cathode, being separated by an ion-exchange membrane. This process uses an electrical current to split water molecules in the anode to e[°], H⁺, and ¹/₂ O₂. The ¹/₂ O₂ combine and leave while the H⁺ pass through an ion-exchange membrane into the cathode compartment where they combine with the electrons and raw bio-oil to create a reduced bio-oil product. During ECH, unsaturated oxygenates such as aldehydes, ketones, and carboxylic acids are saturated into alcohols and polyols making bio-oil less reactive, corrosive, and minimizes the chance for polymerization. ECH is also able to saturate molecules by hydrogenating double bonds which increases the energy density of the molecule. The overall process is visualized below (Figure 1) along with the chemical equations involved (Eqn 1,3,4). To make the reaction more kinetically favorable, an organic substrate can be added to the anolyte to increase the H⁺ and e⁻ content, thereby increasing the faradaic efficiency (F.E.) (Eqn 2).



Figure 1: Basic setup and process of ECH using bio-oil. Water molecules are split and H⁺ migrate to the cathode and combine with bio-oil to form a stabilized product.

Anode:

$$H_2 O \xrightarrow{elec.} \frac{1}{2} O_2 + 2H^+ + 2e^- \tag{1}$$

$$Organic Substrate \xrightarrow{elec.} Oxidized \ product + H^+ + e^-$$
(2)

Cathode:

$$Raw \ bio-oil + nH^+ + ne^- \rightarrow Stabilized \ bio-oil \tag{3}$$

$$2H^+ + 2e^- \to H_2 \tag{4}$$

The F.E., or current efficiency, is a key parameter measured during ECH and represents the fraction of electrons passed that are used for the desired reaction which can be calculated using the formula presented (Eqn 5) and in more detail in Appendix B.

$$\% FE = \left(\frac{mol*F*n}{c}\right) * 100\% \tag{5}$$

In this equation, mol is the number of moles of the desired product, F is the Faraday constant (96,485 C/mol), n is the number of electrons required for the reduction reaction, and C is the total charge passed during the reaction. An ideal reaction happens when there is an F.E. of 100%, meaning all electrons generated are being used for the desired reaction. However, the F.E. is very sensitive and can be affected by pH, temperature, applied voltage, and concentrations of reactants during the reaction. Optimization research on the F.E. is crucial because of its importance in making ECH a profitable, alternative upgrading method.

ECH was explored by Li et al. in 2013, showing its feasibility while also examining the F.E. of the cell and discussing how it could be improved. Focusing on the water-soluble fraction of bio-oil, they were able to show how both the initial concentration of bio-oil compounds decreased and their hydrogenated products increased after ECH. Using gas chromatography results after normalization to the internal standard, the peak area for acetaldehyde dropped from 0.77 before to 0.00 after. The peak area for ethanol, acetaldehyde's hydrogenated product, increased from 0.01 to 0.52. Strategies to increase the F.E. included using a solid polymer electrolyte to decrease the solution's resistance and decreasing the applied voltage to the cell (Li et al., 2014). While ECH seems very promising, optimization is essential to decrease operating costs and make it a viable, profitable solution. More research is being done to optimize factors such as catalyst selection, membrane cost, and different processing strategies (Lam et al., 2020).

As discussed earlier, lignin utilization is necessary to produce a capable biofuel because of its abundance in biomass and energy density. Lignin pyrolysis often produces a variety of unsaturated aromatic molecules. Studies have been done on these to understand the reaction parameters such as temperature, pH, solvents, and type of catalysts to achieve the best conversions, F.E.'s, and selectivities. However, more research on lignin hydrogenation must be done to effectively hydrogenate the aromatic compounds(Garedew et al., 2021).

Garedew et al. studied aromatic compounds from lignin pyrolysis to determine the effect of ECH with different functional groups. ECH was able to hydrogenate the ring of ligninderived, aromatic compounds related to phenol and guaiacol that had different alkyl side chains on the para position of the ring. They also observed partial deoxygenation of alkyl cyclohexanols and alkyl-substituted 2-methoxycyclohexanols where side chain length correlated with conversion rates (Garedew et al., 2019). This was confirmed by Liu et al. in 2020, when they were able to successfully hydrogenate both phenol and guaiacol to cyclohexanol and cyclohexane using silicotungstic acid, a superacid, and platinum (Pt), a noble metal, as a catalyst. Using this technique, conversions and F.E. were 99% toward the hydrogenated products (Liu et al., 2020).

Li et al. performed studies in an H-cell on guaiacol, a compound commonly found at the end of the conifer alcohol group which is included in the G units in lignin. Li's research shows bio-oil stabilization and upgrading using a ruthenium (Ru) catalyst supported on activated carbon cloth (Ru/ACC) at mild temperatures (80°C) and atmospheric pressure. Using this catalyst, they observed guaiacol conversion to cyclohexanol and 2-methoxy-cyclohexanol. The effects of ECH are seen when comparing the chemical structures and energy densities of guaiacol, 28.9 MJ/kg, and its products cyclohexanol, 37.2 MJ/kg, and 2-methoxy-cyclohexanol, 32.7 MJ/kg (Lam et al., 2015). During ECH, guaiacol follows two parallel reaction pathways to convert to cyclohexanol: demethoxylation followed by aromatic ring saturation and vice versa (Wijaya, Smith, et al., 2020b). Results from Li et al.'s study showed that conversions over 70% have been achieved from guaiacol to the major products. Li's team found that temperature had the biggest

effect on the conversion of the system, as higher conversions were associated with higher temperatures within the range studied. Other factors studied were the current and electrolyte, however, no significant effects were observed on conversion. When looking into the F.E., it followed a quadratic function with a peak of about 17.23% at a temperature of 54 °C (Li, Garedew, et al., 2012).

When studying other aromatic compounds such as phenol, 4-methylphenol, and 4methoxyphenol, Song et al. showed conversions to the completely hydrogenated ring products using a rhodium (Rh) catalyst supported on activated carbon. When comparing the ECH results with thermocatalytic hydrogenation results, no significant differences were observed. However, when plotting the concentrations against time, having a hydrophobic methyl group across the ring of the hydroxy group resulted in a decreased reaction rate. Another important aspect of this study was that they showed that ring hydrogenation is favored to hydrogenolysis of the hydroxyl group on a Rh catalyst shown from the final concentrations of 4-methoxycyclohexanol (~25 mol. %) compared to phenol (<10 mol. %) and cyclohexanol (<10 mol. %) (Song et al., 2016).

Benzaldehyde is another aromatic compound commonly used to model bio-oil and will hydrogenate to benzyl alcohol during ECH. In 2018, Song et al. studied the effects of different catalysts, including Pt, palladium (Pd), Rh, and nickel (Ni), on the F.E and hydrogenation of benzaldehyde. They found that Pd was significantly more efficient and active than the other metals because of its selectivity toward the hydrogenation reaction rather than the hydrogen evolution reaction (Song et al., 2018).

While this is an encouraging result for lignin conversion, when utilizing whole biomass, hemicellulose and cellulose compounds must be converted into their saturated forms as well. Studies have been done on the ECH of furfural to verify the effect of ECH on the hemicellulose

fraction of biomass. Furfural is a 5-carbon aromatic furan ring with an aldehyde derived from the dehydration of xylose and arabinose sugars after pyrolysis. Because of its abundance, it has been studied using a variety of different catalysts and conditions to produce a wide range of products. Li et al. showed that ECH could successfully hydrogenate furfural into furfuryl alcohol (FA) and MF in significant amounts using a Ni catalyst. Conversions of more than 80% were observed with selectivities >95% for FA. Both starting concentration of substrate and pH seemed to have significant effects on conversion and selectivities. They also found that F.E. never surpassed 66% which will need to be improved for industrial applications(Li et al., 2012b). When studying the reaction mechanism for the ECH of furfural, Chadderdon et al. concluded that conversion to FA and MF usually happens in series, and that selectivity depends on the reaction conditions. Using production rate analysis, they determined both furfural and H⁺ are absorbed on the catalyst and the reaction conditions determine which atom in the molecule is hydrogenated leading to different product selectivities(Chadderdon et al., 2017). Furfural has also been studied for its selectivity toward FA by Zhao et al using lead (Pb), Ni, Pt, and Copper (Cu) all distributed on activated carbon fibers. They found the highest conversions and F.E. from the lead catalyst however the highest selectivity from the Pt catalyst. When the effects of catalyst loading were studied further with a current varying between 20-30 mA, a voltage of -0.5 V, and a 0.1 M sulfuric acid electrolyte, conversion, selectivity toward FA, and F.E. were at their highest yields of 82%, 99%, and 78%, respectively with a lower amount of catalyst. Drawing from this, they were able to hypothesize that the catalytic activity decreased because of pore blockage in the more densely populated catalysts and increased with an increased surface area. From the study, they were able to conclude that Pt had a higher selectivity toward FA than the other catalysts and that an increase in catalyst loading could result in a decrease of conversion and F.E. (zhao et al.,

