Summer 2014

Production of Renewable Fuels and Chemicals from Biomass-Dervied Furan Compounds

Sara K. Green
University of Massachusetts - Amherst

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PRODUCTION OF RENEWABLE FUELS AND CHEMICALS
FROM BIOMASS-DERIVED FURAN COMPOUNDS

A Dissertation Presented

by

SARA K. GREEN

Submitted to the Graduate School of the
University of Massachusetts Amherst in partial fulfillment
of the requirements for the degree of
Doctorate of Philosophy

SEPTEMBER 2014

Department of Chemical Engineering
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PRODUCTION OF RENEWABLE FUELS AND CHEMICALS
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A Dissertation Presented

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SARA K. GREEN

Approved as to the style and content by:

_________________________________________________________________________________

Paul J. Dauenhauer, Chair

_________________________________________________________________________________

Wei Fan, Member

_________________________________________________________________________________

Scott M. Auerbach, Member

_________________________________________________________________________________

T. J. Mountziaris, Department Head

Department of Chemical Engineering
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ABSTRACT

PRODUCTION OF RENEWABLE FUELS AND CHEMICALS FROM BIOMASS-DERIVED FURAN COMPOUNDS

SEPTEMBER 2014

SARA K. GREEN, B.S., SMITH COLLEGE
PH.D., UNIVERSITY OF MASSACHUSETTS AMHERST

Directed by: Professor Paul J. Dauenhauer

Growing concern over the petroleum supply, energy independence, and environmental impacts associated with fossil fuels, has motivated research into the production of renewable fuels and aromatic chemicals from biomass resources. Specifically, furan-based feedstocks such as furfural, 2-methylfuran (MF) and, 2,5-dimethylfuran (DMF) can be derived from biomass and used to produce a wide variety of desired compounds. These furan-based feedstocks are produced by: (a) the hydrolysis of cellulose and hemicellulose form to glucose and xylose, (b) the dehydration of these carbohydrates to form 5-hydroxymethylfurfural (HMF) and furfural, and (c) the reduction of HMF and furfural to DMF, MF, and furan.

The use of a continuous electrocatalytic membrane reactor presents a novel method of selectively hydrogenating furfural at low temperatures without the use of gaseous hydrogen. Conversion of acetone to isopropanol confirmed that the rate of hydrogenation using gaseous hydrogen is comparable to the rate of hydrogenation using water electrolysis. Evaluation of the electrocatalytic hydrogenation of furfural demonstrated an ability to control product selectivity beyond the capability of
conventional catalysis. Results indicate that production of renewable “electrofuels” in a PEM reactor, utilizing water electrolysis in the place of hydrogen gas, is a viable alternative to conventional methods.

Diels-Alder cycloaddition of furan-based compounds and ethylene is a promising method of sustainably producing valuable base chemicals. Specific molecules of interest include $p$-xylene, the feedstock for polyethylene terephthalate (PET); toluene, an important monomer for polyurethane; and benzene, a precursor for polystyrene. The reaction proceeds via a [4+2] Diels-Alder cycloaddition of the furan feedstock and ethylene to produce an oxa-norbornene intermediate, and the subsequent dehydration of the intermediate to form the desired aromatic. 90% selectivity to $p$-xylene from DMF and 46% selectivity to toluene from MF were achieved over an H-BEA catalyst. Analysis of the reaction rate as a function of catalyst loading revealed two distinct kinetic regimes, whose activation energies correspond with DFT calculated energy barriers for dehydration and cycloaddition rate-limiting steps. Additionally, the reaction network for the MF/ethylene system was expanded to include MF polymers and two isomers of incomplete cycloadduct dehydration. Results demonstrate the complex nature of these reactions and the effect of reaction temperature, catalyst type and loading, and furan feedstock on the product distribution.
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CHAPTER 1
INTRODUCTION

1.1 Motivation

Society depends on petroleum for products such as gasoline, plastics, solvents, asphalt and jet fuel; however, this resource is becoming increasingly expensive and scarce. Additionally, the environmental consequences of using petroleum and its derivatives can no longer be ignored. Renewable fuels and chemicals produced from biomass are commercially feasible and environmentally friendly alternatives that are made using cheap, abundant, renewable resources. The Roadmap for Biomass Technologies predicts that, by 2030, 20% of transportation fuel and 25% of chemicals will be produced from biomass.\textsuperscript{1} The current non-food biomass supply is insufficient to fully replace petroleum as the source of fuels; however, about 10-15% of petroleum is used for the production of high-value chemicals, and it is feasible to replace this feedstock with biomass resources. These chemicals include the BTX series of benzene, toluene, and xylenes, which are used not only in the fuel industry, but also as precursors for valuable plastics. Specifically, benzene is used in the production of polystyrene, toluene is used to make polyurethane foams, and \textit{p}-xylene is a precursor for terephthalic acid and polyethylene terephthalate (PET). These chemicals are not only higher in value than the fuels produced from petroleum, but their production from petroleum also releases a large quantity of CO\textsubscript{2} that it would be beneficial to mitigate.\textsuperscript{2,3,4}

A promising solution is to produce aromatic chemicals using biomass-derived furan feedstocks, as depicted in Figure 1.1. These chemicals include \textit{p}-xylene, toluene, and benzene, which will be focused upon in this dissertation. Additionally, a yield of
80% for phthalic anhydride has recently been achieved from the reaction of biomass-derived furan and maleic anhydride. The furan feedstocks are derived from carbohydrates, such as glucose and xylose, which are produced by the hydrolysis of cellulose and hemicellulose. The furan feedstocks undergo Diels-Alder cycloaddition reactions with additional compounds that add carbon molecules and remove oxygen to produce the desired aromatic chemicals.

Figure 1.1: Potential pathways for production of aromatic compounds from sugar-derived furan feedstocks.

Specifically, p-xylene is produced by the reaction of 2,5-dimethylfuran (DMF) and ethylene. The two steps in the desired pathway are a [4 + 2] Diels-Alder cycloaddition of DMF and ethylene to form an oxo-norborene cycloadduct intermediate, followed by dehydration of the intermediate to form p-xylene, as shown in Figure 1.2. In a non-solvated system, an HY zeolite catalyst produced the highest rates of DMF
conversion and \( p \)-xylene production as compared to other zeolite and amorphous Brønsted and Lewis acid catalysts. A selectivity of 76\% to \( p \)-xylene at >96\% DMF conversion was achieved at 300 °C and with a heptane solvent.\(^6\) More recently, 90\% selectivity to \( p \)-xylene at >99\% was demonstrated using an H-BEA catalyst at 250 °C and with a heptane solvent.\(^7\) It was revealed that similar pathways exist for the production of toluene from 2-methylfuran (MF) and ethylene, and benzene from furan and ethylene. These pathways are also depicted in Figure 1.2. However, selectivity towards these aromatic chemicals is lower than for \( p \)-xylene, which is likely due to the lack of protecting methyl groups on the furan ring and a subsequent higher amount of oligomerization.

Figure 1.2: Reaction schemes for the production of \( p \)-xylene, toluene, and benzene from DMF, MF, and furan reacting with ethylene.
1.2 Project Objectives

The overall objective of this dissertation was to optimize the production of renewable aromatic chemicals from biomass-derived furan feedstocks. Specifically, this project focused on the production of toluene from MF and ethylene, and also investigated the production of p-xylene and benzene from DMF and furan, respectively. Additionally, research was conducted on the use of electrocatalysis in a continuous electrocatalytic membrane reactor as a method of producing furan-based and other biomass-derived feedstocks. The key scientific questions that this project addressed include the following:

- How does the electrocatalytic hydrogenation of biomass-derived oxygenates in a continuous electrocatalytic membrane reactor compare with catalytic hydrogenation in a conventional batch reactor?
- How does electrocatalytic hydrogenation using water electrolysis as a source of protons compare to using hydrogen gas?
- How can we optimize the electrocatalytic hydrogenation of biomass-derived oxygenates in a continuous electrocatalytic membrane reactor?
- What are the reaction kinetics and mechanism for formation of aromatics from the Diels-Alder cycloaddition of ethylene and furan-based feedstocks?
- How does the structure and acidity of the catalyst and structure of the furan feedstock affect the reaction kinetics and product selectivities?
- What side-products are made from the reaction of MF and ethylene?
- How can we design a catalyst and optimize the reaction system to promote the production of aromatics over undesired side-products?
CHAPTER 2

BACKGROUND

2.1 Conventional Production of Petroleum-Based Chemicals

The industrial production of aromatic chemicals uses naphtha fractions of petroleum, pyrolysis gasoline, and coal.\textsuperscript{8,9} Naphtha fractions undergo catalytic reformation to form high octane reformate. The composition of the naphtha fraction and the operating conditions for the reformation process greatly affects the yield of aromatics. High reactor temperatures and low pressures favor the dehydrogenation of napthenes and the dehydrocyclization of parafins, which are the two reactions that produce aromatics. However, these conditions can also decrease the overall reformate yield. Catalysts used for this process include Pt, Re, Ge, Ir, or Pb. Another industrial method for aromatics production is the Cyclar process, developed by UOP/PB, which uses cyclization of propane and butane over zeolites to make aromatics.\textsuperscript{8,9}

Separation is a major component of the industrial production of aromatics. Important purification reactions are the dealkylation of toluene to benzene, the transalkylation of ethylbenzene and toluene to xylenes, and the isomerization of \( m \)-xylene to \( o \)- and \( p \)-xylenes. Distillation is used to separate \( o \)-xylenes from the xylenes mixture; however, the boiling point of \( m \text{- and } p \)-xylenes is sufficiently close that crystallization or adsorption on a molecular sieve is required for the separation of \( p \)-xylene.\textsuperscript{8,9}
2.2 Renewable Production of Biomass-Based Chemicals

2.2.1 Production of Carbohydrates from Biomass Resources

Biomass is comprised of cellulose (40-50%), hemicellulose (25-35%), and lignin (10-30%), as shown in Figure 2.1.\textsuperscript{1,10} Minor components include triglycerides, alkaloids, pigments, resins, sterols, terpenes, terpenoids, and waxes. Cellulose is a polymer made of glucose monomer units with $\beta$-1,4 glycoside linkages. Hemicellulose is an amorphous polymer bound to lignin and interlaced with strands of cellulose. It is comprised of D-xylose, L-arabinose, D-galactose, D-glucose, and D-mannose. Lignin surrounds the cellulose and hemicellulose fractions of biomass, and is an amorphous polymer consisting of highly branched, substituted, mononuclear aromatic polymers.\textsuperscript{1,10}

![Figure 2.1: Lignocellulosic components of biomass.\textsuperscript{10}](image)

Pretreatment methods are required to break apart these three constituents such that the cellulose and hemicellulose can undergo additional processing.\textsuperscript{1,10,11} Physical
treatment methods include milling, steam explosion, and hot water treatments. Chemical treatment methods involve acid hydrolysis in mild conditions. After pretreatment, the biomass is separated into sugar monomers via enzymatic or acid hydrolysis. Hydrolysis of the hemicellulose portion of the biomass produces xylose in high yield (>95%). Enzymatic hydrolysis of cellulose produces high yields of glucose (>90%), while acid catalyzed hydrolysis favors the production of 5-hydroxymethylfurfural (HMF), levulinic acid, and humans with about 70% yield of glucose.\textsuperscript{10,11} Partial acid hydrolysis of cellulose can also produce cellobiose (glucose dimmer), cellotriose (glucose trimer), and cellotetrose (glucose tetramer).\textsuperscript{1}

2.2.2 Conversion of Carbohydrates to Furan Feedstocks

Sugar components can be dehydrated over an acid catalyst (HCL, 423K) to furan compounds such as HMF, 5-methylfurfural, or furfural, as depicted in Figure 2.2. Production of HMF from fructose with an aprotic solvent, such as dimethyl sulfoxide (DMSO), in a biphasic reactor can give a final yield over 90%. Isomerization of the

![Diagram](image.png)

Figure 2.2: Pathways for production of furan feedstocks from biomass.\textsuperscript{12}
glucose to form fructose, often in mild temperatures with a base catalyst, can improve selectivity to HMF.\textsuperscript{11} Despite the tendency of glucose to form oligosaccharides, which can cross-polymerize with HMF, it is often used in industry due to its lower cost.\textsuperscript{12} A yield of 99\% of HMF at 98\% glucose conversion was produced using 12-molybdophosphoric acid (12-MPA) in a solution of 1-ethyl-3-methylimidazolium chloride and acetonitrile, the addition of which suppresses humin formation. Replacing the dehydration catalyst with Pd/C can form DMF at ~30\% selectivity without isolation of the HMF.\textsuperscript{13} A two-step biphasic reactor process was developed by Dumesic and Roman-Leshkov that achieved 89\% selectivity to DMF using 2-butanol as a solvent.\textsuperscript{1,10,14}

The process first involves the acid-catalyzed dehydration of fructose to produce HMF, followed by hydrogenolysis of the C-O bonds to form DMF over a copper-ruthenium catalyst. Additional methods of producing DMF from HMF include hydrogenation over a Pt or Cu catalyst at 7 MPa and 140 °C,\textsuperscript{3} and catalytic hydride transfer (CHT) using secondary alcohols and a Ru/C catalyst.\textsuperscript{15} A selectivity of ~80\% to DMF at ~ 100\% HMF conversion was achieved using CHT and isopropanol as the hydrogen source.

The catalytic dehydration of xylose to form furfural was first developed by the Quaker Oats Company in 1922, using sulfuric acid.\textsuperscript{11,16} A variety of solvents and catalysts have since been examined, with the best performance achieved using sulfonic acid-functionalized MCM-41, with 82\% selectivity at 91\% conversion after 24 h at 140 °C using either DMSO or toluene/water for extraction.\textsuperscript{3,16} Xing and Huber developed a two-step biphasic system uses 67-80\% less energy than current industrial processes, and achieves 90\% yield of furfural using hot water extract containing 10.7\% xylose. The process involves the hydrolysis of xylose oligomers to xylose monomers under mild
conditions in an aqueous media, followed by biphasic dehydration of the monomers to furfural.$^{17}$

2.2.3 Chemical Production from Furfural

Furfural can be used to produce a wide variety of desired chemicals including furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), 2-methylfuran (MF), and 2-methyl-tetrahydrofuran (MTHF), as seen in Figure 2.3. The hydrogenation of furfural produces FA, which is used in the manufacture of resins, and as an intermediate for the production of fragrances, vitamin C, lysine, and THFA.$^{18,19}$ The liquid phase production of FA can have up to 98% selectivity, but requires high temperatures and pressures as well as copper chromate catalysts.$^{12}$ Other catalysts have been examined to reduce the toxicity of the process, and Raney nickel modified with salts of heteropolyacids have achieved 98% selectivity at 98% conversion. Platinum is a well-known catalyst for furfural hydrogenation; however, without doping (ex. Sn, Fe, Ga) the selectivity to FA is low in favor of hydrogenolysis of the C-O bond, ring-opening, and decarbonylation.

![Figure 2.3: Pathways for hydrogenation of furfural.](image)

Figure 2.3: Pathways for hydrogenation of furfural.$^{16}$
reactions. When platinum is deposited on supports (SiO$_2$, γ-Al$_2$O$_3$, MgO, TiO$_2$) and covered with a transition metal oxide monolayer (TiO$_2$, V$_2$O$_5$, ZrO$_2$) a selectivity of 93.8% to FA was achieved, at atmospheric pressure and 423-573 K. High selectivity to FA was also achieved using copper supported on magnesium oxide (98% selectivity at 98% conversion). In the gas phase, Cu-Ca/SiO2 produced a selectivity of 98% at 98% conversion at a temperature of 130 °C. Alternatively, a commercial catalyst containing Cu/Zn/Al/ Ca/Na (59:33:6:1:1) achieved 99.7% conversion and 87% selectivity to MF at 250 °C. At similar conditions, 92.7% selectivity at 98.1% conversion of FA is also achieved.

THFA is obtained from the catalytic hydrogenation of either furfural or FA, and is used a “green” solvent in the chemical industry, in stripping formulations for paint and epoxy coatings, and in agricultural products for pesticides and biocides. Optimal reaction conditions, including solvent and catalyst type, for THFA production depend on whether the reactant is furfural or FA. For example, methanol is a good solvent for producing THFA from FA over Pd/C because it produces a high concentration of dissolved hydrogen; however, the production of THFA from furfural in methanol over Ni leads to a large number of side-products. A 97% yield, and 98% selectivity to THFA at 100% conversion of furfural was achieved in the presence of Ni or Cu at 130 °C and 725 psi. In the conversion from FA, a 98-99% yield at >99% selectivity to THFA was achieved at >99% conversion over Ni supported on silica alumina and containing 59% lead. Production of THFA from FA was also conducted in a slurry reactor at 60 °C and 90 – 580 psi. The most active catalyst for this reactor system was 5% Ru/TiO$_2$, which produced a selectivity of 97% to THFA when using 2-propanol as a solvent.
MF is formed by the hydrodeoxygenation of furfural via FA, and is a potential component of biofuel due to its high energy density.\textsuperscript{22,23} In the gas phase, 95\% conversion of furfural to MF was achieved over Cu, but with a high degree of catalyst deactivation by the thermal polymerization of FA.\textsuperscript{22} Liquid phase reactions, conducted around room temperature, decrease the polymerization reactions. A MF yield of 50 mol\% was achieved using Pd/C or Pd/SiO\textsubscript{2} in ethanol at 36 psi H\textsubscript{2} with trace amounts of HCl.\textsuperscript{22} Recently, a molybdenum carbide catalyst was used to hydrodeoxygenate furfural at 423 K and atmospheric pressure, producing MF at a selectivity of 60\%.\textsuperscript{23} This catalyst also experienced deactivation, likely from polymerization of furfural.

MF can be further processed to yield MTHF, which has an octane number of 74 and is approved by the USDOE for use as a gasoline additive in P Series type fuels.\textsuperscript{16} A two-step process was developed that first produces MF using a Cu catalyst, and then hydrogenates MF to MTHF over a Ni-based catalyst at 100-130 °C.\textsuperscript{16} Another two-step process involves supercritical CO\textsubscript{2} and a combination of CuCrO\textsubscript{4} and Pd/C catalysts.\textsuperscript{22} MTHF can also be produced from levulinic acid.\textsuperscript{1} The overall route is production of gamma valerolactone as an intermediate followed by reduction to 1,4-pentanediol and subsequent dehydration to MTHF.

2.3 Electrocatalytic Reactions

2.3.1 Hydrogenation

The electrocatalytic reduction of organic compounds has been examined using a number of compounds and methods.\textsuperscript{24,25,26,27,28} The reduction of sugars, benzene, and polyhydric alcohols has been investigated using a plexiglass electrobath, a porous tubular
and coaxial electrode membrane reactor, a standard glass H-cell, a conventional filter paper matrix cell, and an electrochemical diaphragm cell.\textsuperscript{25,29,30,31,32,33,34,35} Pintauro used a “solid polymer electrolyte” (SPE) reactor, operated in a batch-recycle mode, to hydrogenate soybean oil.\textsuperscript{36,37,38} Recently, Schröder used both a one chamber cell and a two-chamber standard glass H-cell to perform a two-step electrochemical conversion of levulinic acid to octane via valeric acid.\textsuperscript{39} Additionally, Jackson, Miller, and Saffron succeeded in the mild electrocatalytic hydrogenation and hydrodeoxygenation of model bio-oil phenolic compounds in various solvents in a standard glass H-cell.\textsuperscript{40} They also explored furfural hydrogenation to FA and MF in an undivided electrochemical cell using a sacrificial Ni or Ni–Fe alloy anode with an Al, Fe, Ni, or Cu cathode, and an ammonium chloride electrolyte.\textsuperscript{41} FA production was favored at pH of 5.0 while MF production was favored at pH 1.0. Increasing the current density decreased the reaction rate and efficiency. Chu et al. demonstrated the electrocatalytic hydrogenation of furfural using a nanoporous TiO\textsubscript{2} catalyst with enhanced surface area in an ionic liquid.\textsuperscript{42} In a half-cell reactor, Belgisir studied the electrocatalytic hydrogenation of furfural on Au, Pt, Ni, Cu, and Pb electrodes in different acidic and basic media.\textsuperscript{43} It was determined that a Cu catalyst and a basic solution achieved a high level of furfural conversion.

These previous studies demonstrated the potential of electrocatalytic hydrogenation; however, they were conducted in half-cell or batch type reactors, using sacrificial anode materials, and with the addition of homogenous acids or bases. Industrially, the electrocatalytic reduction of biomass-derived compounds should be done in a continuous reactor with stable catalysts and without added homogeneous acids or bases. The search for a stable catalyst that exhibits high activity in a continuous reactor
is indeed the focus of studies to improve the industrial electrocatalytic conversion of hydrochloric acid to form chlorine. Benziger and Nehlsen have also used a continuous flow “polymer electrolyte hydrogen pump” (PEHP) reactor to study the effect of current density on the electrocatalytic hydrogenation of acetone and decene. Belgsir has investigated the electrocatalytic conversion of furfural using not only a half-cell batch reactor, but also a flow-through reactor. In the flow-through reactor, the oxidation of furfural to furonic acid over a nickel modified graphite felt electrode was coupled with the reduction of furfural to furfuryl alcohol over a copper modified graphite felt cathode. Oxidation took place in a 1 M NaCl + NaOH + LiOH anolyte and reduction in a phosphate buffer (H3PO4 + NaOH, pH 6.6) catholyte.

2.3.2 Oxidation

Electrocatalytic oxidation has also been under investigation, either as a method of producing hydrogen gas or as a potential reaction to couple with electrocatalytic reduction. Bambagioni and coworkers investigated the production of hydrogen through the oxidation of alcohols in an alkaline electrolyzer. Kim et. al. has focused on the electrocatalytic oxidation of biomass-derived compounds such as glycerol. An important discovery was that the use of electrocatalysis allowed high selectivity towards glyceric acid or glyceraldehyde, depending on the applied voltage, which is not possible when using conventional catalysis.
CHAPTER 3

METHODS

3.1 Electrocatalytic Experiments

3.1.1 Materials and Analytical

The following chemicals were used in the study of the continuous electrocatalytic membrane reactor: Acetone (C$_3$H$_6$O, 99.5% Fisher), isopropanol (C$_3$H$_7$OH, 99.5% Fisher), furfural (C$_5$H$_4$O$_2$, 99% Acros Organics), furfuryl alcohol (C$_5$H$_6$O$_2$, 98% Acros Organics), tetrahydrofurfuryl alcohol (C$_5$H$_{10}$O$_2$, 99% Acros Organics), 2-methylfuran (C$_5$H$_6$O, 99% Acros Organics), and 2-methyltetrahydrofuran (C$_5$H$_{10}$O, 99% Acros Organics). Liquid samples were analyzed by an Agilent 7890A gas chromatography system, equipped with an RTX-VMS capillary column and a flame ionization detector (FID). Helium was used as the carrier gas with a column flow rate of 30 ml min$^{-1}$. One microliter liquid sample was injected for each analysis. For the acetone experiments, gas samples were analyzed by a GC-5890 Hewlett Packard gas chromatography system equipped with a packed column and TCD detector. Nitrogen was used as the carrier gas with a column pressure of 47 psi. IPA and hydrogen gas were the only products detected at the cathode. Carbon balances were closed with 80-100% for all experiments reported here.

Commercial membrane electrode assemblies (MEAs) consisted of an unsupported 4.0 mg Pt-Ru per cm$^2$ anode, an unsupported 2.0 mg Pt per cm$^2$ cathode, and a Nafion 117 membrane (Part 590310 www.fuelcellstore.com). In-house MEAs were fabricated using 4.0 mg cm$^{-2}$ Pt–Ru/C anodes and 1.0 mg cm$^{-2}$ Pd/C or Pt/C cathodes. The working electrode used for half-cell experiments was 1.0 mg cm$^{-2}$ Pd/C. Catalyst ink
solutions consisted of 40 wt% Pt–Ru/C, 20 wt% Pd/C, or 20 wt% Pt/C (ETEK) mixed with deionized water, liquid Nafion ionomer (Ion Power, Inc. Dupont DE520 Nafion ® Solution), and 1-propanol (99% Fisher). The ink solution was deposited on teflonized carbon paper (Toray, TGPH-090) using a spray technique at a loading of 1 – 2 mg cm$^{-2}$. MEAs were made using a hot-press at 140 °C and 1500 psi for 3 minutes. The membrane was Nafion 115 from Nara Cell-Tech.

3.1.2 Electrocatalytic Half-Cell Reactor

Electrocatalytic half-cell experiments were conducted using a standard three-electrode set-up. A platinum wire and Ag/AgCl electrode served respectively as the counter and reference electrodes. The working electrode consisted of Pt/C or Pd/C on carbon paper, as described in the previous section. The reaction solution consisted of either 2M acetone or 0.5M furfural in 0.5M H$_2$SO$_4$. The half-cell was capped to maintain an oxygen-free environment, and the solution was purged with N$_2$ for 10 minutes prior to introducing H$_2$ at a flow rate of 20 sccm. Gases were flowed into the half-cell through a glass frit and the solution was stirred throughout the reaction to ensure adequate mixing.

The electrochemically active surface area (EASA) of the commercial and in-house MEA cathodes was determined using cyclic voltammetry measurements conducted using the half-cell. The EASA of the commercial MEA cathode was estimated to be 15.2 m$^2$/g, using unsupported platinum black with a loading of 3 mg/cm$^2$ on the working electrode. The surface area of 20 wt% Pt/C was also determined to be 73.9 m$^2$/g. The EASA of the in-house MEA cathodes was measured as 44.7 m$^2$ g$^{-1}$ and 48.2 m$^2$ g$^{-1}$ for Pd/C and Pt/C, respectively. These measurements used 20 wt% carbon supported metal at
a loading of 1.0 mg cm$^{-2}$. The CVs were recorded within the potential range of −0.2 to 1.0 V (vs. Ag/AgCl) at a scan rate of 50 mV s$^{-1}$.