2014). Under neutral conditions, hydrogenation of furfural was studied by Dhawan et al. who used Zinc (Zn) as their catalyst and compared it to Cu and Ni. In their work, they found that at near-neutral conditions, Zn had significantly higher conversions, yields, and F.E.'s than the others. Their system was able to achieve conversions of 88% with yields toward FA and MF of 40% and 3.5%, respectively and F.E.'s of 73% toward FA and 83% overall, which represents the highest overall F.E. reported in literature (Dhawan et al., 2021). In other studies, researchers have also identified Cu as a catalyst for high furfural conversion to FA and MF and high F.E. In a study done by Liu et al., many catalysts were studied to determine the reaction mechanisms of furfural hydrogenation of each. A key factor that was considered was the hydrogen evolution rate (HER), a measure of how easily hydrogen gas forms from the H⁺ ions generated during electrolysis and absorbed to the catalyst. In this study, Pb was found to have the lowest HER due to a high overpotential, defined as the difference between a reaction's thermodynamically determined potential and the potential at which the reaction is observed. Further, low exchange current density, defined as the current at zero net electrolysis and zero overpotential, also lowers the HER. The second-lowest HER was observed on the Cu catalyst and the highest occurred on the Pt catalyst. In these studies, Cu was the most successful catalyst for furfural hydrogenation due to its low HER rate and the difference in its onset potential without vs. with furfural. When looking at the mechanism of furfural hydrogenation using Cu as the electrode, Liu et al. found that the first step in the reaction is to hydrogenate the aldehyde group and produce a free radical on the carbonyl, then transform to FA through saturation of the free radical. When running batch experiments, they were able to see that while FA was the dominant product, after 6 hrs, FA began to convert into MF through hydrogenolysis of the hydroxyl group (Liu et al., 2017). For hydrogenation of furfural to MF, Jung and Biddinger used a Cu catalyst to find the optimal

reaction conditions, which also involved minimizing side reactions. They found that as the pH of the electrolyte decreased, the selectivity toward MF increased. In their study, they also noted that mass balances showed that side reactions had a significant effect. Side reactions from mildly acidic solutions may be promoted by charge transfer on the Cu electrode while in strongly acidic solutions, the side reactions were acid-promoted. These side reactions can be controlled using a variety of parameters including the amount of organic cosolvent, reaction time, initial concentration, potential, and pH of the experiment (Jung and Biddinger, 2016) (May and Biddinger, 2020). While Cu is one of the best catalysts for conversion of furfural to FA and MF, the dimer product, hydrofuroin, is a valuable, chiral compound used in resins, jet fuel, and other pharmaceutical molecules. On the market, it can achieve costs greater than \$800 per gram. Dixit et al. showed both Cu and Ni by themselves could produce both molecules in significant quantities but that with a bimetallic Cu and Ni catalyst, they were able to produce both FA and hydrofuroin at even higher rates achieving yields of 118.7 and 176.3 µmol h⁻¹ cm⁻² in an alkaline electrolyte, respectively(Dixit et al., 2021). For biofuel production, Nigles and Schröder focused on converting furfural and 5-HMF into MF and 2,5-dimethylfuran (DMF). The results of this study showed that Cu presented the highest product selectivity of furfural toward MF in an acidic electrolyte and significant conversion of 5-HMF to DMF. Because a high energy density is required to have a competitive biofuel, the effects of ECH on increasing the energy density of a molecule are clearly shown in this study. The conversion of furfural to MF and 5-HMF to DMF results in an energy difference between products and reactants of 217 and 382 kJ/mol, respectively (Nilges and Schröder, 2013). 5-HMF is another product derived from cellulose- and hemicellulose-pyrolysis that has been studied because of its ability to produce potential biofuels. Kwon et al. studied this molecule to see which catalysts were more selective to its different
hydrogenation products, 2,5-dihydroxymethylfuran (DHMF) and 2,5-dimethyl-2,3-dihydrofuran (DMDHF), in an acidic solution. They showed that of the metals studied, Ni was the most active in converting 5-HMF into DHMF and Antimony was the most effective for DMDHF conversion. Also, like the previous studies, they concluded that the pH of the solution plays a significant role as it can lower the activation energy needed for 5-HMF hydrogenation and furan ring saturation (Kwon et al., 2015).

One factor that significantly affects F.E.'s and yields of any ECH system working with furfural are the polymerization reactions of furfural and furfuryl alcohol that occur during the process. These reactions can be electrocatalyzed, promoted by charge transfer, which will form a dimer product. This happens when an H⁺ is added to the oxygen of the aldehyde and an e⁻ to the carbon creating a radical e⁻. When two of these molecules contact each other, the radicals combine to form the dimer product (Figure 2) (Cao and Noël, 2019).



Figure 2: Reaction pathway for the electrocatalyzed dimerization of furfural.

Other polymerization reactions that occur involve resinification which can form full polymers of both furfural and furfuryl alcohol. In furfural, this happens in one of two different ways. First, when the partial positive charge on the carbon (C) connected to the aldehyde is attracted to the delocalized electron system of the furan ring and forms a bond with the C across the ether bond from the aldehyde forming a difuryl ketone called 5-(furan-2-carbonyl) furan-2-carbaldehyde (1). Second, the oxygen in the aldehyde combines with 2 other H⁺ from 2 furan

rings of different molecules and leaves the molecule as H_2O . This leaves a negative charge on the carbonyl it left and a positive charge on the 2 carbon atoms in the furan rings. These are attracted to each other and bond forming a trifurylic dialdehyde called 5,5'-(furan-2ylmethylene)bis(furan-2-carbaldehyde) (2) which can continue to polymerize (Figure 3).



Figure 3: Self-resinification reaction of furfural where (1) is 5-(furan-2-carbonyl) furan-2-carbaldehyde and (2) is 5,5'-(furan-2-ylmethylene) bis(furan-2-carbaldehyde) formation that can continue to polymerize.

Furfuryl alcohol can undergo a resinification reaction like reaction (1) in Figure 3. In this reaction, the primary alcohol is protonated and binds with the furan ring of another FA molecule in an electrophilic aromatic substitution reaction (Figure 4) (Hoydonckx et al., 2007).



Figure 4: Self-resinification of FA to form a linear polymer (Hoydonckx et al., 2007).

To decrease this polymerization of furfural, Kim et al. investigated the use of an organic solvent to reduce the rate of polymerization. Using UV-Raman experiments, they observed that

using an alcohol solvent such as ethanol or butanol significantly hindered the rate of polymerization. This was caused by a shielding effect where hydrogen bonding between the oxygen of the aldehyde and the hydrogen of the alcohol decreased its attraction to other furan rings (Kim et al., 2013).

Studying individual monomers is good to gain an understanding of how each molecule will react. However, in lignin, many dimers exist with the most common link between them being the β -O-4 linkage. Using model compounds with alcohol- and ketone-containing linkages, Zhou et al. were able to successfully demonstrate cleavage of the β -O-4 linkage using a skeletal Ni electrode and proposed mechanisms for both the alcohol- and ketone-containing linkages. However, they did find that any substituent methyl or methoxy groups had a significant effect on cleavage through the prevention of Ni binding or C–H insertion. Using this data, they were able to establish a cleavage rate hierarchy based on the functional groups present in the linkage that will allow for more accurate predictions of the reaction and better control over product selectivity (Zhou et al., 2020). Song et al. also did work with dimers and showed that aromatic dimers could have both aromatic rings saturated or become monomers through cleavage of the ether linkage.

The use of individual model compounds to understand how they react among different reaction conditions provides valuable information towards the hydrogenation of whole bio-oil. However, the individual compounds studied alone do not provide data regarding their interactions with other molecules. Sanyal et al. took this into account when they studied how furfural and benzaldehyde would react in the presence of phenol on Ru, Rh, Pd, and Cu catalysts. When comparing the turnover frequencies (TOF) of each catalyst on furfural in the absence and presence of phenol, they noticed an increase in the Pd, Rh, and Cu catalysts when phenol was

added but showed no change in the Ru catalyst. This increase in TOF did not correspond to the F.E. as only Cu increased slightly, both Pd and Rh decreased and Ru showed no change. For the comparison of the benzaldehyde reaction in the absence and presence of phenol, the TOF increased most significantly in the following order with the addition of phenol: Cu >> Pd > Ru > Rh. The F.E. for this reaction increased only in Cu, remained constant for Pd, and decreased significantly for Ru and Rh. The results of the study suggest a significant interaction between molecules where the hydrogen-bonded complexes between the alcohol of the phenol with the aldehyde group on furfural and benzaldehyde allow for easier hydrogenation of the aldehyde (Sanyal et al., 2021).

Another area of interest in ECH is the production system. In a study done by Wijaya et al., ECH was conducted in a stirred slurry electrochemical reactor (SSER) using a Pt catalyst and guaiacol in a variety of different electrolytes characterized by their pH. These experiments were conducted in an H-cell, however, instead of using a support for the catalyst, a catalyst containing slurry was added to the catholyte. The different pairs of catholytes and anolytes were evaluated to determine their effect on conversion, selectivity, and F.E. The results of their study showed that in the SSER production system using a Pt catalyst, the most effective combinations occurred when the anolyte was acidic and the catholyte was acidic or neutral. The results showed that conversion, cyclohexanol selectivity, and F.E. for the acidic-acidic pair and the acidic-neutral pair were 38%, 19%, 82% and 36%, 28%, and 94%, respectively(Wijaya, Grossmann-Neuhaeusler, et al., 2020).

In their review, Garedew et al. investigated other areas of ECH that could be improved, and costs could be mitigated to make production more economically feasible. The first area identified was the anode erosion and the material used to prevent it. While precious metals remain the best choice for anode selection due to their ability to function in harsh oxidative environments, they are very rare, costly, and have a limited reserve. This has sparked a search for earth-abundant metals for the anode. In ECH, earth-abundant metals, such as Ni, have been used as a sacrificial anode meaning that these metals have a lower overpotential than water so they are also oxidized during the reaction. However, once they are oxidized and eroded, they are deposited on either the cathode or the catalyst to create a fresh surface and improve F.E. as reported in studies done with aliphatic compounds (Garedew et al., 2020). An increase in F.E. would be ideal as it would result in more hydrogenation using the same amount of current thereby reducing overall costs.

While the stand-alone and integrated refineries techno-economic analysis mentioned previously are very promising, another suggestion to decrease the MFSP is to alter the supply chain to create a decentralized system involving localized depots for bio-oil production and upgrading using ECH. This upgraded bio-oil could be transported to a central refinery which would utilize hydroprocessing or catalyst cracking for further purification. This was first suggested by Lam et al. to reduce transportation costs by hauling upgraded bio-oil to a refinery instead of bulk biomass. Lam et al. compared energy, mass, and carbon yields of the proposed biomass upgrading depot (BUD) production scheme to a cellulosic ethanol facility. Corn stover was chosen as the feedstock (16.498 MJ/kg wet weight, HHV) at a rate of 1 billion dry tonnes/yr for both facilities. After analysis, it was found that the finished fuel after upgrading in the refinery of the BUD scheme had a superior energy yield, mass yield, and carbon yield of 89%, 38%, and 63%, respectively (Lam et al., 2017). This concept was explored more in a dissertation by Das in 2020.