3.1.3 Continuous Electro catalytic Membrane Reactor

Continuous electrocatalytic membrane reactor experiments were conducted using a PEM fuel cell (www.fuelcelltechnologies.com) with a 5 cm$^2$ surface area. Serpentine flow channels for the anode and cathode were set in graphite blocks, and liquid flow rates were controlled by Eldex® Optos Metering Pumps. Electrocatalytic acetone experiments were conducted with either 200 sccm humidified hydrogen gas or 0.25 ml min$^{-1}$ water at the anode and 0.167 ml min$^{-1}$ acetone at the cathode. The hydrogen gas was humidified to ensure that, in combination with the liquid feedstock at the cathode, the membrane was sufficiently hydrated. Electrocatalytic furfural experiments were conducted with either 0.6 ml min$^{-1}$ water or 60 sccm humidified hydrogen gas at the anode. The cathode contained either 5 wt% furfural, 5 wt% furfuryl alcohol, or 5 wt% furfural sparged with 30 sccm hydrogen gas. The liquid flow rate at the cathode was 0.2 ml min$^{-1}$. The residence time of the cathode reaction mixture was approximately 20-30 minutes.

The fuel cell was purged with the anode and cathode feeds for 20 minutes prior to applying a voltage and 20 minutes after applying a voltage to ensure the cell was fully saturated with fresh feedstock and that current had reached steady state. Samples were collected at the end of the initial 20 minute purge to demonstrate the catalytic activity of the fuel cell without any external applied voltage. Time on stream data was collected for 7 hours; steady state was reached after one hour and no catalyst deactivation was observed. Data points for subsequent experiments were either averaged from samples
collected at 1, 2, and 3 hours, or single points from samples taken at 2 or 3 hours. Gas samples at the cathode outlet were collected by sparging the liquid product with N2. Voltage application and current measurements were performed with a Metrohm Autolab Potentiostat, PGSTAT302N, coupled with a 10 Amp Current Booster, BSTR10A. Pressure was controlled using Swagelok back-pressure regulators (KCB Series) connected to the outputs of both the anode and the cathode.

3.1.4 Conventional Catalytic Batch Reactor

Conventional catalytic batch reactor experiments were conducted to compare with results from the continuous electrocatalytic membrane reactor for experiments using acetone. The batch reactor was a 100 ml Parr Reactor that was operated at a pressure of 15 psi. Catalyst samples for the Parr reactor consisted of 0.05 grams of commercial 20 wt% Pt/C (BASF). The catalyst amount in the Parr reactor was chosen to equal the platinum loading on the cathode of the PEM reactor. Samples from the Parr reactor were collected from the sampling port into a chilled container and filtered using a 0.22 μm Millipore syringe filter. Samples were taken at five-minute intervals for thirty minutes. A linear regression analysis of the data was conducted to determine the reaction rate. The analysis showed a clear dependence of IPA concentration on reaction time ($R^2 > 99\%$).

3.1.5 High-throughput reactor (HTR) experiments

HTR experiments were conducted to screen potential catalysts for hydrogenation of furfural in the continuous electrocatalytic membrane reactor. Monometallic catalysts were prepared by the incipient wetness impregnation method with the following metal
precursors: [Pd(NH3)4](NO3)2, [Pt(NH3)4](NO3)2, Ru(NO)(NO3)3 and Ni(NO3)2·6H2O (Strem Chemicals Inc.). The 5 wt% Rh/Al2O3 catalyst was purchased from Strem Chemicals Inc. Gamma- alumina (γ-Al2O3) was employed as a support, formed from Boehmite (Sasol) pretreated in a conventional oven at 600 °C for 4 hours. The catalysts were reduced under H2 flow at 300 °C for Pd, Pt, Ru, and Rh and 400 °C for Ni for 2 hours and purged with He flow for 30 minutes. After reduction, the catalysts were cooled down to room temperature under He flow, then sealed, and stored in a glove box. The metal dispersions of the prepared catalysts were determined by H2 chemisorption using a Quantachrome Autosorb iQ Automated Gas Sorption system. Before chemisorption, all catalysts were reduced in situ under H2 flow up to 300 °C (Pd, Pt, Ru and Rh) and 400 °C (Ni) with a heating rate of rate 1 °C min$^{-1}$, held for 140 minutes, and cooled to room temperature.

The aqueous-phase hydrogenation (APH) of furfural and FA was conducted using a HTR (HEL Group CAT24) consisting of 24 wells machined into a high-pressure stainless steel cylindrical chamber. The temperature, pressure, and stirring speed were controlled and monitored by WinIso E670 system software. Prior to the reaction, 5–10 mg of catalyst was loaded into a glass tube reactor placed on the HTR wells in the glove box and the catalysts were reduced under H2 flow at 200 °C for 12 hours in case re-oxidation occurs. After reduction, the catalysts were cooled down to room temperature under He flow, then sealed, and moved to the glove box. In the glove box, magnetic stir bars and 2 ml of 4.8 wt% furfural and FA solutions were loaded into glass tube reactors containing reduced catalysts. The HTR was then sealed with closed valves and transported to the reactor system bench. The HTR was first pressurized to 650 psia and
then heated to 100 °C for the APH of furfural and 80 °C for the APH of FA at a rate of 20 °C min\(^{-1}\), after which it was pressurized to a final pressure of 800 psia. The temperature and pressure were kept constant during the reaction, and a stirring speed of 800 rpm was used. Once a reaction set finished, the HTR was cooled down to room temperature at a rate of 14 °C min\(^{-1}\). The HTR was then depressurized to atmospheric pressure, and samples from each well are taken and filtered at 0.2 microns.

### 3.2 Diels-Alder Experiments

#### 3.2.1 Materials and Analytical

The reaction solution for Diels-Alder experiments consisted of a n-heptane solvent (Alfa Aesar, 99%), the furan reactant (DMF, Alfa Aesar, 98%; MF, Alfa Aesar, 98%, furan, Sigma Aldrich, 99%), and n-tridecane (Alfa Aesar, 98%) as an internal standard. Liquid samples were analyzed using an Agilent 7890A gas chromatograph with a Restek Stabiliwax® -DA column. A Shimadzu high performance liquid chromatograph with a mobile phase consisting of 90% methanol and 10% water and equipped with a Waters C\(_{18}\) column, a refractive index collector, and a 10A Fraction Collector was used to separate individual products. These samples were analyzed with NMR using deuterated dimethylsulfoxide (Cambridge Isotope Laboratories, Inc., DMSO) as a solvent. Mass spectrometry analysis was conducted using a Agilent 7890A connected to a 5975C inert XL MSD with Triple-Axis Detector.
3.2.2 Catalyst Characteristics and Preparation

Zeolite catalysts were obtained from Zeolyst and included CBV600 (FAU, Si/Al=2.6), CP814C (BEA, Si/Al=19), CP814E (BEA, Si/Al=12.5) and CBV3024E (MFI, Si/Al=15). Prior to reaction, the microporous materials were calcined in a tube furnace under air flow with an online drierite tube to remove moisture present in the gas. The calcination was carried at 550 °C for 12h with a ramping rate of 1 °C min⁻¹. Gamma alumina (STREM) was pretreated at 500 °C for 12h with the same ramping rate. Niobic acid (HY-340, CBMM) was pretreated for 3 h at 100 °C. Catalyst characteristics are included in Table 3.1. The concentration of Brønsted acid sites was determined using

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Si/Al ratio</th>
<th>surface area</th>
<th>Na₂O content</th>
<th>Brønsted acid sites</th>
<th>Total acid sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-BEA (CP814E)</td>
<td>12.5</td>
<td>680</td>
<td>0.05</td>
<td>0.70</td>
<td>1.12</td>
</tr>
<tr>
<td>H-BEA (CP814C)</td>
<td>19</td>
<td>710</td>
<td>0.05</td>
<td>0.56</td>
<td>1.21</td>
</tr>
<tr>
<td>H-Y (CBV600)</td>
<td>2.6</td>
<td>660</td>
<td>0.2</td>
<td>0.36</td>
<td>0.99</td>
</tr>
<tr>
<td>H-ZSM-5 (CBV3024E)</td>
<td>15</td>
<td>405</td>
<td>0.05</td>
<td>0.71</td>
<td>1.10</td>
</tr>
<tr>
<td>Niobic Acid</td>
<td>NA</td>
<td>118[b]</td>
<td>-</td>
<td>0.05[b]</td>
<td>0.13[b]</td>
</tr>
<tr>
<td>γ-Al₂O₃</td>
<td>NA</td>
<td>200[b]</td>
<td>-</td>
<td>-</td>
<td>0.21[b]</td>
</tr>
</tbody>
</table>

isopropylamine temperature programmed desorption – thermogravimetric analysis (TPD-TGA). The number of total acid sites were calculated using the concentration of Brønsted acid sites and the ratio of Brønsted acid sites to Lewis acid sites measured using FT-IR on pyridine absorbed catalysts.\(^7\)

3.2.3 Reactor Design

High temperature, high pressure batch reactions were conducted using a 160ml Parr Reactor and a 100 ml reaction solution. In a given reaction, the reaction vessel was loaded with the liquid reaction solution and the solid catalyst before being sealed. The reactor was purged with N\(_2\) to ensure that no air was present during the reaction. The system temperature was then increased to between 200 and 300 °C and, once the desired temperature was achieved, 200 psi partial pressure of ethylene was introduced to the reactor vessel. An initial liquid sample was collected at this time, which represents the 0 minute reaction time.

Analysis of potential mass transport limitations between the gas and liquid phases was conducted by determining the second Damköhler number, which compares the chemical reaction rate to the rate of diffusive mass transfer. The mass transfer rate was determined by measuring the change in reactor pressure as a function of time once ethylene was added to the reactor. The change in pressure was used to calculate the concentration of ethylene in solution, and Figure 3.1 shows the natural log of the concentration of ethylene as a function of reaction time. The slope of the trend line of this plot is equal to the mass transfer coefficient, \(k_a = 0.0660 \text{ sec}^{-1}\). The reaction rate was measured and plotted as the natural log of DMF concentration versus reaction time,
as seen in Figure 3.1. The slope of the resulting trend line is the reaction rate constant, $k_{\text{rxn}} = 3.93 \times 10^{-5} \text{ s}^{-1}$. The ratio of these two values yields $D_{\text{aIl}} = 0.0006$, which is significantly less than 1. Therefore, it was concluded that no transport limitations exist between the gas and liquid phases in the reaction system.

The reaction system was also analyzed for potential diffusion limitations related to the catalyst. Figure 3.2 depicts the rate of production for Diels-Alder products from the reaction of DMF and ethylene as a function of catalyst particle size for the H-BEA catalyst. It is apparent that, as the catalyst particle size increases, diffusion limitations
cause the rate of production of Diels-Alder products to decrease. The particle size of the commercial H-BEA catalyst is unknown and cannot be measured due to natural variation. However, the horizontal line in the graph represents the measured reaction rate over the commercial H-BEA, which is comparable to the non-diffusion limited reaction rate over the smallest catalyst particle size. Therefore, it can be concluded that no intraparticle diffusion limitations are exhibited by the system when using the commercial H-BEA catalyst.

Figure 3.2: Rate of production of Diels-Alder products as a function of catalyst particle size for the reaction of DMF and ethylene over H-BEA catalysts at 250 °C. The solid line represents the reaction rate over the commercial H-BEA catalyst (Si/Al = 12.5).
CHAPTER 4

ELECTROCATALYTIC REDUCTION OF ACETONE IN A PEM REACTOR: A MODEL REACTION FOR THE ELECTROCATALYTIC REDUCTION OF BIOMASS

4.1 Introduction

Biofuels offer an environmentally friendly alternative to conventional petroleum fuels, and are compatible with our existing infrastructure. There exists a range of techniques for producing biofuels from biomass-derived feedstocks, most of which require the use of hydrogen gas. These include the hydrogenation of fermentation broths (including organic acids) and the hydrodeoxygenation of carbohydrates, vegetable oils, and pyrolysis oils. The hydrogen consumption for these processes ranges from 0.0074 - 0.047 kg of H\textsubscript{2} per kg of sugar feedstock, to 0.034 kg H\textsubscript{2} per kg of water soluble bio-oil feedstock, to 0.017 – 0.019 kg of H\textsubscript{2} per kg of vegetable oil feedstock. Often times the cost of the hydrogen in these processes can be comparable or more than the cost of the biomass itself. The cost of hydrogen also varies with location. For example, hydrogen costs are low (i.e. $1 per kg) near petroleum refineries where there are ample natural gas and hydrogen pipelines and facilities to produce hydrogen. In remote locations, where biomass resources are abundant, hydrogen would have to be trucked in, which increases the cost by 100 times or more. Consequently, there is a clear need for being able to inexpensively produce hydrogen at remote locations if we are to use our biomass resources in a cost effective manner.

One promising method for hydrogen production is through the oxidation of compounds at the anode of a proton exchange membrane (PEM) fuel cell. PEM fuel
cell technology is a well-known, existing technology that has primarily been developed as a method of producing electricity from hydrogen and oxygen. Exciting recent advances in the field of PEM fuel cell technology have led to highly efficient membranes, anode materials, and cathode materials. The PEM technology can also be used in reverse, where electricity is consumed to produce hydrogen by the electrolysis of water.

A continuous electrocatalytic membrane reactor uses electricity to simultaneously electrolyze water to form protons and hydrogenate a second compound using those protons. A schematic of the reactor is shown in Figure 4.1. Water is fed into the anode where protons, electrons, and oxygen are produced, as shown by Equation 1. The protons migrate through the proton exchange membrane to the cathode, where they reduce the biomass-derived molecules. A potential series of reactions that occur on the cathode of

![Figure 4.1: Schematic of the continuous electrocatalytic membrane reactor.](image-url)
the PEM reactor, using acetone as a model feedstock and isopropyl alcohol (IPA) as the desired product, are shown in Equations 2 to 6, where “S” denotes a surface active site. Equations 2 and 3 represent the absorption of protons and acetone onto the catalyst to make hydrogen and acetone surface species. Equation 4 is the reaction of surface hydrogen with surface acetone to form absorbed IPA and two free surface sites. Equation 5 is the de-absorbance of surface IPA. Equation 6 represents the evolution of hydrogen gas, which is a competitive reaction that consumes hydrogen surface species before they can react with acetone surface species. The overall reaction for the PEM reactor, including reactions on both the anode and the cathode, is shown in Equation 7.

\[
\begin{align*}
\text{H}_2\text{O} & \rightarrow 2\text{H}^+ + 2\text{e}^- + \frac{1}{2}\text{O}_2 & (1) \\
2\text{H}^+ + 2\text{e}^- + 2\text{S} & \rightarrow 2\text{H} - \text{S} & (2) \\
\text{C}_3\text{H}_6\text{O} + \text{S} & \rightarrow \text{C}_3\text{H}_8\text{O}-\text{S} & (3) \\
2\text{H}-\text{S} + \text{C}_3\text{H}_6\text{O}-\text{S} & \rightarrow \text{C}_3\text{H}_8\text{O}-\text{S} + 2\text{S} & (4) \\
\text{C}_3\text{H}_8\text{O}-\text{S} & \rightarrow \text{C}_3\text{H}_6\text{O} + \text{S} & (5) \\
2\text{H}-\text{S} & \rightarrow \text{H}_2 + 2\text{S} & (6) \\
2\text{C}_3\text{H}_6\text{O} + 2\text{H}_2\text{O} & \rightarrow 2\text{C}_3\text{H}_8\text{O} + \text{O}_2 & (7)
\end{align*}
\]

The electroreduction of acetone to form IPA is of minimal practical importance. However, it paves the way for the electroreduction of more commercially relevant biomass-derived feedstocks, such as converting glucose to hexane (Reaction 8).

\[
2\text{C}_6\text{H}_{12}\text{O}_6 + 2\text{H}_2\text{O} \rightarrow 2\text{C}_6\text{H}_{14} + 7\text{O}_2 \quad (8)
\]
Reaction 8 has the potential to produce 22.8 MJ of liquid fuel (HHV) per kg of glucose. In comparison, the fermentation of sugars to ethanol produces 15.2 MJ of liquid fuel (HHV) per kg of glucose. Therefore, the electrocatalytic reduction of carbohydrates has the potential to produce 50% more liquid fuel per kg of carbohydrates than the fermentation of sugars. However, electrocatalytic reduction does require electricity as an input. Reaction 8 requires 1.76 kWh of electricity (6.34 MJ) per kg of glucose. This value is based on the Gibb’s free energy for Reaction 8, 1139.43 kJ/mol, and assumes 100% conversion efficiency and 100% total electrical efficiency. This electricity could be obtained from any source (e.g. solar power, wind power, coal power). Additionally, the electrocatalytic PEM reactor can be used to “store” the electrical energy from intermittent sources during off-peak hours in the form of a fungible liquid fuel.74,75

4.2 Gibb’s Free Energy, Standard Cell Potential, and Reactor Efficiencies

Table 4.1 lists the Gibbs free energy and the standard cell potential for the reactions that occur during the electrocatalytic reduction of acetone. These reactions include the hydrogenation of acetone using hydrogen gas (Equation 9), the electrolysis of water (Equation 10), and the hydrogenation of acetone coupled with the electrolysis of water (Equation 11). The Gibb’s free energy for each reaction was calculated using the standard heat of formation and standard molar entropy for each component, obtained from NIST’s Chemistry Webbook (http://webbook.nist.gov/chemistry/). The standard cell potential was calculated using the Gibb’s Free Energy, Faraday’s constant, and the number of moles of electrons being exchanged in the reaction ($E^\circ = -nF\Delta G^\circ$). A negative Gibb’s Free Energy value, such as the value for Equation 9, indicates that a reaction is
Table 4.1: Gibbs free energy and standard cell potentials for the electrocatalytic reduction of acetone

<table>
<thead>
<tr>
<th>Equation</th>
<th>Electrocatalytic Reaction</th>
<th>$\Delta G^0$ (kJ/mol)</th>
<th>$E^\circ_{cell}$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>$\text{C}_3\text{H}_6\text{O} + \text{H}_2 \rightarrow \text{C}_3\text{H}_7\text{OH}$</td>
<td>-23.0</td>
<td>0.12</td>
</tr>
<tr>
<td>10</td>
<td>$\text{H}_2\text{O} \rightarrow \text{H}_2 + 0.5\text{O}_2$</td>
<td>236.3</td>
<td>-1.23</td>
</tr>
<tr>
<td>11</td>
<td>$\text{H}_2\text{O} + \text{C}_3\text{H}_6\text{O} \rightarrow \text{C}_3\text{H}_7\text{OH} + 0.5\text{O}_2$</td>
<td>213.3</td>
<td>-1.11</td>
</tr>
</tbody>
</table>

spontaneous and will generate a voltage when conducted in a fuel cell. Conversely, a positive Gibb’s free energy value, such as the values for Equations 10 and 11, indicates the reaction is non-spontaneous and will require an applied voltage from an external source to react. Because the standard cell potential is directly related to the Gibb’s free energy of a reaction, different voltages can be applied to the same reactants to selectively produce different products. The electrical power that is used by the PEM reactor is determined by the product of the applied voltage and the current, ($\text{Power} = VI$). The amount of electrical energy that is available to be converted into chemical energy depends on both the magnitude of the voltage and current and on the reactor efficiency.

There are several different measurements of reactor efficiency. The total electrical efficiency of the PEM reactor relates how much electrical energy is converted to usable chemical energy. Excess electrical energy can be converted to heat or contribute to undesired chemical reactions. The total electrical efficiency is determined by the product of the voltage efficiency and the current efficiency (Table 4.2).76 The ratio of the standard cell potential and the experimental applied voltage is the voltage efficiency.
Table 4.2: Reactor efficiency equations

<table>
<thead>
<tr>
<th>Total Electrical Efficiency</th>
<th>$\eta_T = \eta_V \eta_I$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage Efficiency</td>
<td>$\eta_V = E^o / V_{cell}$</td>
</tr>
<tr>
<td>Current Efficiency</td>
<td>$\eta_I = I_{rxn} / I_{cell} = (mol_{rxn})nF / I_{cell}\Delta t$</td>
</tr>
<tr>
<td>Power Efficiency</td>
<td>$\eta_P = \frac{HHV \text{ Fuel Output}}{(HHV \text{ Fuel Input} + \text{Electrical Power Input})}$</td>
</tr>
</tbody>
</table>

Where:

- $E^o = \text{Standard cell potential}$
- $V_{cell} = \text{Experimental applied voltage}$
- $I_{rxn} = \text{Portion of current contributing to desired product}$
- $I_{cell} = \text{Overall cell current}$
- $mol_{rxn} = \text{Number of moles of product}$
- $n = \text{Number of electrons participating in reaction}$
- $F = \text{Faraday’s constant (96485.34 C/mole)}$
- $\Delta t = \text{Operational Time}$

Current efficiency is the ratio of the portion of current contributing towards the desired product to the overall current. As the only two products from the acetone system are IPA and hydrogen gas, the current efficiency is equal to the reaction selectivity through stoichiometry and Faraday’s constant. Several factors can reduce the performance and efficiency of the PEM reactor.\textsuperscript{76,77} Increasing the applied voltage will increase the reaction rate and the electrical energy, but will decrease the voltage efficiency. The resistances of the reactor components, including the feedstocks, connecting elements, and catalyst, can decrease the current, which decreases the electrical energy. Fuel crossover through the Nafion membrane decreases the amount of reactant available to react at one
electrode and can introduce competing reactions at the other electrode. Finally, mass transfer limitations can occur, which can decrease the reaction rate of the product formation. The power efficiency is defined as the ratio of the higher heating value (HHV) of the fuel output to the HHV of the fuel input plus the electrical power input (Table 4.2). In this system, the fuel output is IPA and the input is either the consumed acetone or consumed acetone and hydrogen gas.

4.3 Results

4.3.1 Electrocatalytic Hydrogenation of Acetone with Hydrogen Gas in PEM Reactor:

The Electrocatalytic Acetone/Hydrogen System

The electrocatalytic hydrogenation of acetone to IPA using hydrogen gas in a PEM reactor is thermodynamically favorable with a Gibb’s free energy of -23 kJ/mol. In the PEM reactor this reaction should generate a voltage of 0.12V. With no externally applied voltage, a current density of ~0.0386 mA/cm$^2$ (with 0.5M acetone) was experimentally measured and IPA was detected in the product stream. This suggests that the reaction can occur purely catalytically, without an external voltage. However, current density increased drastically with the application of an external voltage (~138 mA/cm$^2$ with 0.5M acetone). The application of an external voltage also increased the reaction rate and conversion of acetone to IPA by 2-4 times. Figure 4.2 shows the increase in current density and input power as a function of applied voltage. Current density is calculated using the area of the MEA, 5 cm$^2$.

Figure 4.3.a depicts the effect of increasing an externally applied voltage on the electrocatalytic acetone/hydrogen system. Conversion and reaction rate increase with
Figure 4.2: The variation in current density and input power as a function of applied voltage for the electrocatalytic acetone/hydrogen system. Reaction conditions: 30°C, 2M acetone at 0.167 ml/min, 200 sccm H₂.

Increasing applied voltage. The current efficiency decreases with applied voltage, indicating that the increase in current contributing towards IPA production is not as large as the increase in overall current. This is discussed further in the Discussion, and is attributed to excess protons on the cathode reacting to form hydrogen gas. Gas samples collected from the cathode outlet confirmed that the concentration of hydrogen gas increases as a function of applied voltage. The measured concentration of hydrogen gas was within experimental error to the theoretical difference between the total amount of hydrogen gas (calculated from the total current) and the hydrogen required to produce IPA. This confirms that protons not reacting with acetone to form IPA instead evolved into hydrogen gas.
Figure 4.3: Conversion, current efficiency, and reaction rate for the hydrogenation of acetone to IPA using hydrogen gas in an electrocatalytic PEM reactor as a function of a) applied voltage, b) reactor temperature, c) acetone concentration, and d) cathode pressure. Reaction conditions: a-d) 0.167 ml/min acetone, 200 sccm hydrogen, a) 30ºC, 2M acetone, b) 0.1V, 2M acetone, c) 0.1V, 30ºC, and d) 0.1V, 30ºC, & 2M acetone.
The acetone conversion, reaction rate, and current efficiency increased with increasing temperature, as shown in Figure 4.3.b. The increase in reaction rate as a function of temperature is more pronounced than that caused by an increase in applied voltage. Figure 4.3.c shows the effects of increasing the liquid acetone concentration on conversion, current efficiency, and reaction rate. The acetone conversion decreased with increasing acetone feedstock concentration. The rate of IPA production went through a maximum with acetone concentration. This suggests that this reaction may have a Langmuir-Hinshelwood-Hougen Watson type rate equation where the rate initially increases with concentration and then decreases due to product inhibition. This is described in further detail by Benziger and Nehlsen.\textsuperscript{47} The current efficiency also goes through a maximum with acetone concentration.

Increasing the pressure at the anode and cathode initially increases the conversion, reaction rate, and current efficiency, as shown in Figure 4.3.d. The horizontal axis reports only the cathode pressure. The data point at 0.034 MPa represents an 0.034 MPa differential pressure between the electrodes, where the cathode was at 0.034 MPa and the anode was at 0 MPa (gauge). All other data points have the same pressure at the anode and at the cathode. The loss of performance at pressures above 0.1 MPa could be attributed to acetone fuel crossover to the anode through the polymer membrane. This is a known disadvantage in PEM technology.\textsuperscript{47,78} The data point at 0.034 MPa shows that applying a pressure differential between the anode and cathode, which should decrease crossover, slightly increases performance.