In the techno-economic analysis of a bio-oil production plant proposed earlier by Li et al., it was assumed that each bio-oil production facility was considered a stand-alone plant and that upgrading and purification could be done either at the biorefinery or at a pre-existing oil refinery. However, using a much milder approach in ECH for upgrading, the system could be decentralized as discussed by Lam et al. Sabyasachi Das explores this system in a technoeconomic analysis using 2018 dollar equivalents where pretreatment, pyrolysis, and ECH are done in localized depots and stable bio-oil is transported to refineries for further upgrading. The central refinery would process 2,000 tonnes of bio-oil/day (tpd), which was the input combined from all depot outputs. Some of the key economic parameters used were a plant life of 30 years, an internal rate of return of 10%, and a working capital of 5% of the fixed capital investment. By-products produced by the system included biochar, which can be sold for additional revenue, however, is not sold in the study due to limited information, H_2 gas, which is partially combusted, and excess is sold for additional revenue at \$2/kg, and NCG, which are combusted to heat the pyrolysis reactor. For the study, it was found that the optimum depot size for the refinery was 500 tonnes bio-oil produced/day because at this size the economics of scale and transportation costs equate. Therefore, to feed the central refinery processing 2,000 tonnes biooil processed/day, four depots would be optimum.

Supply chain costs included the transportation and biomass costs. In determining the transportation costs, a rate of \$1.82/mile was assumed, therefore the total transportation costs within the production scheme were \$7.82/tonne of biomass. The total cost of biomass delivered from the farm to the depot was calculated to be \$61.30/tonne of biomass. Grower payments were determined to be the highest contributor to the supply chain cost at \$38.62/tonne of biomass with

harvesting costs next at \$16.51/tonne of biomass. Storage and handling costs were equivalent to the transportation costs.

The depot's total capital investment was calculated to be \$29 million for a single depot. Direct costs, which included equipment, warehouse, site development, and additional piping, summed to \$17.1 million while the indirect costs covered portable costs, field expenses, home office and construction, and project contingency and totaled to \$10.7 million. The direct costs were dominated by the ECH reactor at \$9.92 million while the home office and construction formed the bulk of the indirect costs at \$3.42 million. The operating costs of the depot were also evaluated and were determined to be \$25.5 million per year. Variable operating costs included raw material, grid electricity, fresh water, and ECH stack replacement. This totaled \$24.7 million per year with grid electricity and raw material representing about 63% and 36%, respectively. Fixed operating costs included worker salaries, labor burden, maintenance, and property insurance and totaled \$846,000 per year. Overall, the variable costs outweighed the fixed costs by a ratio of almost 30:1.

From the depot, stable upgraded bio-oil is transported to a central refinery for further upgrading to produce a fuel product. When evaluating the refinery, the total capital investment was determined to be \$227 million where the direct cost and indirect costs were calculated and found to be \$134 million and \$80.4 million, respectively. Equipment costs, including hydroprocessing, electrolysis, and storage, represented \$114 million of the direct costs. The majority was spent on electrolysis (58%) and hydroprocessing (42%) equipment with storage having a negligible contribution (<1%). The operating costs were also evaluated and totaled \$161 million per year. The variable operating costs for the refinery included raw material, grid electricity, natural gas, electrolyzer stack replacement, and hydroprocessing catalyst

replacement, and summed to \$154 million. This is caused by the high raw material costs of stable bio-oil at \$100 million per year. The fixed operating costs included salaries, labor burden, maintenance, and property insurance which totaled \$7.08 million.

The MFSP for the depot system was determined to be \$3.62/gallon of gasoline equivalent from the fuel produced by the refinery. When conducting a sensitivity analysis, electricity costs and raw material costs had the biggest impact on the system with other factors being the economics of scale-up, current efficiency, catalyst price, and whether biochar is sold or not. If these factors were to become more favorable, such as a decrease in feedstock or electricity cost, the MFSP could drop to about \$2.57/gallon of gasoline equivalent (Das, 2020).

Das's work with a techno-economic analysis represents a major barrier that has been overcome when it comes to electrocatalytic hydrogenation. Other areas of work that will need to be addressed in the future for the commercialized ECH of bio-oil involve DFT calculations, spectroscopic studies, separation and purification technologies, cost-effective processing strategies, and a better understanding of catalytic mechanisms (Li and Sun, 2018).

5. Benefits of Continuous Processing

One way to reduce the MFSP of ECH systems is to operate them continuously. Continuous electrochemical systems are used in industry due to their simple and integrated design that results in increased energy efficiency, a smaller capital cost, and safe operation. For instance, in the food industry, the FDA identified these advantages and has been pushing for more continuous systems to reduce the operating costs associated with food manufacturing (Chatterjee, 2012).

In a techno-economic analysis of a production process within the pharmaceutical industry, Schaber et al. discuss the potential cost savings of switching from a batch to a continuous process. During batch processes, which were used as the study's base case, multiple reactors are used to add key intermediates to make the active pharmaceutical ingredients (API) that are loaded into tablets. After evaluating the current process, Schaber et al. proposed a new continuous process with a recycling option and two different downstream options and compared each combination to the base case. The determined yield of the base case scenario of a large pharmaceutical manufacturer was set to 79%. While yields of the continuous processes are generally much higher than batch processes and increase further when using a recycle within the process. In this analysis, the process yield was set to 79% when recycling is included, and 69% without recycling. Even before cost savings were calculated, the proposed continuous system saved significant amounts of resources such as water and solvents compared to the base case. After evaluating the monetary component at varying costs of the key intermediate and loadings of API into the tablets, the continuous system showed savings in the total capital costs between 20-76% depending on the scenario used with higher savings being achieved at higher API loadings and higher key intermediate costs. The annual operating costs were also compared, and it was found that only the recycling option offered savings from 6-40% at all three key intermediate prices and two API loadings. Without recycling, the operating costs could increase about 8-9% at low and high API loadings with high key intermediate costs. Present cost differences for all processing options showed savings of between 9-40% with recycling, however, without recycling, savings were only seen at the low and medium key intermediate costs for both API loading values. If yields for the continuous systems decreased by 10%, at low key intermediate costs and different API loadings, savings of between 27-35% and 14-16% were

still seen with and without recycling, respectively. As key intermediate costs increase,

production costs increased to 20% from the base case without recycling at high API loading. If continuous system yields increase 10% from the base case, production costs decrease in all cases with maximum savings of 44% production cost reduction at a low key intermediate cost and high API loading without recycling. With this study, Schaber et al. showed that in the pharmaceutical industry, even at lower yields, continuous systems can offer significant cost savings compared to batch systems (Schaber et al., 2011).

6. Continuous Electrocatalytic Hydrogenation

When specifically looking at the continuous system for ECH, productivity could be improved, rate-specific information could be more easily obtained, and the whole system could be more suitable for industrial application. Continuous upgrading would require less energy and catalyst inputs while also increasing the yield of stabilized products to be processed into fuel. In this continuous strategy, reactors can be operated as divided or undivided cells for hydrogenation in continuous operation. The most common type of reactor is the proton exchange membrane (PEM) fuel cell configuration where a Nafion membrane is used to separate the anode and its electrolyte, anolyte, from the cathode and its electrolyte, catholyte. In this type of reactor, solutions containing organic compounds flow into the cell, contact the catalyst, and then exit the cell. However, one problem with this design is that mass transfer rates of liquid reactants in laminar flow conditions are low (Akhade et al., 2020). According to Garedew et al. continuous systems would be much better adapted for industrial applications and have the same synthetic freedom as a batch processing method. These continuous systems can be designed in single or multi-step processes where modifying temperature, flow rate, solvent composition, or pressure can be performed to optimize yield and selectivity. The flexibility offered by flow

electrochemistry has excellent potential to enable biomass conversion for bio-based drop-in chemicals and fuel production (Garedew et al., 2020b).

While the continuous ECH of bio-oil compounds remains nascent, studies using different metals, such as Cu, Ni, Pt, and Pd, have shown that continuous ECH is possible. In a study done by Sanyal et al., both Cu and Pd were impregnated on carbon cloth and analyzed in a continuous system using benzaldehyde, furfural, and acetophenone as model compounds in solutions that flowed over them. Overall, Pd was found to be the most active catalyst with higher F.E. and conversion rates than Cu. Based on the results of their study, general trends between the two catalysts showed that as the current increased, F.E. decreased and conversion rates increased. The experiments showed that continuous ECH was able to both deoxygenate and hydrogenate the compounds and suggested that the type of catalyst plays a very significant role in determining product selectivities (Sanyal et al., 2018). Another study performed by Wang et al. explored the use of mono- and bimetallic Ni and tungsten (W) catalysts with varying temperatures and flow rates in batch and continuous platforms. In their experiments, furfural was studied as the model compound for bio-oil in an isopropanol solvent. A bimetallic catalyst achieved a higher selectivity toward MF at slower flow rates, however, the monometallic Ni catalysts showed much more conversion (Wang et al., 2018). Both studies show that ECH is possible in a continuous system to stabilize and upgrade bio-oil.

For industrial scale-up purposes, Roessler et al. devised a feasibility study that focused on using data from batch experiments on the ECH of indigo to leuco-indigo to create a continuous process using a PEM reactor. In the study, different parameters including pH, temperature, current density, and cosolvent, were all varied to determine the optimum conditions for conversion. They found that with an initial indigo concentration of 10 g/L, a higher initial pH

resulted in a higher reduction rate and a maximum conversion at a current density of 0.02 amps per centimeter² (A/cm²), and a temperature of 70 °C. They also found that of the different organic cosolvents with water at 20% (v/v), methanol had the highest conversion rate of up to 43.1% at a current efficiency of 6.9%. The authors were successful in showing that continuous ECH can hydrogenate indigo to leuco-indigo and were able to identify optimum parameter values needed for industrial scale-up (Roessler et al., 2003). Sáez et al. used a PEM fuel cell to evaluate the feasibility of continuous ECH processing using acetophenone to make 1phenylethanol, and the effects of current density and cathode catalyst loading were investigated. The current density was varied from 0.01-0.02 A/cm² and the catalyst loading ranged from 0.025-0.2 milligrams of Pd/cm². The study was successful in determining that continuous ECH increased conversions as the total charge and catalyst loading increased. It also showed that the system was highly selective for the desired product 1-phenylethanol (>87%) for all conditions, which is promising for industrial scale-up (Sáez et al., 2013).

Pintauro et al. examined continuous ECH using a PEM reactor and soybean oil. The system utilized a Pd-black powder catalyst on the cathode and a Pt-black powder catalyst on the anode which were combined with a Teflon-30 and Nafion dispersion. These were then coated onto carbon cloth and hot-pressed onto the Nafion 117 membrane at 16,000 kPa and 120 °C for 90 seconds (s). Soybean oil was pumped into the cathode while H₂ was pumped into the anode instead of water. The soybean oil was characterized by its fatty acid profile that was initially found to be 4.2% stearic acid (C18:0), 25.3% oleic acid (C18:1), 53.1% linoleic acid (C18:2), and 6.6% linolenic acid (C18:3). In labeling these acids, the first number is the number of carbon atoms on the molecular chain and the second number is the number of double bonds existing in the chain. When initial hydrogenation experiments were run on the soybean oil, both electrical

current densities and oil flow rate, measured in milliliters per minute (mL/min), were varied. Their results showed that when temperature and oil flow rate were held constant at 70 °C and 30 mL/min, respectively, and the current density was varied across the cell, both C18:0 and C18:1 values increased while the C18:2 and C18:3 values decreased with increasing current density. The oil flow rate was also varied, while holding the current density constant at 0.16 A/cm² and temperature at 70 °C, but it did not have an impact on the hydrogenation. Overall, this study showed that continuous ECH is successful at hydrogenating soybean oil characterized by longer carbon-carbon chains than most molecules present in pyrolysis bio-oil (Pintauro et al., 2005).

A study in 2013 by Green et al. focused on the continuous conversion of furfural into its four major products: FA, THFA, MF, and 2-methyltetrahydrofuran (MTHF). First, Pd, Pt, Ru, Rh, and Ni catalysts were all investigated to determine their activity in the system. Pd was the most active and offered the highest TOF when studying the hydrogenation of both furfural and FA. Pd also offered the highest F.E. at values between 24-30%, meaning most of the energy supplied by the electricity was used for H₂ formation instead of hydrogenation. Next, the effect of the applied voltage was varied from 1.15-1.75 V to show the effect of voltage toward product selectivities using a Pd catalyst. At low voltages and low conversion rates, FA was the dominant product at 100% selectivity since FA is the first step in the reaction. However, as the voltage and conversion percentage increased, the selectivity for FA dropped and the other molecules increased. Since the conversion of FA to THFA and MF requires 1.01 V and 1.09 V, respectively, THFA production was favored to MF. Since FA was the initial product of furfural hydrogenation, the ECH of FA was also tested and compared to furfural. At low power inputs, FA had a much higher conversion rate, and the selectivity of products showed the same reaction pathway as furfural. However, at power inputs greater than 0.12 W, the furfural conversion rate was higher than the FA conversion rate.

Green, et al. were also able to determine the energetics of furfural hydrogenation to MTHF and determined that it was more energetically favorable to hydrogenate the aldehyde, hydrogenate the ring, and finally cleave the hydroxyl group. The study concluded that the Pd catalyst was the most active, that the applied voltage played a role in product selectivities, and that selectivity toward THFA and MF increased with increasing applied voltage. One area of concern the group noted was the low F.E. at only 24-30% meaning 70-76% of the electrical energy was used to produce H_2 instead of hydrogenating the furfural (Green et al., 2013).

In studying furfural and its redox reactions, Chamoulaud et al. ran a continuous flow cell with a Cu catalyst on the anode and Ni on the cathode. However, furfural was run on both sides of the cell because both its hydrogenated and oxidized products, furfuryl alcohol and furoic acid, are valuable products,. At a flow rate of 1.5 mL/min, the best conversions, yields, and selectivities were found when the cell was operated between 1.5-2 times the theoretical current needed to saturate the entire solution (Chamoulaud et al., 2001). By coupling the oxidation reaction with the reduction reaction, the cell was able to produce two products rather than just one. This improves the overall productivity of the cell which could decrease the operating costs of ECH at a biorefinery. This could also be applied to 5-HMF to produce both 2,5-furandicarboxylic acid (FDCA), a chemical building block toward polyethylene furanoate, and 2,5-dimethyltetrahydrofuran, a potential biofuel as identified by Kwon et al. in their review in 2016 (Kwon et al., 2016). Li et al. explored this concept further using the same reactor design as Chamoulaud et al. but for the redox of 5-HMF. After seeing high conversions in both the oxidation and reduction reactions of 5-HMF in a batch environment, they ran the experiment in a

continuous system. In their study, they operated a continuous reactor in full recycle mode using a vanadium nitride (VN) catalyst on the anode and a Pd/VN catalyst on the cathode. At a constant current of 100 mA and a flow rate of 130 mL/min leading to 70 cycles through the reactor per hr, they saw conversions of 92% and 87% in the oxidation to FDCA and hydrogenation to 2,5-dihydroxymethyltetrahydrofuran (DHMTHF), respectively (Li et al., 2019). The results show the potential of pairing electrocatalytic hydrogenation with oxidation reactions in making large-scale bio-oil upgrading profitable.

This work serves to extend the potential for electrochemistry using a continuous process that is better suited for industrial applications and scale-up, identified by Lucas et al. in their review of electrochemical processes. A continuous application could improve the economics associated with ECH scale-up by improving yields and productivities when using electrocatalysts (Lucas et al., 2021).

7. Ruthenium as a Catalyst

Catalysts are essential for the ECH reaction as they lower a reaction's activation energy thereby increasing reaction rates. They also play a role in determining product selectivities based on their interaction with molecules shown in Dixit et al.'s study evaluating the production of FA and hydrofuroin. These interactions can be impacted by the reaction conditions such as pH, temperature, and concentration.

Reaction conditions can impact the interaction of molecules with a catalyst during ECH. The pH of the solution can have a significant effect on the catalyst's HER and ECH rate. Shao et al. studied the HER between Ru and Pt on activated carbon cloth and observed that in an alkaline medium, the Ru catalyst had a higher HER than when in an acidic environment, which is unlike other catalysts including Pt. Because of this, they hypothesized that Ru on carbon cloth adsorbed a high amount of hydrogen leading to increased molecular hydrogen evolution. Because of hydrogen adsorption and Ru's strong ability to disassociate water, Ru was shown to have a higher HER than Pt in alkaline mediums (Shao et al., 2021).

The support structure of the catalyst also should be considered. A common catalyst support is activated carbon cloth due to high absorptivity. However, Zhang et al. tested ordered mesoporous carbon as their support because of its porosity, durability, and inertness. They were able to evenly disperse and uniformly embed smaller Ru particles into the mesoporous carbon using silica as a template. Increased conversion rates, alcohol production, and F.E. were observed in water-soluble bio-oil with the meoporous carbon than with the Ru on activated carbon cloth support (Zhang et al., 2018).

Another important factor is the binding energy of a catalyst toward a specific molecule compared to its binding energy for hydrogen. Since bio-oil has a variety of aldehyde-containing molecules, a catalyst that can reduce different kinds of aldehydes is ideal. Lopez-Ruiz et al. studied both noble metal catalysts (Pd, Ru, Rh) and base metal catalysts (Cu, Ni, cobalt (Co), and Zn) to determine their ECH and HER rates and the effect carbon rings have on the rates and binding energies for furfural, heptanal, cyclohexane-carboxaldehyde, and benzaldehyde. Pd had the highest TOF for benzaldehyde and furfural but had lower rates for heptanal and cyclohexanecarboxaldehyde. Ru had sufficient TOFs for all molecules and had the highest for cyclohexanecarboxaldehyde and had the highest HER of the catalysts studied (Lopez-Ruiz et al., 2019). In literature, Cu and Ni have both demonstrated a high ability for ECH but are also prone to dimerization and deoxygenation. Table 2 shows the specific TOF of the ECH reaction for the metals recorded by Andrews et al.

	ECH Rate (mmol $g_{cat}^{-1} h^{-1}$)				
Catalyst	Benzaldehyde	Furfural	Cyclohexane-	Heptanal	
			carboxaldehyde		
Pd	3.6	2.2	0.31	0.14	
Ru	2.2	1.6	0.67	0.68	
Rh	0.23	0.37	0	0	
Cu	2.4^{*}	1.1^{**}	0.49	0.56	
Ni	1.2^{*}	1.5**	0	0.54	
Со	0.15	0.25	0.5	1.1	

Table 2: Specific ECH Rates of catalysts recorded (Andrews et al., 2020).

^{*}also showed dimerization product hydrobenzoin

***also showed the deoxygenated product, MF, and dimerization product, hydrofuroin

Catalyst interaction can also determine the selectivity of products. The interaction between Ru and furfural was studied by Banerjee and Mushrif in 2017. In their study, they investigated reactions and energetics of furfural conversion to its potential products using density functional theory (DFT) studies. The results showed that furfural interacts with a catalyst's surface in two different ways depending on the catalyst: 1) through the oxygen of the aldehyde and 2) through both the furan ring and the oxygen in the aldehyde group. The first interaction is present in Cu which explains why both FA and MF are produced with such high efficiency, though THFA is not observed. The second interaction is present in catalysts such as Pd, Ni, and Ru allowing them to hydrogenate the furan ring after the aldehyde producing THFA. Their study concluded by presenting reaction pathway energetics for furfural hydrogenation indicating why different products are produced from furfural on a Ru catalyst (Banerjee and Mushrif, 2017).