The results from the electrocatalytic acetone/hydrogen system show that PEM reactor performance is a complicated function of the applied voltage, reactor temperature,
acetone concentration, and reactor pressure. The initial analysis suggests that the reactor should be operated at high temperatures, low concentrations and pressures, and an applied voltage that balances reaction rate with efficiency. However, additional engineering analysis is needed to understand these effects and others in more detail. For example, water flux in a PEM is believed to be a function of both diffusion and electro-osmotic drag (EOD), where the proton current drags water molecules from the anode to the cathode. Benziger demonstrated that interfacial water transport is also a major factor and that the current in PEM fuel cells is self-regulated by the feedback between EOD and membrane resistance. This indicates that, in the electrocatalytic PEM reactor, the transport of water across the Nafion membrane and MEA interfaces may change the resistance of the system and decrease the local concentration of acetone near the surface of the cathode. This would affect the reaction rate and current efficiency. Additionally, much work has been conducted on modeling the steady state and dynamic behavior of H₂/O₂ PEM fuel cells, direct methanol fuel cells, and solid oxide fuel cells. Much of this work involves gaseous feedstocks or liquid feedstocks with different properties (i.e. density, viscosity, surface tension etc) than biomass-derived compounds of interest, such as pyrolysis oils. These types of models must be adapted to biomass-derived feedstocks to fully optimize the PEM reactor.

4.3.2 Electrocatalytic Hydrogenation of Acetone Coupled with the Electrolysis of Water in a PEM Reactor: The Electrocatalytic Acetone/Water System

The overall Gibb’s Free energy for the electrocatalytic reduction of acetone using protons generated by the electrolysis of water is +213.33 kJ/mol (Equation 11 Table 4.1).
This is a thermodynamically unfavorable reaction that requires a theoretical voltage of 1.11V to occur. Experimentally, 1.3V was required for the reaction to occur. Any IPA production below 1.3V was attributed to the purely catalytic reaction of acetone with protons already present in solution. At an applied voltage of 1.3V, the voltage efficiency of the PEM reactor is 85%. In comparison, the electrolysis of water requires a theoretical voltage of 1.23V and an experimental voltage of 1.482V.\textsuperscript{76} This equates to a voltage efficiency of 83%. Figure 4.4. depicts the increases in current density and input power as a function of applied voltage.

![Figure 4.4](image)

Figure 4.4: The variation in current density and input power as a function of applied voltage for the electrocatalytic acetone/water system. Reaction conditions: 30ºC, 2M acetone at 0.167 ml/min, H$_2$O at 0.25 ml/min.

At values of applied voltage above 1.3V, conversion and reaction rate increase with increasing applied voltage (Figure 4.5.a). This is similar to the electrocatalytic acetone/hydrogen system. However, conversion and reaction rate are higher for the
acetone/hydrogen system than the acetone/water system. This is because the current is higher in the acetone/hydrogen system, which equates to a higher flux of protons through the membrane. The lower flux in the acetone/water system is due to the energy requirement for the electrolysis of water. This may also explain why the current efficiency of the acetone/water system increases with applied voltage while the current efficiency of the acetone/hydrogen system decreases. Excess electrical energy in the acetone/hydrogen system can contribute to hydrogen gas generation, as discussed in the previous section. However, in the acetone/water system this electrical energy can also be used for the electrolysis of water. The acetone hydrogenation rates in the acetone/water system are lower to those measured by Benziger and Nehlsen in their PHEP reactor. Both systems have an operating power input ranging from 0.03W to 0.35W. The PEM reactor in this paper used a 15% by volume solution of acetone and generated an acetone hydrogenation rate of $0.02 - 0.42 \text{ nm/cm}^2/\text{sec}$. The PEHP reactor used a 10% by volume solution of acetone and had rates of $0.28 - 2.67 \text{ nm/cm}^2/\text{sec}$.\(^{47}\)

Increasing the cell temperature increases the current efficiency, reaction rate, and conversion for the acetone/water system as shown in Figure 4.5.b. This is similar to the effect of increasing temperature for the acetone/hydrogen system. Conversion and reaction rate are both lower for the electrocatalytic acetone/water system than for the electrocatalytic acetone/hydrogen system. As described in the previous paragraph, this is because the flux of protons from the anode to the cathode is higher for the acetone/hydrogen system than for the acetone/water system.

Figure 4.5.c depicts the effect of increasing liquid acetone concentration on conversion, current efficiency, and reaction rate. The current efficiency and conversion
Figure 4.5: Conversion, current efficiency, and reaction rate for the hydrogenation of acetone to IPA coupled with the electrolysis of water in an electrocatalytic PEM reactor as a function of a) applied voltage, b) temperature, c) acetone concentration, and d) cathode pressure. Reaction conditions: a-d) 0.167 ml/min acetone, 0.25 ml/min water, a) 30°C, 2M acetone, b) 1.5V, 2M acetone, c) 1.5V, 30°C, and d) 1.5V, 30°C, & 2M acetone.
decrease slightly with concentration. The reaction rate did not change significantly with acetone concentration. These results do not show evidence of product inhibition. This may be due to the overall lower reaction rates for the acetone/water system, thus sufficient product is not present for inhibition. Overall, the current efficiency is higher for the acetone/water system than for the acetone/hydrogen system. This could be attributed to the use of electrical energy for the electrolysis of water as opposed to hydrogen gas production.

Increasing pressure on the anode and cathode appears to have little or no effect on the electrocatalytic acetone/water system (Figure 4.5.d). As in Figure 4.3.d, the horizontal axis reports only the cathode pressure. The data point at 0.034 MPa represents a pressure differential between the two electrodes in which the cathode was at 0.034 MPa and the anode was at 0 MPa (gauge). All other data points have the same pressure at the anode and the cathode. Fluctuations could be attributed to leakage from the cell or mixed potentials from acetone crossover to the anode. Acetone concentration at the anode was analyzed using GC and found to increase with increasing pressure and increasing acetone concentration at the cathode. The analysis of the acetone/water system suggests that the reactor should be operated at high voltages and temperatures and low concentrations and pressures.

4.3.3 Conventional Catalytic and Half-Cell Electrocatalytic Hydrogenation of Acetone with Hydrogen Gas

Hydrogenation in a conventional catalytic Parr batch reactor, using hydrogen gas, was conducted to compare reaction rates with those from the acetone/hydrogen system in
the electrocatalytic PEM reactor. The PEM reactor used an unsupported Pt cathode while the Parr reactor used a 20 wt% Pt/C catalyst. To better compare these two systems, acetone hydrogenation was also conducted in an electrocatalytic three-electrode half-cell reactor with a 20 wt% Pt/C catalyst. Figure 4.6 shows a comparison of the rate of IPA production for these three systems. The rate obtained by the acetone/hydrogen system is significantly greater than the rates measured in the Parr reactor and half-cell system. This result was expected due to the relationship between partial pressure of hydrogen in a standard three-phase reactor, flux of hydrogen to the catalyst surface, and current density in an electrocatalytic reactor, as described by Benziger and Nehlsen.\textsuperscript{47} The reaction rate

![Figure 4.6: Reaction rates for the hydrogenation of acetone to IPA for the electrocatalytic acetone/hydrogen system, the conventional Parr reactor, and the electrocatalytic half-cell system. Reaction conditions: acetone/hydrogen system: 30 °C, 0.12 W, 2M acetone at 0.167 ml min\(^{-1}\), and 200 sccm H\(_2\); Parr reactor: 30 °C, 2M acetone, 103 kPa H\(_2\), 30 min; half-cell: 30 °C, 0.12 W, 2M acetone in 0.5M H\(_2\)SO\(_4\), 40 sccm H\(_2\), 30 min.](image)
of the half-cell system is comparable to that of the Parr reactor. This is likely to be because the current density in the half-cell is about 43% of that in the PEM reactor. These results signify that electrocatalytic reduction performs at least equally as well as, if not significantly better, than conventional catalytic reduction at atmospheric pressures.

4.3.4 The Role of Diffusion Limitations in the Electrocatalytic System

We calculated the Weisz Modulus, the fraction of resistance due to film mass transfer, the film temperature gradient, and the catalyst pore temperature gradient to reveal the extent to which diffusion limitations play a role in the electrocatalytic hydrogenation of acetone, as shown in Table 4.81 Bulk liquid acetone concentration and observed reaction rate were obtained directly from the experiments. Acetone surface concentration was assumed to be equal to the bulk concentration. The heat of reaction was calculated using the enthalpies of formation of products and reactants. The diameter of the Pt catalyst particles, which was used to calculate the particle characteristic length, was 10 micrometers as given by the MEA manufacturer. We could find little information on the diffusivity of acetone in Pt catalysts, therefore the effective diffusivity was estimated as that of isopropanol in palladium.82 The mass transfer coefficient was calculated using the Higbie penetration theory, as described by Outili et al., using the Table 3 we determined that all diffusion parameters for both electrocatalytic systems were negligible for all experimentally measured reaction rates and concentrations. These results suggest that there are no mass or heat transfer limitations, including pore diffusion limitations, present.
Table 4.3: Diffusion limitation equations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Equation</th>
<th>Parameter Range Acetone/ H₂ System[^a]</th>
<th>Parameter Range Acetone/ Water System[^b]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weisz Modulus</td>
<td>[ M_w = \frac{-r_{\text{obs}} L^2}{C_{AS} D_e} ]</td>
<td>2.6e⁻⁶ – 7.9e⁻⁵</td>
<td>1.1e⁻⁶ – 1.4e⁻⁵</td>
</tr>
<tr>
<td>Fraction of Resistance due to</td>
<td>[ F = \frac{-r_{\text{obs}} L}{k_g C_{Ag}} ]</td>
<td>1.0e⁻¹⁰ – 3.1e⁻⁹</td>
<td>4.5e⁻¹¹ – 5.5e⁻¹⁰</td>
</tr>
<tr>
<td>Mass Transfer across Film</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature Gradient across Film</td>
<td>[ \Delta T_{\text{Film}} = \frac{(-\Delta H_r)(-r_{\text{obs}}) L}{h} ]</td>
<td>2.4e⁻¹⁰ – 2.8e⁻⁹</td>
<td>3.2e⁻¹⁰ – 6.1e⁻¹⁰</td>
</tr>
<tr>
<td>Temperature Gradient across Catalyst Pore</td>
<td>[ \Delta T_{\text{Pore}} = \frac{D_e C_{AS} (-\Delta H_r)}{k_{\text{eff}}} ]</td>
<td>3.4e⁻⁶ – 3.5e⁻⁴</td>
<td>2.8e⁻⁵ – 3.3e⁻⁴</td>
</tr>
</tbody>
</table>

[^a]: Concentration 0.07 – 7.5M, reaction rate 0.81 – 9.5 moles IPA/moles Pt min.
[^b]: Concentration 0.61 – 7.1M, reaction rate 1.1 – 2.0 moles IPA/moles Pt min

Where:
\( r_{\text{obs}} \) = Observed reaction rate
\( L \) = Characteristic length (1/3 particle diameter)
\( C_{AS} \) = Acetone surface concentration
\( D_e \) = Acetone effective diffusivity
\( k_g \) = Acetone mass transfer coefficient
\( C_{Ag} \) = Acetone bulk concentration
\( \Delta H_r \) = Enthalpy of reaction
\( h \) = Acetone heat transfer coefficient
\( k_{\text{eff}} \) = Acetone thermal conductivity
4.4 Discussion

A PEM reactor can be used to electrocatalytically reduce oxygenated compounds by coupling the hydrogenation of biomass compounds with the electrolysis of water. This method has some key advantages over current methods of biomass conversion. The most significant advantage is that no hydrogen gas is required. This is especially important in remote locations where hydrogen gas is expensive. All protons required for the chemical reactions are produced at the anode of the PEM reactor through the electrolysis of water or, potentially, the oxidation of alcohols or other compounds. Figure 4.7 shows that comparable rates of IPA production are possible using water as the source of protons as compared to hydrogen gas. However, the acetone/water system requires a much higher power input to achieve these rates. This requirement is due to the energy needed for water electrolysis. Figure 4.7 also displays the rate of hydrogen

![Graph showing reaction rates for the production of IPA and H₂ gas as a function of power.](image)

Figure 4.7: Reaction rates for the production of IPA and H₂ gas as a function of power.

Reaction conditions: 30°C, 2M acetone at 0.167 ml/min acetone or 60 sccm N₂ at cathode, and 200 sccm of H₂ or 0.25 ml/min of water at anode.
production when using either H₂ or water at the anode with N₂ gas at the cathode. Current, or current density, is directly related to the rate of H₂ production through Faraday’s constant. Comparing the rates of H₂ production to IPA production emphasizes why current efficiency decreases with increasing applied voltage in the acetone/hydrogen system, but increases in the acetone water system. The high increase in H₂ production using hydrogen gas results in a decrease in current efficiency in the acetone/hydrogen system at high power input. However, H₂ production using water electrolysis has rates similar to IPA production in the acetone/water system over a range of power inputs. The result is that increasing the applied voltage of the acetone/water system causes either an increase or no change to the current efficiency. This also suggests that the acetone/water system will have higher current efficiencies overall. The power efficiency of the two electrocatalytic systems is compared in Figure 4.8 as a function of reaction rate. This

![Figure 4.8: Power efficiencies for the production of IPA as a function of reaction rate in the PEM reactor. Reaction conditions: 30°C, 2M acetone at 0.167 ml/min acetone at cathode, and 200 sccm of H₂ or 0.25 ml/min of water at anode.](image)
data again shows that a region of overlap exists wherein comparable rates for IPA production are obtained regardless of the source of protons. The power efficiency of the acetone/hydrogen system is higher overall than the acetone/water system. This trend is the opposite of that seen with the current efficiency. This is because the power efficiency does not take into account H\textsubscript{2} gas produced at the cathode.