III. Goals and Objectives

The goal of this study is to determine the technical feasibility of continuous ECH using a Ru/ACC catalyst. Initial concentration and current density effects on F.E. and product yields will be examined by analysis of variance (ANOVA). Ru has shown to be proficient at hydrogenating furfural and saturating the furan ring in batch studies. However, since batch operations are less productive and have a higher capital cost, continuous systems are preferred for industrial applications. The proposed continuous system offers safety, technical, and economic advantages when considering bio-oil stabilization methods. Using the data collected from experimental trials, the point where F.E. and product yield are the highest within the range studied will be found from ANOVA. Hypothetically, the current has a more significant impact on the F.E because it affects product conversion. Product yields are expected to be impacted more by concentration than current. These results will then be applied to demonstrate the hydrogenation of the furan ring in furfural, FA, and 5-HMF while using Ru/ACC catalyst.

IV. Materials and Methods

1. Design of Experiments

Furfural was chosen as the model compound for this study due to its importance in the world today. Its derivatives, both hydrogenated and oxidized, availability, and chemical properties make it an ideal candidate molecule for continuous ECH in an industrial application. The continuous ECH of furfural to its derivatives could provide a start toward an economically favorable production scheme for bio-oil upgrading based on its F.E. and product yield while also producing value-added byproducts.

To find the maximized value in the range studied for continuous furfural ECH, a duplicated full factorial design of experiments was conducted using concentration in moles per liter (M), and current in milliamps (mA), as experimental factors (Table 3). A center point was also included and duplicated to determine whether any curvature was present. During these experiments, the reactor was operated in a recycle mode for 1 hr.

Table 3: Concentration and current levels examined by th	e factorial	design.
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Level	Current (mA)	Concentration (M)
+1	50	0.2
-1	100	0.02
0	75	0.11

ANOVA was performed using the experimental results to show the significant effects of the current and concentration. Once ANOVA tables were obtained, the point with the highest combined F.E. and product yield within the range studied was found using the main effects of the factors. Both responses were considered because producing hydrogenated products at a high F.E. will often result in the reaction being run with a low current that will achieve low conversion rates. However, for high conversion rates, experiments are often run with higher currents that will result in a decreased F.E.

Trials were also run to better evaluate the system. To determine the effects that adsorption had on the overall process a combination of furfural, FA, and THFA at known initial concentrations were processed in a recycle mode without current and the final amount of each was calculated and evaluated. To observe catalyst deactivation, the reactor was operated in a single-pass mode with a constant concentration of 0.02 M furfural and a current of 100 mA passing through it until evidence of catalyst deactivation was observed.

At the point chosen, furfural (Sigma Aldrich, 99%), furfuryl alcohol (Sigma Aldrich, 98%), and 5-HMF (Sigma Aldrich, >99%) were individually run for 2 hrs to demonstrate ring hydrogenation in significant quantities.

2. Reactor Design

To build the reactor, a direct methanol fuel cell (DMFC) (Fuel Cell Store, Product Code: 3101601) was modified to function as a PEM fuel cell by drilling a hole into the pre-existing cutout in the acrylic endplate across from another pre-existing hose fitting. A pair of specially ordered brass hose fittings (Fuel Cell Store) was inserted into the cutout and held in place with silicone glue (Figure 5). This allowed the solution the ability to flow through each side of the reactor using an additional graphite monopolar plate (Fuel Cell Store, Product code: 590328) and two additional 1/8" Push-to-connect fittings (Fuel Cell Store, Product Code: 202174). The two sides were separated by a membrane electrode assembly consisting of Teflon gaskets on both sides, an activated carbon cloth on the anode side, and a Ru/ACC catalyst on the cathode side of a Nafion 117 membrane (Fuel Cell Store, Product Code: 591239). As the solutions flow into the cell, they are forced into the channel of the graphite plate, undergo ECH, and exit the reactor.



Figure 5: Front of each acrylic plate of the reactor after modifications to install brass hose fittings highlighted in the red circle.

The reactor was designed to attain a higher geometric surface-area-to-volume ratio to increase the ECH rate. The reactor has a higher geometric surface-area-to-volume ratio (60 cm⁻¹) than the batch reactors commonly used in our lab (0.69 cm⁻¹). In the reactor, chemicals are continuously adsorbed and desorbed by the catalyst cloth that is pressed directly against the membrane.

3. Experimental Procedure

During experiments, a peristaltic pump (Fischer Scientific) circulated 20 mL of a 30% (v/v) ethanol in water solution containing the desired concentration of furfural at a flow rate of 0.75 mL/min. This resulted in an average residence time in the reactor of about 24 s, based on the void volume of the cell. On the anode side, 20 mL of nanopure water was pumped into the cell and electrolyzed. Oxygen and excess water left the system through the hose connected to the bottom of the reactor, while H⁺ crossed the Nafion 117 membrane and bonded with the furfural. Furfural was able to combine with the H⁺ on the catalyst cloth then exit the reactor as the hydrogenated products. The reactor was run in recycle mode where the input feed and output

products were kept in the same container. The experimental setup is shown in Figure 6. All experiments were conducted in a fume hood at a constant temperature.



Figure 6: Experimental setup where the catholyte (green) and the anolyte (red) solutions are pumped along the path indicated by the arrows into and out of their respective compartments.

4. Catalyst Preparation

Because of its ability to sufficiently hydrogenate different aldehyde-containing molecules, shown by Lopez-Ruiz et al. among others, Ru/ACC was used for this study. The catalyst cloths were made in batches of 30 using an incipient wetness impregnation technique.

First, pieces of activated carbon cloth (Charcoal House, Double Weave- Activated Carbon Cloth) were cut to 1.5 cm x 3 cm and stirred in a water bath for 12 hrs so that any loose fibers would be removed before being oven-dried at 150 °C for 1 hr to remove most of the water. After the cloths were dried, they were individually soaked in a mixture of 1.01 g hexaammineruthenium (III) chloride (Strem >99%), 1.96 mL ammonium hydroxide (Sigma Aldrich), and 13.02 mL of nanopure water for 1 minute each, and excess liquid was removed. The cloths were then placed in a desiccator and vacuum dried for 12 hrs. Once they had been vacuum dried, they were placed into a Parr mini reactor (Parr Instrument Company, Series 4560) in batches of eight to reduce the Ru. The Parr reactor first had to be purged three times with argon gas and twice with hydrogen gas to remove any air in the vessel. The reactor was then pressurized to maintain a temperature of 310 °C at 3,447 kPa for 12 hrs. After 12 hrs, the reactor was allowed to cool and the catalyst clothes were placed in a desiccator.

5. Product Analysis

The sample collection and product analysis were divided into four distinct parts: catholyte dewatering, anolyte dewatering, catalyst cloth extraction, and adsorption extraction. To analyze the catholyte and the anolyte, the volumes of each were recorded and 1 mL samples from each were mixed with 0.4 g sodium chloride (NaCl) (Marcon Fine Chemicals), then with 2 mL of dichloromethane (DCM) (Fischer Chemical) to extract the organic material from the aqueous phase. From this, 1 mL was taken from the DCM phase and used for analysis. The catalyst cloth was extracted using 5 mL of DCM and placed into an ultrasonic bath for 15 min. After this, 1 mL was used for analysis. Because adsorption was identified as a source of loss in the system after the factorial design, 20 mL of methanol was circulated throughout the system for 1 hr after the catalyst cloth had been removed to extract any organic material from the system. After 1 hr, the volume of methanol was recorded, and 1 mL was used for analysis. All trials were analyzed using gas chromatography and mass spectrometry (GC/MS). The area of each compound on the chromatogram produced was multiplied by a response factor given as the trendline coefficient from the evaluation of standards and multiplied by the volume of solution they were extracted from to determine the approximate number of moles in each sample (Appendix B).

The system was evaluated using the F.E., FA and THFA yields, and the mass balance was calculated using equations (6), (7), and (8). The product yield was chosen rather than conversion because many side reactions could occur causing the conversion percentage to be misleading.

$$FE (\%) = \frac{electrons \ for \ hydrogenated \ products}{total \ electrons \ passed} * 100 = \frac{\Sigma(mol_i * n_i) * F}{I * t} * 100$$
(6)

$$Yield(\%) = \frac{moles \ of \ desired \ product \ produced}{initial \ moles \ of \ substrate} * 100$$
(7)

$$Mass Balance (\%) = \frac{(moles of furfural+moles of FA+moles of THFA)}{initial moles} * 100$$
(8)

Where the number of moles of each product is represented as mol_i and the number of electrons required to hydrogenate the product is n_i , F represents Faraday's constant 96,485 C/s, and I represents the current passed over time, t.

V. Results and Discussion

1. Operational control verification

When conducting this study, control trials were implemented to evaluate the need for both electrical current and catalyst. These trials were run using a current without catalyst and a catalyst without current to verify that both are needed for ECH to proceed (Figure 7). In these control experiments, a furfural solution of 0.02 M was circulated through the system for 1 hr with a current of 100 mA when applicable.





Without current, ECH does not occur as evidenced by the 0% yield to furfural's first hydrogenated product, FA, and 0% F.E. Without the catalyst, the reaction is still able to proceed as the current can split the water molecules but the FA yield and F.E. are both at low levels and there is no hydrogenation of the furan ring to form THFA. This is because the current alone can

hydrogenate the aldehyde but is not enough to hydrogenate the furan ring. The mass balance of less than 100% shows that throughout the experiments, there is some form of loss that will be discussed later. The mass balance with the current was lower than the run without the current, indicating that electrical current leads to a source of mass loss.

A key side reaction that may have affected the F.E. was the production of 1,1diethoxyethane from the ethanol cosolvent. Paleti et al. showed this reaction using a copper catalyst. Evidence of this reaction was first observed upon GC/MS analysis of Ru/ACC extracts from the control experiments and observed in most experiments afterward (Appendix A). This reaction occurs when the oxygen in ethanol binds to a catalyst active site resulting in the oxidative addition of the ethanol. This causes the removal of the hydrogen in the alcohol group and a hydrogen from the attached carbon atom to form acetaldehyde leading to a nucleophilic attack of the electrophilic carbon by the oxygen in another ethanol molecule. The oxygen of the second ethanol binds to the electrophilic carbon atom forming a hemiacetal and H⁺. Another hydrogen is removed from the same carbon to form ethyl acetate leading to another nucleophilic attack of the electrophilic carbon atom from another ethanol molecule forming an oxonium ion intermediate. Finally, the oxonium ion is rearranged to form 1,1-diethoxyethane and a water molecule and leaves the catalyst site (Paleti et al., 2019). The full reaction scheme is presented in Figure 8. This acetalization reaction also occurs with the aldehyde group of the furfural molecule to form 2-(diethoxymethyl)furan. However, this only occurred in insignificant quantities and did not severely impact the mass balance of the system.