The PEM reactor must be economically competitive to be viable in the current energy market. It has been calculated that the capital investment cost of a PEM fuel cell electrolyzer is in the range of $13/GJ for a 530 MW\textsubscript{e} system.\textsuperscript{67} Results show that the acetone/hydrogen system is capable of producing 55.3 moles of IPA/kWh whereas the acetone/water system produces 4.1 moles of IPA/kWh. This difference is attributed to the energy cost for the electrolysis of water. Therefore, the cost of electricity must be less than the cost of hydrogen to justify this technology.

The economic potential of the PEM reactor is explored further using a more commercially relevant feedstock: biomass-derived glucose. Economic potential of the PEM reactor is defined as the difference between the selling price of the products and the prices of the raw materials. In our case, the raw materials are the biomass feedstock and electricity. The price of the biomass feedstock varies based on the type of biomass and its location. We estimate the cost of sugar to be $0.289/kg, based on the average price for sugar from 2001-2011 as documented by the USDA Economic Research Service (www.ers.usda.gov). Sugar streams could also be available from sugarcane (http://english.unica.com.br/), or cheaper options such as black liquor from pulp and paper, hemicellulose from steam explosion of wood and the Kraft Mill process,\textsuperscript{83,84} or reducing sugars from cassava bagasse,\textsuperscript{85,86} We estimate the cost of electricity to be 8.59
cents/kWh, based on the average retail price of electricity to US customers for the commercial and industrial sectors in 2011.\textsuperscript{87} This price will change based on whether the electricity is used during peak or off-peak hours, and if a renewable source of electricity were used. The number of kilowatt hours used depends on the Gibb’s Free energy of the desired chemical reaction, the amount of desired product and the total electrical efficiency of the PEM reactor. The selling price of the desired product is estimated at $2.797/gallon based on the spot price of gasoline in the US in 2011 (www.eia.gov).

Figure 4.9 depicts the estimated economic potential for the production of 80 million gallons of hexane per year from glucose using a PEM reactor. The economic potential is calculated as a function of the chemical conversion efficiency and the total electrical efficiency. The chemical conversion efficiency is defined as the amount of

![Figure 4.9: The economic potential of the electrocatalytic PEM reactor in generating 80 million gallons of hexane per year using glucose, electricity, and water as feedstocks. Economic potential is calculated as the difference between the selling price of the products and the cost of the raw materials.](image)
product produced as compared to the theoretical amount of product that could be
produced given the amount of reactant. The total electrical efficiency is a function of the
voltage efficiency and the current efficiency, and defines how efficient the reactor is at
converting electrical energy to chemical energy. The results of the cost analysis indicate
that positive profit margins are indeed feasible if the chemical conversion efficiency is
greater than 90% and the total electrical efficiency is greater than 70%. Chemical
conversion efficiency and total electrical efficiency can be increased by increasing the
temperature of the reactor, optimizing the applied voltage and feedstock concentration,
and increasing the activity of the catalyst.

A benefit of the PEM reactor is that it can be powered using any source of
electricity. This is especially important in remote locations where biomass is plentiful
and a wind turbine or solar panel could be used to provide electricity. A distinction of the
PEM reactor is its ability to directly convert and “store” this intermittent electrical energy
into chemical energy in the form of renewable fuels that fit into our existing fuel
infrastructure. A different approach would be to use the electricity to directly generate
hydrogen gas, which could then be used in another method of biomass conversion.
However, using this method the issues of pressurizing and storing the hydrogen gas, and
the associated cost, still exist. The PEM reactor is the only technology able to directly
use unpressurized hydrogen to produce biofuels. Since the rate of biofuel production is
estimated to be lower than hydrogen production, one possibility is splitting the system
into two or more PEM reactors. The first reactor would be a PEM electrolyzer used only
for making hydrogen and oxygen gas. The hydrogen gas would flow to the anode of a
second, or a second and third, PEM reactor, and react with biomass molecules at the
cathode. A benefit of using this method is that only those PEM reactors used for reducing biomass molecules would be susceptible to catalyst poisoning by the organic compounds.

The most expensive component of operating the electrocatalytic PEM reactor are the platinum catalyst electrodes.\textsuperscript{88,89} Degradation of the MEA can occur in any layer (i.e. the platinum catalyst, carbon support, or Nafion membrane) and is caused by high temperatures, high voltages, humidity, pH, and the presence of poisonous species.\textsuperscript{88,90,91} Once degradation has occurred, there exist no methods for regenerating catalytic activity, and the MEA must be replaced. However, high operating temperatures are required to achieve practical reaction rates. Additionally, operating at high voltages can increase conversion and reaction rate, though decrease efficiency. To operate at higher temperatures and voltages, additional research must be conducted in membrane and catalyst technology or reactions must be conducted in a different type of fuel cell.\textsuperscript{92,93,94,95,96} Poisoning of the catalyst is also a concern due to the use of organic species at the cathode. The two PEM reactor approach mentioned above could mitigate catalyst degradation, as the organic species would only be present in the second of the two reactors. The cost of MEAs and, subsequently, the cost of PEM reactors will decrease as more durable, stable MEAs are developed that use non-Pt catalysts, Pt catalysts alloyed with other metals, and non-carbon or novel carbon supports.\textsuperscript{90,91,97}

This reactor concept is currently limited in that it has only been demonstrated with the electrocatalytic reduction of acetone. The development of a realistic electrocatalytic PEM reactor requires the reduction of other biomass-derived oxygenates, such as glucose or pyrolysis oils. These reactions require the use of catalysts that can
hydrogenate other types of linkages like furans and C-O-C bonds. A challenge is that some catalysts that are known to hydrogenate these linkages, such as Raney Nickel, are incompatible with the Nafion membrane. This is due to the acidic environment of the membrane, which causes dissolution of non-precious metals that then diffuse into the membrane and decrease the activity of the catalyst.\textsuperscript{98,99} Therefore, the ability of a catalyst to reduce the desired biomass-derived oxygenate must be balanced with the compatibility of that catalyst with the Nafion membrane. Future experiments will examine the use of different types of catalysts to expand the number and type of reduction reactions that can be conducted using the PEM reactor.

4.5 Conclusion

In this study we demonstrated the electrocatalytic conversion of acetone to IPA at the cathode of a PEM reactor using protons generated from either hydrogen gas or the electrolysis of water at the anode. Electrocatalytic hydrogenation in the acetone/hydrogen system was confirmed to have a higher reaction rate than conventional catalytic hydrogenation in a Parr reactor. The rate of electrocatalytic hydrogenation was lower for the acetone/water system than for the acetone/hydrogen system. This is due to the energy required for water electrolysis. A subsequent result is that the acetone/water system has a higher current efficiency than the acetone/hydrogen system. Diffusion limitations were determined to not play a role in either of the electrocatalytic systems. The investigation of different operating conditions indicated that, to maximize performance of the electrocatalytic acetone/water system, the PEM reactor should be operated at:
• as high a temperature as possible without degrading the MEA;
• an applied voltage that maximizes total electrical and power efficiencies without degrading the MEA;
• a space velocity, based on feedstock concentration and flow rate, that maximizes rate and efficiency; and
• no applied pressure at the anode or cathode. This applies to PEM fuel cells capable of maintaining an internal pressure of 0.07 MPa or less.

While the electrocatalytic hydrogenation of acetone itself is of minimal interest, this reaction can be used as a model for the electrocatalytic hydrogenation of more commercially relevant biomass-derived feedstocks, like glucose or a pyrolysis oil. Results from the electrocatalytic hydrogenation of acetone show that production of renewable “electrofuels” in a PEM reactor is a potentially viable alternative to current conventional methods, and removes the need for hydrogen gas as a feedstock. Additional research should be conducted on pressurizing PEM reactors that are able to maintain higher internal pressures. Also, exploring the use of high temperature MEAs or fuel cells may yield more practical reaction rates. Finally, alternate process designs involving two or more PEM reactors could increase efficiencies and mitigate catalyst poisoning.
CHAPTER 5

THE ELECTROCATALYTIC HYDROGENATION OF FURANIC COMPOUNDS IN A CONTINUOUS ELECTROCATALYTIC MEMBRANE REACTOR\textsuperscript{100}

5.1 Introduction

Many current methods of biomass conversion require the use of high quantities of hydrogen gas. This usage of hydrogen gas constitutes a large fraction of the overall operating cost of these technologies.\textsuperscript{10,11,16,55} An example is the hydrodeoxygenation of carbohydrates, vegetable oils, and pyrolysis oils, which can require up to 0.12 kg H\textsubscript{2} per kg feedstock.\textsuperscript{62,63,64,65} The cost of hydrogen gas is about $1/kg near hydrogen pipelines, but can increase 10 times or more when storage and transportation are required.\textsuperscript{67} This is especially important in remote locations, where biomass is plentiful and inexpensive. Assuming $2/ kg H\textsubscript{2}, the cost of the hydrogen gas feedstock could be as high as $0.13/gallon diesel fuel for hydrodeoxygenation (HDO) of vegetable oils and $1.00/gallon of gasoline for the HDO of bio-oils and sugars.\textsuperscript{62,63,64,65} These costs amount to a significant portion of the overall price of the product. This example illustrates the need for methods of biomass conversion that minimize consumption of hydrogen gas.

We recently demonstrated that proton exchange membrane (PEM) technology can be used to electrocatalytically hydrogenate acetone to isopropyl alcohol (IPA) using protons generated from the electrolysis of water.\textsuperscript{54} Water electrolysis requires an electrical power input (defined as the product of applied voltage and measured current). The required cell potential for water electrolysis is proportional to the Gibbs free energy via the number of electrons transferred and Faraday’s constant ($\Delta G = -nFE_{\text{cell}}$). Cell
current has a complicated relationship with cell potential, which was simplified by Datta into a model based on charge balances, mass balances, and Butler-Volmer kinetics.  

The electrocatalytic hydrogenation of biomass-derived oxygenates has several key advantages over other methods of biomass conversion. The most significant advantage is that no hydrogen gas is required. This is especially important in remote locations where hydrogen gas is expensive. Another advantage is that this technology stores electricity as a liquid transportation fuel that fits into existing infrastructure. This technology could thus be used for electricity storage, especially when the electricity is generated from renewable sources like wind turbines. Compared to the fermentation of glucose to ethanol, the electrocatalytic HDO of glucose to hexane in a continuous electrocatalytic membrane reactor has the potential to produce 50% more energy as a liquid fuel. HDO of biomass produces a wide range of products including alcohols, polyols, and alkanes that can be used for fuel blendstocks or sold into the commodity chemicals market. Thus PEM technology could be used to produce a wide range of products from the electrocatalytic hydrogenation of biomass-derived molecules. Both the anodic water electrolysis and the cathodic biomass hydrogenation take place in one single continuous reactor that could easily be scaled up to a commercial level. Having one single reactor vessel could reduce the capital cost of a facility for biomass conversion. The simplicity of the reactor design would also decrease the operating costs. Finally, one of the most important advantages of electrocatalysis compared to conventional catalysis is the ability to manipulate the size of the activation barrier by controlling the electrode potential. Therefore, reactions that require high temperatures and pressures in a conventional catalytic system (e.g., hydrolysis of water) will readily occur at atmospheric temperatures.
and pressures in the continuous electrocatalytic membrane reactor due to the application of a voltage.\textsuperscript{104,105} Additionally, controlling the electrode potential has the ability to affect reaction selectivity, as high potentials may promote the formation of secondary or side-products. Based on the required power input, electrocatalytic hydrogenation in a continuous electrocatalytic membrane reactor will be most economically profitable when hydrogen gas is expensive and electricity is cheap.

Furfural is a, commercially relevant, platform molecule that can produce a wide range of products by hydrogenation reactions (Figure 5.1) and shows significant potential for electrocatalytic hydrogenation.\textsuperscript{12,16,17,106,107} Products from furfural hydrogenation include furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA), 2-methylfuran (MF), and 2-methyltetrahydrofuran (MTHF). Furfural is produced from the acid-catalyzed dehydration of xylose at around 300,000 metric tons per year, and cannot be used directly as a fuel due to its tendency to polymerize at room temperatures.\textsuperscript{12} However, MTHF has an octane number of 74 and can be blended into p-series gasoline fuel.\textsuperscript{16,106} Additionally,

![Reaction Scheme for the hydrogenation of furfural.](image)

Figure 5.1: Reaction Scheme for the hydrogenation of furfural.
THFA is a “green” solvent used in industrial applications such as biocides and pesticides, coatings and dyes, and stripping formulations. The Gibbs’s free energies and standard cell potentials for the electrocatalytic formation of these products from furfural are presented in Table 5.1. As mentioned above, reactions using protons generated from water electrolysis require a higher cell potential, and thus a greater power input. The formation of THFA and MF from FA requires 1.01V and 1.09V, respectively. This indicates that hydrogenating the furan ring to form THFA is marginally more favorable than hydrogenolysis of the conjugated hydroxyl group to form MF. Similarly, hydrogenating the furan ring in MF to form MTHF (1.5V) is more favorable than hydrogenolysis of the non-conjugated hydroxyl group in THFA to form MTHF (2.06V).