Figure 8: Possible 1,1-diethoxyethane formation pathway from ethanol on a Ru catalyst based on Paleti et al.'s research using Cu. Solid lines between atoms represent bonds while dashed lines represent hydrogen bonds or partial bonds. The solid dark line represents the catalyst layer.

2. Effect of electric current and concentration

Once the need for both current and Ru was established, the factorial experiments to find the optimal conditions for industrial application were run. Using Garedew et al.'s work, which showed that the F.E. was dependent on both the concentration and current, both were varied as shown in Table 3 and the results are shown in Figure 9.



Figure 9: Results from the factorial experiments to find the optimal reaction conditions where the current varies from 0.05 - 0.1 A (first category) and the concentration varied from 0.02 - 0.2 M (second category). All values were calculated in terms of percentages.

This study demonstrated that preliminary continuous ECH trials can achieve results consistent with previous batch ECH trials. The results show that the F.E. seemed to follow the hypothesized trend that lower current provides higher F.E and is a more significant factor than the initial concentration. F.E.'s in this study ranged from 10-30% with an average of 18%, which is similar to the system presented by Green et al. The low F.E. can be attributed to Ru's HER, which is more than three times its ECH rate of furfural, and binding energy with furfural shown by Andrews et al. and Lopez-Ruiz et al. The yields recorded seemed to be most affected by the initial concentration where a lower concentration indicated a higher yield for both products regardless of the current. In this study, the combined product yields, FA and THFA, averaged

about 17% and ranged from 5-35%. Both responses displayed evidence of curvature from their respective significant main effects based on the p-value of each linear model. The mass balances were affected most by the initial concentration and mass closure averages 62%, with a range of 47-76%, where 76% was found to be on the high end of reported literature values.

Extraction from the catalyst cloth is also a key aspect that should be techno-economically evaluated. During the factorial experiment, the extraction rate of furfural and its products off the catalyst cloth was over 65% of the number of moles recorded. A higher extraction rate will yield more material in the solution instead of adsorbed to the catalyst cloth. Higher extraction rates will provide simple handling of material and eliminate the need to manually extract the catalyst cloth saving time during the manufacturing process.

Using the data from the factorial experiments, ANOVA tables for both F.E. and overall product yield, of both FA and THFA combined, were generated to determine the significant factors and interactions. For the F.E., the only significant factor was the linear effect of the electrical current. This had a negative coefficient based on a linear model developed from the ANOVA table results indicating the lower current had a higher F.E. confirming the hypothesis. When analyzing the overall product yield, the first-order main effect of concentration was the most significant factor and had a negative coefficient from the linear model. The results of the ANOVA table can be seen in Figure 10, which is arranged so that each category has a column and a row. Moving down a column shows the category in the x-axis while moving across a row will show the category on the y-axis. For example, to find the panel showing the effect of concentration with the row of overall product yield. In this panel, the concentration and overall yield are on the

x and y-axis, respectively. The intersection panel of concentration and current gives the points of the experimental design that are shown in Table 3.



Figure 10: Results of the ANOVA table showing the significant statistical effects. Categories are listed within the figure and moving down a category's column will show the category in the x-axis while moving horizontally will show the category on the y-axis.

From Figure 10, the significant effects on the F.E. and product yield can be seen in their respective panels confirming the original hypothesis that current would be more significant to the F.E. and initial concentration would be more significant to the overall product yield. Thus, this point is where the current and concentration are at the lowest levels studied, 50mA and 0.02 M for a 1-hr recycle trial. The results presented are consistent with the conclusions drawn by Garedew et al. showing that the batch and continuous cell act in similar ways concerning the F.E. and product yield for the ECH of furfural.

3. Mass balance evaluation

As seen in Figures 7 and 9, the mass balance closure for all experiments ranges from 47-76%. These values are comparable to the values presented by Jung and Biddinger, and Li et al. Possible sources for loss in the system include adsorption to the system components, migration across the membrane to the anode, evaporation, byproduct formation, and polymerization. Considering the high boiling point of furfural and its products, and the length of time of the trial, losses due to evaporation were assumed to be negligible. To quantify the migration across the membrane, the anolyte was analyzed in the same manner as the catholyte and quantified. The number of moles found in the anolyte was less than 10% of each product's final calculated moles. To better understand the effect of adsorption on the system, trials were run without current, but otherwise, the reactor was operated in the same way as the factorial trials. The solutions were made based on real data collected during the factorial experiments and all three compounds were analyzed at the same time to simulate the effect of competitive adsorption. The solution was circulated through the system for 1 hr and analyzed using the same technique as the factorial experiments. The results revealed how much of each analyte was adsorbed and are shown in Figure 11.



Figure 11: Adsorption trial data where the Adsorption (%) is the amount of (a) furfural and (b) FA and THFA adsorbed by the system during each trial. Logarithmic functions were fit to the collected data.

Since adsorption generally follows a period of steep incline followed by saturation like a logarithmic function, a portion of a logarithmic trendline was plotted to determine where on the curve each point resides. All furfural concentrations are speculated to be at the maximum absorbance past the saturation point. FA seems to have concentrations that are split where at the lower concentrations, absorbance appears very low while at higher concentrations, the system seems saturated. All THFA concentrations are near the saturation point. The adsorption studies showed that the amount of adsorption to the system was directly related to the initial concentration. Since a cosolvent, ethanol, was added to help prevent adsorption during the trial, the trend also shows that the higher ratio of furfural, FA, or THFA to ethanol results in a higher amount of adsorption within the system. To quantify as much of the adsorbed material as possible, methanol was run through the system after each experiment and analyzed. This occurred after the Ru catalyst was removed and methanol was circulated through the system for 1 hr to extract any compounds adsorbed to the components of the system such as tubing, membrane, or graphite plate. However, small amounts of the substrate and products were found after analysis meaning adsorption had a minor effect on the system.

Another source of loss that was observed was the acetalization reaction between the furfural and ethanol to form 2-(diethoxymethyl)furan. This occurred when the oxygen atom in the aldehyde group bonded with the Ru/ACC which allowed for a nucleophilic attack of the electrophilic carbon by the oxygen in the ethanol molecules. However, the extent of acetalization was minimal based on the chromatogram peaks and did not significantly change the overall mass balance closure of the system.

The final source of loss identified in the system was polymerization of furfural and FA discussed by Jung and Biddinger and Hoydonckx et al. Prevention of polymerization was attempted, in part, by the addition of the cosolvent, ethanol, which disrupts the polymerization due to hydrogen bonding as discussed by Kim et al. These polymer products were unable to be quantified by GC/MS but are assumed to account for a significant quantity of the mass balance.

When combined, these sources of loss proved to occur in significant quantities. While it was unable to be quantified, it appeared that the polymerization reaction was the most significant source of loss within the system. All other sources were able to be quantified or were considered negligible. As the most significant source of mass loss, quantification and prevention of the polymerization reaction should be investigated in future studies to obtain the most accurate data possible

4. Deactivation studies

Catalyst deactivation, important for techno-economic models and future commercialization, can be readily studied using continuous ECH. A time-on-stream study was performed to collect data to plot the catalyst deactivation profile and build an understanding of deactivation mechanisms. In this study, a 0.02 M furfural solution was continuously pumped through the reactor, collected at the end, and analyzed to assess catalyst deactivation. To

determine the onset of deactivation, two conditions were developed from the control experiment with Ru catalyst over each sample's time period: 1) FA yield was less than 5%, and 2) THFA yield was 0%. The FA yield requirement of less than 5% was chosen because of the 10% FA yield found from two passes in the control. Since the current alone could hydrogenate the aldehyde but hydrogenation of the furan ring required a catalyst, the THFA yield requirement of 0% was chosen. The results are presented below where FA yield and the mass balance are evaluated along the left axis and the THFA yield is evaluated along the right axis (Figure 12).



Figure 12: Results from the Ru/ACC deactivation study where FA yield and mass balance closure are read using the left axis and THFA yield is read using the right axis. Catalyst deactivation continued for 8

hrs.

The results show that the catalyst was active for at least 3 hrs and exhibited significant signs of deactivation during the 4th hr until final deactivation by the 8th hr. The most active time for the catalyst was during the first hour after the system was saturated which is reflected in both

the FA and THFA yield. The low yield rates of both products were expected as conversion also depends on the time molecules are used in reactions. It is important to note that there is still conversion toward FA due to the current being applied. Such quick deactivation can be attributed to either catalyst leaching due to the flow of solution over the cloth, or active site blocking from any reactants and products that were not extracted off the cloth or the reactor configuration itself.

The lower initial concentration and current within the range studied will result in the point where the highest combination of overall product yield and F.E. is observed. Four potential sources of loss in the system have been identified and quantified using GC/MS. The catalyst life-span in this configuration was studied for deactivation which was observed over 8 hrs. These points provide a basis for further investigations into continuous ECH for bio-oil upgrading.

5. Furan ring hydrogenation

Next, the effect of different functional groups on the hydrogenation of the furan ring using Ru/ACC was explored. Using the data collected earlier, additional experiments were run operating at 0.02 M and 50 mA, in a recycle mode, for 2 hrs so that adequate conversion to their hydrogenated products could be seen. The furanic compounds studied in this section were furfural, FA, and 5-HMF.

Furfural was investigated to show its complete ring hydrogenation to THFA according to the reaction pathway from literature which can be seen below (Figure 13).



Figure 13: Hypothesized reaction pathway for the ECH of furfural observed from experimental results which is consistent with Kwon et al., 2016.