In fact, though MTHF can be produced from THFA in conventional catalysis, this route is highly unlikely to occur electrocatalytically because the formation

Table 5.1: Gibbs Free Energy and Standard Cell Potentials for the hydrogenation of furfural using hydrogen gas and water electrolysis.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Hydrogen Gas</th>
<th>Water Electrolysis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ΔG (kJ/mol)</td>
<td>E&lt;sub&gt;cell&lt;/sub&gt;</td>
</tr>
<tr>
<td>1. Furfural → FA</td>
<td>-35.95</td>
<td>0.19</td>
</tr>
<tr>
<td>2. FA → THFA</td>
<td>-80.97</td>
<td>0.21</td>
</tr>
<tr>
<td>3. FA → MF</td>
<td>-25.27</td>
<td>0.13</td>
</tr>
<tr>
<td>4. MF → MTHF</td>
<td>104.78</td>
<td>-0.27</td>
</tr>
<tr>
<td>5. THFA → MTHF</td>
<td>160.48</td>
<td>-0.83</td>
</tr>
</tbody>
</table>
of hydrogen gas, requiring 1.23V, is significantly more thermodynamically favorable and, subsequently, faster.

Several catalysts have been studied as replacements for the toxic copper chromate catalyst historically used for furfural hydrogenation. These catalysts include: carbon supported copper,\textsuperscript{108,109} a copper/iron catalyst,\textsuperscript{110} Raney Ni,\textsuperscript{111} and monometallic and bimetallic Pt, Pd, Sn, and Ru.\textsuperscript{20,112,18,19,113} These catalysts can also be employed in electrocatalysis. Miller, Jackson, and Saffron explored furfural hydrogenation to FA and MF in an undivided electrochemical cell using a sacrificial Ni or Ni-Fe alloy anode with an Al, Fe, Ni, or Cu cathode, and an ammonium chloride electrolyte.\textsuperscript{41} FA production was favored at pH of 5.0 while MF production was favored at pH 1.0. Increasing the current density decreased the reaction rate and efficiency. Chu et al. demonstrated the electrocatalytic hydrogenation of furfural using a nanoporous TiO$_2$ catalyst with enhanced surface area in an ionic liquid.\textsuperscript{42} Belgsir has investigated the electrocatalytic conversion of furfural using both a flow-through reactor and a half-cell batch reactor.\textsuperscript{43,48} In the flow-through reactor, the oxidation of furfural to furonic acid over a nickel modified graphite felt electrode was coupled with the reduction of furfural to furfuryl alcohol over a copper modified graphite felt cathode.\textsuperscript{48} Oxidation took place in a 1M NaCl + NaOH + LiOH anolyte and reduction in a phosphate buffer (H$_3$PO$_4$ + NaOH, pH 6.6) catholyte. In the half-cell reactor, the electrocatalytic hydrogenation of furfural was studied on Au, Pt, Ni, Cu, and Pb electrodes in different acidic and basic media.\textsuperscript{43} It was determined that Cu was active towards furfural conversion and that the highest conversion was achieved in a basic solution.
From an economic viewpoint it would be desirable to do the electrocatalytic hydrogenation of furfural in a continuous flow reactor using stable electrodes without the use of a liquid electrolyte. Previous work has suggested that hydrogenation is most favorable in a basic media; however the Nafion membrane used in PEM fuel cells is acidic. The environment in the membrane electrode assembly (MEA) therefore limits the types of metal catalysts that can be used for hydrogenation without degradation. In this paper we will study the electrocatalytic hydrogenation of 5 wt% furfural and 5 wt% furfuryl alcohol in water in a continuous electrocatalytic membrane reactor with an MEA consisting of an acidic Nafion polymer electrolyte, Pt-Ru/C anode, and Pd/C or Pt/C cathodes. The reactor schematic for this study is depicted in Figure 5.2.

Figure 5.2: Continuous electrocatalytic membrane reactor schematic for the electrocatalytic hydrogenation of furfural over Pd/C or Pt/C using protons derived from the electrolysis of water over Pt-Ru/C.
5.2 Results

5.2.1 Catalyst Selection

The initial activity of different alumina supported monometallic catalysts including Pd, Pt, Ru, Rh, and Ni for the APH of furfural and FA was investigated. Figure 5.3 shows the comparison of initial turnover frequencies (TOFs) for the APH of furfural and FA according to catalyst type. The initial activity for the APH of furfural decreased as follows: Pd > Ni > Ru > Pt > Rh (at 100 °C). The initial TOF of the 3 wt% Pd catalyst was 8.5 times higher than the initial TOF of the 3 wt% Pt catalyst for the APH of furfural. The order of initial activity for the APH of FA followed: Pd > Ni > Ru > Rh ~ Pt (at 80 °C). The 1wt% Pd catalyst exhibited the highest initial TOF (244 h⁻¹), which was 15.3 times as high as the initial TOF of the 1 wt% Pt catalyst. Ni also showed a high initial

![Figure 5.3](image1.png)

(a) (b)

Figure 5.3: Comparison of initial TOFs over different monometallic catalysts for (a) the PAPH of furfural at 100 °C and 800 psia for 75 minutes with 4.8 wt% furfural solution as feedstock, and (b) the APH of FA at 80 °C and 800 psia for 3 hours with 4.8 wt% FA solution as feedstock.
activity for the APH of furfural and FA. However, Ni catalysts have been reported to solubilize in acidic environments and thus Ni is not a suitable monometallic PEM catalyst.\textsuperscript{98} Although Pt had a low activity for furfural and FA hydrogenation, it was investigated further using the continuous electrocatalytic membrane reactor due to its popularity as both a fuel cell catalyst and as a conventional catalyst for furfural hydrogenation.\textsuperscript{19,72,113,114}

The electrocatalytic hydrogenation of aqueous solutions of 5 wt\% furfural in a continuous electrocatalytic membrane reactor was investigated using both Pd/C and Pt/C cathodes, as shown in Figures 5.4 and 5.5. Figure 5.4 shows the relationship between current density and power input as a function of applied voltage for the (a) Pd/C and (b) Pt/C cathode catalysts. The power input is defined as the product of the applied voltage and the measured system current. The weight hourly space velocity (WHSV), defined as the ratio of the mass flow of furfural to the mass of the metal catalyst present in the MEA, was held constant for both of the catalytic systems. Both the current density and the power input are slightly higher for Pt/C than for Pd/C. This shows that the Pt/C catalyst has a higher electrochemically active surface area and lower overpotential than Pd/C.\textsuperscript{115} The higher current density produced by Pt/C translates directly to a higher flux of protons, using Faraday’s constant, as compared to Pd/C.

The current efficiency at a given power input is up to 50 times higher for Pd/C compared to Pt/C as shown in Figure 5.5.a. The current efficiency is the ratio of current contributing to furfural hydrogenation divided by the overall current. Current that does not contribute to furfural hydrogenation instead produces hydrogen gas (that is not used
Figure 5.4: Current density and power input as a function of applied voltage for the
electrocatalytic hydrogenation of furfural to form FA and THFA over a) Pd/C and b) Pt/C. Reaction conditions: 30°C, cathode: 111.7 hr\(^{-1}\)WHSV furfural over 1.0 mg/cm\(^2\) Pd/C or Pt/C, anode: H\(_2\)O at 0.6 ml/min over 4.0 mg/cm\(^2\) Pt-Ru/C.

to hydrogenate furfural) at the cathode. The high current efficiency for the Pd/C catalyst
indicates that Pd/C is a better catalyst than Pt/C for furfural conversion, while Pt/C is a
better catalyst for producing hydrogen gas. This is further demonstrated in Figure 5.5.b,
which depicts the rate of furfural conversion as a function of power input. The rate of
furfural conversion is up to 5 times higher with the Pd/C catalyst as compared to the Pt/C
catalyst. Additionally, furfural hydrogenation over Pd/C at a power input of 0.05 W or
more produced FA, THFA, MF, and MTHF. However, no MF or MTHF was detected
from furfural hydrogenation over Pt/C (results not shown). THFA was only present at a
power input of 0.3W. Based on the higher rate of furfural conversion and higher current efficiency, Pd/C was used as the cathode catalyst for all additional experiments.

![Graphs showing current efficiency and rate of furfural conversion as a function of power input for electrocatalytic hydrogenation of furfural.](image)

**Figure 5.5**: (a) Current efficiency and (b) rate of furfural conversion as a function of power input for the electrocatalytic hydrogenation of furfural. Reaction conditions: 30°C, anode: H₂O at 0.6 ml/min over 4.0 mg/cm² Pt-Ru/C, cathode: 111.7 hr⁻¹ WHSV furfural over 1.0 mg/cm² Pd/C or 1.0 mg/cm² Pt/C.

5.2.2 Effect of applied voltage

The effect of applied voltage on the electrocatalytic hydrogenation of furfural using a Pd/C cathode was investigated over a voltage range of 1.15V to 1.75V. The results for current efficiency (Figure 5.5.a) and reaction rate (Figure 5.5.b.) are presented as a function of total power input. The current efficiency ranged from 24-30%. This signifies that 70-76% of the current contributed to the evolution of hydrogen gas, rather than the hydrogenation of furfural. Liquid product selectivity is reported as a function of
conversion in Figure 5.6.a and as a function of applied voltage in Figure 5.6.b. FA was the main product with 100% selectivity at low conversion and applied voltage. This result was expected given the theoretical standard cell potential values in Table 5.1. As furfural conversion increased, the FA selectivity decreased and other products were observed. As shown in Table 5.1, a cell potential of 1.04V is required for converting furfural to FA, which is below the applied voltages of 1.15 and 1.3V. Converting FA to THFA or MF requires 1.01 and 1.09V respectively. However, at low conversion there is only low quantities of FA present and these products are not observed. As conversion increases to 2%, THFA, MF, and MTHF are detected at selectivities of 8-10%. Increasing the applied voltage to 1.75V increases conversion to 6% under the reaction

![Selectivity graphs](a) and (b)

Figure 5.6: Selectivity as a function of a) conversion and b) applied voltage for the electrocatalytic hydrogenation of furfural over Pd/C. Reaction conditions: 30°C, cathode: 111.7 hr⁻¹ WHSV furfural over 1.0 mg/cm² Pd/C, anode: H₂O at 0.6 ml/min over 4.0 mg/cm² Pt-Ru/C.
conditions used in this study. At this voltage, THFA was the second most abundant product with a selectivity of 26%. MF and MTHF remain at 8% selectivity. The high selectivity for THFA, as compared to MF or MTHF, was expected based on the thermodynamic calculations. The high standard cell potential (2.06V) for THFA hydrogenation to MTHF is consistent with these experimental results and indicates that the main route for formation of MTHF is through MF.

Figure 5.7 compares the rate of hydrogen production, furfural conversion, and hydrogen production plus furfural conversion (“combined rate”) as a function of power input for two different systems: 1) H₂O on the anode/furfural on the cathode (H₂O/Furfural System); and 2) H₂O on the anode/hydrated N₂ on the cathode (H₂O/N₂ System). Hydrogen gas was collected at the cathode by sparging the liquid product with nitrogen gas. The highest measured rate of hydrogen production was from the H₂O/N₂

![Graph showing reaction rate as a function of power input.]

Figure 5.7: Reaction rate as a function of power input. Reaction conditions: 30°C, cathode: 111.7 hr⁻¹ WHSV furfural or 60 sccm N₂ over 1.0 mg/cm² Pd/C, anode: H₂O at 0.6 ml/min over 4.0 mg/cm² Pt-Ru/C.
system. At power inputs less than 0.05W, the rate of hydrogen production was comparable for both systems. However, as the power input increases, the rate of hydrogen production for the H₂O/Furfural system decreased compared to the rate of hydrogen production for the H₂O/N₂ system. The rate of furfural conversion in the H₂O/Furfural system increased with increasing power input, but is up to 16 times lower than the rate of hydrogen production in the same system. Also shown in Figure 5.7 is the rate of hydrogen production plus the rate of furfural conversion for the H₂O/Furfural system. This “combined rate” is similar to the rate of hydrogen production in the H₂O/N₂ system, especially for power inputs below 0.1 W. Thus, it can be inferred that, at power inputs below 0.1 W, the furfural does not inhibit the rate of water electrolysis. The difference between hydrogen production in the H₂O/N₂ system and the “combined rate” in the H₂O/Furfural system increases with increasing power input. This difference coincides with a decrease in the current density of the H₂O/Furfural system. One possible cause could be that the liquid furfural feedstock at the cathode of the H₂O/Furfural system results in a higher overpotential, and thus a lower current, than the gaseous N₂ in the H₂O/N₂ system.