As seen from the reaction pathway, the first step is the reduction of the aldehyde to a primary alcohol (1) followed by either hydrogenation of the furan ring or hydrogenolysis of the hydroxyl group (2), and the third step is the opposite of the second step (3). This pathway is validated in literature and by factorial experiments showing much higher yields of FA than THFA. In the previous studies, only conversion to THFA was seen, however, it was hypothesized that MTHF could form on the catalyst cloth from THFA if the reaction time was longer. Therefore, to increase the conversion, the run time was doubled so that the molecules would pass through the reactor four times instead of two. When comparing the results of the 1-hr validation experiment from the factorial design and the 2-hr study, run time increases conversion to hydrogenated products (Figure 14). The differences between the validation experiment and factorial design trials can be explained from the catalyst preparation method, which is subject to variability in the surface deposition of Ru, or from variability within experiments due to operational control and analytical error.


Figure 14: Differences between the 1- and 2-hr trials. Both experiments were run at 0.02 M and 50 mA at a catholyte flow rate of 0.75 ml/min.

In this comparison, the difference in yield can be seen and the effect of extra passes through the reactor is significant as the yields of FA and THFA increase by about 10% and 8%, respectively with a similar F.E. and mass balance. When running the 2-hr experiments, it was also noted that trace amounts of MTHF appeared on the catalyst cloth, an expected product since it is the final step in the reaction pathway (3).

To verify the pathway presented in Figure 13 and compare the effect of an alcohol with an aldehyde, FA was run through the system at the same conditions. By eliminating the first step in this pathway, it resulted in an increased THFA yield of about 15% while also verifying that THFA is produced from FA ECH (Figure 15).



Figure 15: Effect of alcohol vs. aldehyde on ECH of a furan ring when furfural and FA are compared using 0.02 M initial concentration, 50 mA, and a 2-hr. run time.

Results from the study suggest that the aromatic ring is hydrogenated first forming THFA rather than hydrogenolysis of the hydroxyl group. Thus, when eliminating the first step in furfural hydrogenation, THFA yields increase substantially while the F.E. and mass balance remain similar. The mass balance closures were similar due to the same sources of loss; however, FA mass closure was slightly higher as polymerization was less likely to occur. Trace amounts of MTHF were also extracted from the catalyst cloth as well.

Another furan-containing molecule that was studied using the continuous system was 5-HMF, a compound commonly derived from the pyrolysis of cellulose and hemicellulose and dehydration of glucose and other sugar monomers. Using this molecule, the effect of having another hydroxymethyl group opposite the aldehyde on the furfural molecule was studied. However, results were not able to be quantified due to the unavailability of chemical standards for the hydrogenated products. Therefore, all results for this study were assessed using the chromatogram and mass spectrum (Appendix A). The results from the chromatogram support what has been reported in literature as the reaction pathway for 5-HMF which is similar to furfural. First, the hydrogenation of the aldehyde occurs (1) followed by a competing reaction between the hydrogenation of the furan ring (2a) and the recombination and dehydration of a hydroxy group (2b) (Figure 16). While the results of this portion of the study were not quantified, they were confirmed by MS as the four products shown in Figure 16 appear in significant quantities (Yang et al., 2019).



Figure 16: Hypothesized reaction pathway for the ECH of 5-HMF observed from experimental results which is consistent with Kwon et al., 2016.

In this study, continuous ECH has been effective and efficient at hydrogenating both furfural and 5-HMF in significant quantities. For the reaction to proceed, both an electric current and catalyst are needed for significant yields of products and F.E.s. The linear effect of the current was the most significant effect on the F.E. while the product yield was impacted by both the linear and quadratic effects of the concentration. Due to the increased geometric surface areato-volume ratio within the reactor, chemical species were able to interact more and may have led to a higher chance of polymerization which is assumed to account for some of the mass loss. When studying the reaction pathway of furfural, the pathway in the cell favored the furan ring hydrogenation compared to the hydrogenolysis of the hydroxy group. This was confirmed when FA was run through the system and produced only THFA and trace amounts of MTHF. Catalyst deactivation also occurred very quickly inside the reactor, possibly due to catalyst leaching and active site blocking from the polymerization or reactor design.

VI. Conclusion and Future Recommendation

The results of this study suggest that when using Ru/ACC in a continuous system, ECH can proceed at least two steps to hydrogenate the furan ring of both furfural and 5-HMF with significant results in short reaction times. Because of the higher geometric surface area-to-volume ratio, chemical species were subjected to continuous interaction with the catalyst cloth while passing through the reactor causing quicker and further hydrogenation in their respective reactions. For both furfural and 5-HMF, hydrogenation of the furan ring seemed to be favored over hydrogenolysis of the hydroxyl group. For industrial applications, the current and concentration are significant factors affecting the F.E. and product yield. At a lower concentration and current within the ranges studied, the system demonstrated the ability to hydrogenate the furan ring of furfural, FA, and 5-HMF, all of which are biomass pyrolysis products.

While this is a promising start toward the industrial implementation of ECH reactors for bio-oil upgrading, there is much more research required. Investigation into the time-on-stream studies and catalyst deactivation should be made to determine the cause of deactivation. Understanding the mole balance and how to quantify and ultimately prevent the polymerized product of both furfural and furfuryl alcohol could result in improved yields of the desired product. Kinetic modeling is needed to better quantify and understand reaction rates to further maximize yields and F.E.'s. More resources and research should be given to understand the continuous system as a whole and its potential use in the industry. Results gained from further studies will inform future techno-economic analysis and life cycle assessment for systems that make stable bio-oil and other value-added products.

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The transportation industry currently produces the most CO_2 through the combustion of non-renewable, petroleum-based products. Therefore, liquid biofuels represent the fastest way to reduce the effects of climate change through the recycling of CO_2 emissions. This research serves as a push toward efficiently and effectively producing a greener, value-added fuel product that could be used to displace fossil fuels in the world today.

APPENDICES

APPENDIX A

Chromatograms for all experiments

Ru and current control experiment results

The chromatograms of the experiments to verify the need for both current and the Ru catalyst are presented in this section of Appendix A. Chart titles were added to show the control experiment and location each sample was taken from.



No Ruthenium Control-Catholyte

Figure 17: No Ru control experiment where the catholyte extract is analyzed and (1) is furfural.







No Current Control-Catholyte

Figure 19: No electrical current control experiment where only the catholyte extract is analyzed and (1) is furfural.

Factorial experiments results

In this section, the chromatograms for each experimental run in the factorial design are presented. Table 3 gives the values of the reaction conditions. Titles are given to each chart to show which reaction conditions, duplicate, and area of system they are taken from. C means the sample was taken from the catholyte, and Ru/ACC means the sample was taken from the catalyst cloth. In these chromatograms, the major products are labeled in the following order: (1) is diethoxyethane, (2) is furfural, (3) is THFA, and (4) is FA. 2-(diethoxymethyl)furan is also present in these samples on the catalyst cloth, however, is not labeled due to its insignificant quantity. Differences along the y-axis between each duplicate can be attributed to the use of a new tuning, or calibration, file. This was accounted for in calculations using external standards. Due to significant differences in the data, the experiments with medium current and medium concentration, and low current and high concentration were run three times and therefore have three chromatograms for each catholyte and catalyst value. The first and third experimental runs for both conditions were the two with the closest values and were used for further calculations.



Figure 20: First duplicate of high current and low concentration experiment taken from the catholyte

extract.



Figure 21: Second duplicate of high current and low concentration experiment taken from the catholyte

extract.



High current, Low concentration 1-Ru/ACC

Figure 22: First duplicate of high current and low concentration experiment taken from the Ru catalyst cloth extract.



Figure 23: Second duplicate of high current and low concentration experiment taken from the Ru catalyst

cloth extract.



Low current, Low concentration 1-C

Figure 24: First duplicate of low current and low concentration experiment taken from the catholyte

extract.



Figure 25: Second duplicate of low current and low concentration experiment taken from the catholyte

extract.



Low current, Low concentration 1-Ru/ACC

Figure 26: First duplicate of low current and low concentration experiment taken from the Ru catalyst cloth extract.





cloth extract.



Low current, High concentration 1-C

Figure 28: First duplicate of low current and high concentration experiment taken from the catholyte

extract.





extract.



Low current, High concentration 3-C

Figure 30: Third replicate of low current and high concentration experiment taken from the catholyte

extract.



Figure 31: First duplicate of low current and high concentration experiment taken from the Ru catalyst

cloth extract.



Low current, High concentration 2-Ru/ACC

Figure 32: Second duplicate of low current and high concentration experiment taken from the Ru catalyst cloth extract.



Figure 33: Third replicate of low current and high concentration experiment taken from the Ru catalyst

cloth extract.



High current, High concentration 1-C

Figure 34: First duplicate of high current and high concentration experiment taken from the catholyte extract.





extract.



High current, High concentration 1-Ru/ACC

Figure 36: First duplicate of high current and high concentration experiment taken from the Ru catalyst cloth extract.





catalyst cloth extract.



Medium current, Medium concentration 1-C

Figure 38: First duplicate of medium current and medium concentration experiment taken from the catholyte extract.





catholyte extract.



Medium current, Medium concentration 3-C

Figure 40: Third replicate of medium current and medium concentration experiment taken from the catholyte extract.





catalyst cloth extract.



Medium current, Medium concentration 2-Ru/ACC

Figure 42: Second duplicate of medium current and medium concentration experiment taken from the Ru catalyst cloth extract.



Figure 43: Third replicate of medium current and medium concentration experiment taken from the Ru catalyst cloth extract.

Furan ring conversion results

In this section of Appendix A, the chromatograms for the 2 hr ring conversion studies are presented. These were done all using the same tuning file, therefore, absolute intensity values will be similar between trials. Titles are given to each chart to show which molecule was used, duplicate, and area of system they are taken from where C means from the catholyte, Ru/ACC means the sample was taken from the catalyst cloth, Anolyte means it was taken from the anolyte to determine the amount of crossover occurred, and MeOH stands for the absorbed material that methanol could extract after 1 hr. In these chromatograms, the major products are labeled in the caption.







furfural, (2) is THFA, and (3) is FA.

Figure 45: Second duplicate of 0.02 M furfural at 50 mA for 2 hrs taken from the catholyte where (1) is furfural, (2) is THFA, and (3) is FA.









Figure 47: Second duplicate of 0.02 M furfural at 50 mA for 2 hrs taken from the Ru catalyst cloth where (1) is MTHF, (2) is diethoxyethane, (3) is furfural, (4) is THFA, and (5) is FA.





furfural,	(2)	is	THFA,	and	(3)	is	FA.
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Figure 49: Second duplicate of 0.02 M furfural at 50 mA for 2 hrs taken from the anolyte where (1) is furfural, (2) is THFA, and (3) is FA.









Figure 51: Second duplicate of 0.02 M furfural at 50 mA for 2 hrs taken from the 1-hr methanol rinse where (1) is furfural, (2) is THFA, (3) is FA, and (4) is unknown.







5-MF, (2) is DHMTHF, (3) is DHMF, and (4) is 5-HMF.

Figure 53: Second duplicate of 0.02 M 5-HMF at 50 mA for 2 hrs taken from the catholyte where (1) is 5-MF, (2) is DHMTHF, (3) is DHMF, and (4) is 5-HMF.







(1) is 5-MF, (2) is DHMTHF, (3) is DHMF, (4) is 5-HMF, and (5) is diethoxyethane.



5-HMF 2-Ru/ACC

Figure 55: Second duplicate of 0.02 M 5-HMF at 50 mA for 2 hrs taken from the Ru catalyst cloth where (1) is 5-MF, (2) is DHMTHF, (3) is DHMF, (4) is 5-HMF, and (5) is diethoxyethane.



Figure 56: First duplicate of 0.02 M 5-HMF at 50 mA for 2 hrs taken from the anolyte. There were no

products observed.



Figure 57: Second duplicate of 0.02 M 5-HMF at 50 mA for 2 hrs taken from the anolyte. There were no products observed.





(2) is DHMTHF, (3) is DHMF, and (4) is 5-HMF.



5-HMF 2-MeOH

Figure 59: Second duplicate of 0.02 M 5-HMF at 50 mA for 2 hrs taken from the 1-hr methanol rinse where (2) is DHMTHF, (3) is DHMF, and (4) is 5-HMF.









Figure 61: Second duplicate of 0.02 M FA at 50 mA for 2 hrs taken from the catholyte where (1) is THFA, and (2) is FA.









Figure 63: Second duplicate of 0.02 M FA at 50 mA for 2 hrs taken from the Ru catalyst cloth where (1) is THFA, (2) is FA, and (3) is diethoxyethane.





and (2) is FA.



Figure 65: Second duplicate of 0.02 M FA at 50 mA for 2 hrs taken from the analyte where (1) is THFA,

and (2) is FA.





is THFA, and (2) is FA.





Figure 67: Second duplicate of 0.02 M FA at 50 mA for 2 hrs taken from the 1-hr methanol rinse where (1) is THFA, and (2) is FA.

Time-on-stream study results

In this section of Appendix A, the chromatograms for the time-on-stream study (TOS) are presented. These were done all using the same tuning file, therefore, absolute intensity values will be similar between trials at the same time but will differ throughout the experiment. Titles are given to each chart to show the time the sample was taken, and which duplicate trial it came from. In these chromatograms, the major products are labeled where (1) furfural, (2) is THFA, and (3) FA.



Figure 68: Sample was taken after 15 minutes of the first TOS duplicate.


Figure 69: Sample was taken after 15 minutes of the second TOS duplicate.



Figure 70: Sample was taken after 30 minutes of the first TOS duplicate.



Figure 71: Sample was taken after 30 minutes of the second TOS duplicate.



Figure 72: Sample was taken after 45 minutes of the first TOS duplicate.



Figure 73: Sample was taken after 45 minutes of the second TOS duplicate.



Figure 74: Sample was taken after 60 minutes of the first TOS duplicate.



Figure 75: Sample was taken after 60 minutes of the second TOS duplicate.



Figure 76: Sample was taken after 90 minutes of the first TOS duplicate.



Figure 77: Sample was taken after 90 minutes of the second TOS duplicate.



Figure 78: Sample was taken after 120 minutes of the first TOS duplicate.



Figure 79: Sample was taken after 120 minutes of the second TOS duplicate.

TOS 1-180

7.0E+6 6.0E+6 (1) Absolute Intensity 5.0E+6 4.0E+6 3.0E+6 2.0E+6 1.0E+6 (3) 0.0E+0 (2) 7 12 17 27 32 37 42 47 22 Time (min)

Figure 80: Sample was taken after 180 minutes of the first TOS duplicate.



Figure 81: Sample was taken after 180 minutes of the second TOS duplicate.



Figure 82: Sample was taken after 240 minutes of the first TOS duplicate.



Figure 83: Sample was taken after 240 minutes of the second TOS duplicate.



Figure 84: Sample was taken after 360 minutes of the first TOS duplicate.



Figure 85: Sample was taken after 360 minutes of the second TOS duplicate.



Figure 86: Sample was taken after 480 minutes of the first TOS duplicate.



Figure 87: Sample was taken after 480 minutes of the second TOS duplicate.



Figure 88: Sample was taken after 600 minutes of the first TOS duplicate.



Figure 89: Sample was taken after 720 minutes of the first TOS duplicate.



Figure 90: Sample was taken from the Ru catalyst cloth after the first TOS duplicate.



Figure 91: Sample was taken from the Ru catalyst cloth after the second TOS duplicate.

APPENDIX B

Formulas and calculations

This appendix contains all formulas used during calculations. The calibration curves are also given in this section and were used to calculate the number of molecules for furfural, furfuryl alcohol, and THFA. Multiple calibration curves were used during the project all with R^2 values of > 0.99. The coefficient was used to calculate the concentration of the vial and multiplied by the volume of the solution it was extracted from. There was no standard for 5-HMF therefore all the results were interpreted from the chromatogram.



Figure 92: Calibration curve used for furfural calculations during control experiments and first duplicates

of the factorial experiment.



Figure 93: Calibration curve used for FA and THFA calculations during control experiments and first duplicates of the factorial experiment.







Figure 95: Calibration Curve for FA (blue) and THFA (orange) used for calculations of FA and THFA in second duplicates of the factorial experiments and adsorption trials.



Figure 96: Calibration Curve for furfural (blue), FA (orange), and THFA (grey) used for calculations of the third trials in the factorial experiments.



Figure 97: Calibration curves for furfural (blue), FA (orange), and THFA (grey) used for calculations of the ring conversion studies and catalyst deactivation studies.

The following equations were used to quantify the number of molecules in the catholyte (Eqn 9), on the catalyst cloth (Eqn 10), in the anolyte (Eqn 11), and extracted using methanol (Eqn 12). These were done individually for each molecule during calculations however, the equations are the same. In the equations, m_{moles, I} is the number of moles taken from the Ith category, GC Area is the area for the integration of the GC peak over 3 seconds, and CF is the response factor from the GC Area. For the catholyte and anolyte, there is also a dewatering and dilution factor of ½ that was used during the extraction. The catalyst cloth was extracted using 5 mL of DCM.

$$m_{moles,Catholyte} = GC Area * CF * \frac{Volume of solution (mL)}{1000} * 2$$
(9)

$$m_{moles,Catalyst\ Cloth} = GC\ Area * CF * \frac{5\ mL}{1000}$$
(10)

$$m_{moles,Anolyte} = GC Area * CF * \frac{Volume of solution (mL)}{1000} * 2$$
(11)

$$m_{moles,Methanol} = GC Area * CF * \frac{Volume of solution (mL)}{1000}$$
(12)

The final parameters were calculated using the following equations. The total moles of each molecule, M_I, was calculated by summing the moles found in each part of the system (Eqn 13). The initial concentration of each of the experimental runs, Initial Conc, is listed by its molarity and multiplied by the starting volume (20 mL) to obtain the initial amount of moles and is used to calculate the yields, Y_I, (Eqn 14), and mass balance, MB, (Eqn 15). The final F.E., yields, and mass balance are listed as a percent and given a conversion factor of 100. When calculating the F.E. (Eqn 16), the number of electrons was calculated as a function of current, measured in amps, I, and time, measured in seconds, t. The number of electrons, n_i, used by the products was multiplied by faraday's constant, F to obtain the number of coulombs.

$$M_I = m_{moles,Catholyte} + m_{moles,Catalyst\ Cloth} + m_{moles,Anolyte} + m_{moles,Methanol}$$
(13)

$$MB = \frac{M_{furfural} + M_{FA} + M_{THFA}}{Initial \ Conc * \frac{20}{1000}} * 100$$
(14)

$$Yield(\%) = \frac{M_{I}}{Initial \ Conc * \frac{20}{1000}} * \ 100$$
(15)

$$FE(\%) = \frac{\Sigma(M_i * n_i) * F}{I * t} * 100$$
(16)

APPENDIX C

Additional data collected

To find the true optimum conditions, a central composite design was to be used originally and is shown below (Figure 94). However, due to a calculation error, the experiments on the outside circle were run incorrectly and the data was not used in further calculations but is presented here (Table 4). The box and center point remained intact and were further used to find the point with the highest F.E. and product yield.



Figure 98: Central composite design of experiments where the current is varied along the x-axis and concentration along the y-axis. The points labeled are the points to be originally run at.

Furfural Concentration (M)	Current (A)	Faradaic Efficiency (%)	FA Yield (%)	THFA Yield (%)	Mass Balance (%)
0.237	0.075	27.21	6.56	0.49	62.29
0.237	0.075	25.07	6.07	0.44	60.53
0.11	0.015	22.14	2.53	0.09	74.09
0.11	0.015	16.68	1.76	0.12	67.65
0.11	0.135	13.67	12.73	0.97	63.54
0.11	0.135	11.73	8.93	1.50	77.93
0.017	0.075	8.97	15.37	7.18	54.21
0.017	0.075	6.81	14.00	4.67	36.30

Table 4: Additional experimental results.

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