5.2.3 Effect of Reactor Temperature

The temperature of the continuous electrocatalytic membrane reactor was increased from 30°C to 70°C to investigate the effect of reaction temperature. Figure 5.8.a shows that the current density increases while the current efficiency decreases, with increasing temperature. The decreasing current efficiency signifies an increase in the production of hydrogen gas. These results indicate that the increase in temperature
promotes water electrolysis and production of hydrogen gas but not furfural hydrogenation. This is confirmed by Figure 5.8.b, which shows no change in the furfural conversion rate, despite the increase in power input. There is also no statistically significant change in liquid product selectivity as the temperature increases (results not shown). In non-electrocatalytic systems furfural hydrogenation is generally conducted at temperatures greater than 120°C.\textsuperscript{115} The Nafion membrane used in the continuous electrocatalytic membrane reactor is only stable up to 80°C, and therefore, additional experiments could be conducted using a high temperature membrane, such as a Celtec®P membrane from BASF, or a high temperature fuel cell to further increase temperature and study its effects on reaction rate and efficiency.\textsuperscript{95,96}

![Graphs showing current density, current efficiency, and furfural conversion rate as a function of temperature.](image)

Figure 5.8: (a) Current density, current efficiency and (b) and furfural conversion rate, power input as a function of temperature for the electrocatalytic hydrogenation of furfural. Reaction conditions: 1.45V, cathode: 111.7 hr\textsuperscript{-1} WHSV furfural over 1.0 mg/cm\textsuperscript{2} Pd/C, anode: H\textsubscript{2}O at 0.6 ml/min over 4.0 mg/cm\textsuperscript{2} Pt-Ru/C.
5.2.4 Electrocatalytic hydrogenation of Furfuryl Alcohol

Figure 5.9 depicts results from the electrocatalytic hydrogenation of FA. Figure 5.6 shows that at low conversion and low applied voltage only FA was produced for furfural conversion. It was explained that sufficient voltage was applied for producing MF and THFA but that insufficient FA was present for these reactions. At higher voltages, where there was a higher degree of furfural conversion, MF and THFA were produced. Given this explanation, the electrocatalytic reduction of FA should produce MF and THFA at an applied voltage of 1.15V. This is confirmed by the results in Figure

![Graphs](image)

Figure 5.9: (a) Reactant concentration as a function of applied voltage and (b) reactant conversion rate as a function of power input for the electrocatalytic hydrogenation of furfuryl alcohol. Furfural conversion is included in Figure 9b for the purpose of comparison. Reaction conditions: 30°C, cathode: 111.7 hr⁻¹ WHSV furfuryl alcohol (or 111.7 hr⁻¹ WHSV furfural) over 1.0 mg/cm² Pd/C, anode: H₂O at 0.6 ml/min over 4.0 mg/cm² Pt-Ru/C.
5.9.1, which show that MF and THFA are produced at approximately 3.8 mM at an applied voltage of 1.15V. However, at 1.15V no MTHF is observed, likely because there is insufficient MF present for further reaction. FA conversion and concentrations of THFA and MTHF increase as applied voltage increases. However, the concentration of MF increases from 1.15V to 1.45V, but then decreases when voltage is increased to 1.75V. This trend appears to further confirm that MF is an intermediate for MTHF, as was discussed for Figure 5.6.b.

The FA conversion rate increased with increasing power input, as shown in Figure 5.9.b. Initially, the rate of FA conversion is higher than the rate of furfural conversion. Furfural hydrogenation produces primarily FA at low power input, which involves only hydrogenating the aldehyde functionality. FA hydrogenation produces THFA, which involves hydrogenating the furan ring, and MF, which involves hydrogenolysis of the hydroxyl group. Therefore, the rate of hydrogenating the aldehyde functionality in furfural appears lower than the sum of the rates of hydrogenating the furan ring and hydrogenolysis of the hydroxyl group in FA. At power inputs greater than 0.12W, the rate of furfural conversion is higher than the rate of FA conversion. This result indicates that the rate of furfural conversion increases due to the added reactions of FA to THFA, FA to MF, and MF to MTHF.

5.2.5 Electrocatalytic hydrogenation using Hydrogen Gas

The rate of furfural hydrogenation at low power input using protons derived from hydrogen gas (the H$_2$/Furfural System) was found to be comparable to the rate of furfural hydrogenation at higher power input using protons derived from water electrolysis (the
H$_2$O/Furfural System), as shown in Figure 5.10. This is similar to results obtained for the electrocatalytic hydrogenation of acetone.$^{54}$ Figure 5.10 also shows that the H$_2$/Furfural system has a lower current efficiency, at all investigated power inputs, as compared to the H$_2$O/Furfural system. Therefore, the H$_2$/Furfural system not only has a higher rate of furfural conversion but also a higher rate of hydrogen gas production. Both systems have comparable liquid product selectivities of MF and MTHF. Selectivity of THFA is slightly higher in the H$_2$/Furfural system and selectivity of FA is slightly lower in the H$_2$/Furfural system, as compared to the H$_2$O/Furfural system.

![Figure 5.10: Current efficiency (CE) and furfural conversion rate as a function of power input for the electrocatalytic hydrogenation of furfural using hydrogen gas or water at the anode. Reaction conditions: 30°, cathode: 111.7 hr$^{-1}$ WHSV furfural over 1.0 mg/cm$^2$ Pd/C, anode: H$_2$O at 0.6 ml/min or 30 sccm H$_2$ over 4.0 mg/cm$^2$ Pt-Ru/C.](image-url)
5.3 Discussion

The main challenge in electrocatalytic hydrogenation using a continuous electrocatalytic membrane reactor is that a large fraction of the current goes towards generating hydrogen gas that is not used in the hydrogenation reaction. Thus, to make this system more practical is highly desirable to increase the rate of hydrogen consumption due to hydrogenation reactions over the rate of hydrogen gas evolution. This is based not only on the low rate of furfural hydrogenation (0.6 moles furfural/moles Pd min), but also the low current efficiency (24-30%), which indicates that the majority of protons are going towards hydrogen gas evolution. One method of increasing the furfural hydrogenation rate is to increase the applied voltage, which equates to an increase in power input. However, this also increases the rate of hydrogen evolution and thereby affects the efficiency of the reactor. It was shown in Figure 5.6.b that current efficiency for furfural conversion is between 24-30%, and increases with increasing power input. Power efficiency is defined as the sum of the higher heating value of the hydrogenated products divided by the sum of the higher heating value of the reactants plus the electrical power input. Figure 5.11 shows that there is an initial drop in power efficiency as a function of power input, followed by a graduate decrease at inputs greater than 0.05W. Therefore, a small decrease in current or power efficiency may be a worthwhile penalty for a higher rate of furfural hydrogenation. However, the applied voltage also affects selectivity, and thus increasing it may increase overall reaction rate but not promote the desired product (ex. FA at 1.3V vs FA at 1.75V as seen in Figure 6). One method of manipulating applied voltage without influencing selectivity is to change the species being oxidized at the anode. For example, Rodriguez-Rivera et al. found that
the rate of cathodic hydrogen gas evolution is comparable for oxidation of an aqueous solution of polyoxometalates (POM), which occurs at ~0.62V, as compared to oxidation of water at ~2.0V.\textsuperscript{116}

![Power Efficiency Graph](image)

Figure 5.11: Power efficiency as a function of power input for the electrocatalytic hydrogenation of furfural. Reaction conditions: 30°C, cathode: 111.7 hr\textsuperscript{-1} WHSV furfural over 1.0 mg/cm\textsuperscript{2} Pd/C, anode: H\textsubscript{2}O at 0.6 ml/min over 4.0 mg/cm\textsuperscript{2} Pt-Ru/C.

A second method of increasing the rate of furfural hydrogenation is to increase the reactor temperature. However, the temperature of the continuous electrocatalytic membrane reactor is limited by the Nafion membrane and, as discussed earlier, either a high temperature membrane or another type of fuel cell is required to achieve temperatures over 80°C.\textsuperscript{95,96} Additionally, increasing reactor temperature was seen to decrease current efficiency (Figure 5.8.a). A third option to increase reaction rate is to change the catalyst or its support. Ni, Fe, and Cu have been used for electrocatalytic furfural hydrogenation and shown high conversion and selectivity to FA, despite leaching...
of these metals. These metals could be readily incorporated into an MEA for an alkaline fuel cell. Using conventional catalysis, it has been shown that Pt/titania results in higher selectivity to FA and THFA while Pt/silica and Pt/magnesia have higher selectivity towards MF, 2-pentanol, and 2-pentanone. Extensive research has been conducted on improving the kinetics for H₂/O₂ fuel cells, which could be applicable to electrocatalysis of biomass derived molecules. Research to improve oxygen reduction reactions (ORR) has examined Pt monolayers on Au, Rh, Pd, Ru, and Ir supports as well as monolayers of Pt-M (M = Ir, Ru, Rh, Pd, Au, Re, or Os) deposited on the surfaces of Pd (111) single crystal or carbon supported Pd nanoparticles. To decrease CO poisoning and improve reaction kinetics at the anode, Pt alloys such as PtRu, PtMo, and PtSn have been examined. An added difficulty in choosing the proper catalyst is that the catalyst represents a large portion of the cost of the overall process. The aforementioned Pt monolayers drastically decrease the amount, and therefore, cost of Pt in the catalyst. Even cheaper substrates made from tungsten carbide, have also been found to have a similar hydrogen binding energy and activity to bulk Pt, when only a Pt monolayer is present.

Alternate reactor designs could also be used for this process, as shown in Figure 5.12. One of the most basic methods of hydrogenating furfural would be to produce hydrogen in a PEM electrolyzer and then use the hydrogen in a conventional catalytic reactor, as seen in Figure 5.12.a. The disadvantage of this design is that the hydrogenation of furfural requires high-pressure hydrogen. Therefore a compressor would be needed to recompress the hydrogen gas after reaction. In addition, this approach requires a separate high-pressure reactor. The continuous electrocatalytic
membrane reactor proposed in this study was depicted in Figure 5.2. In this design, water is electrolyzed at the anode of the electrocatalytic reactor and the generated protons are used to reduce furfural at the cathode. The benefit of this design, as compared to that shown in Figure 5.12.a, is that it does not require pressurization, storage, or transport of hydrogen gas and takes place all in one reactor, thereby minimizing energy and materials usage.

The continuous electrocatalytic membrane reactor could be further developed to recycle hydrogen and/or furfural from the cathodic product stream and/or to include a second catalytic bed to further hydrogenate remaining furfural (Figure 5.12.b). The second catalytic bed could be conventional, and thus require a compressor, or electrocatalytic. A recycle loop for water exiting the anode could also be incorporated. The purpose of recycling hydrogen gas in the cathode feedstock is not only to conserve resources but also to increase the rate of furfural hydrogenation. However, experiments conducted with hydrogen gas sparged at the cathode inlet showed no statistically relevant changes in furfural conversion rate or product selectivity.

5.4 Conclusion

In this paper we studied the electrocatalytic hydrogenation of furfural in a continuous electrocatalytic membrane reactor using protons derived from water electrolysis. Pd/Al2O3 was 15.3 times more active than Pt/Al2O3 for hydrogenation of furfural in a batch reactor. Consistent with the batch reactor experiments, Pd/C was 4.4 times more active than Pt/C for hydrogenation of furfural at the cathode of the continuous electrocatalytic membrane reactor. Identified products from furfural hydrogenation over
Figure 5.12: Reactor schematics for the hydrogenation of furfural using protons generated from water electrolysis. (a) PEM water electrolyzer coupled with a conventional catalytic reactor. Hydrogen gas is produced from water electrolysis in the PEM electrolyzer, which is then used in a conventional catalytic reactor to hydrogenate furfural. (b) Single continuous electrocatalytic membrane reactor with second catalytic bed (electrocatalytic or conventional catalytic) and recycle loops.

Pd/C were FA, THFA, MF, and MTHF. The product selectivity changed as a function of applied voltage. The FA selectivity decreased and the THFA selectivity increased with increasing voltage. Selectivity towards MF and MTHF was 8% at power inputs over
0.02W. The current efficiency was 24-30%, which indicates that up to 76% of the overall current contributed towards the evolution of hydrogen gas instead of furfural hydrogenation. Adjusting the temperature between 30-70°C was not found to affect the rate of furfural conversion. The electrocatalytic hydrogenation of FA resulted in high selectivities of THFA and MF, and a faster initial rate of conversion than furfural hydrogenation. Using hydrogen gas as the source of protons instead of water electrolysis resulted in a comparable rate of furfural conversion at a lower power input. Sparging hydrogen gas at the cathode had no statistically significant effect on the reaction rate.
CHAPTER 6

PRODUCTION OF P-XYLENE FROM THE DIELS-ALDER CYCLOADDITION OF DMF AND ETHYLENE

The reaction of DMF and ethylene involves a Diels-Alder cycloaddition to produce a cycloadduct intermediate, followed by dehydration of the intermediate to produce p-xylene (shown in Figure 1.1). Williams et al. investigated the non-solvated system, and discovered that the highest selectivity to p-xylene was 51.9%, achieved at 300 °C over HY. This catalyst also produced the highest rate of DMF conversion as compared to HBEA, H-ZSM-5, Siliceous BEA, Silicalite-1, and Mulite. Additionally, different Si/Al ratios for H-Y (Si/Al = 2.6) and H-Y (Si/Al = 40) produced statistically similar reaction rates. These results indicate that catalyst structure plays an important role in catalytic activity. Specifically, the structure of H-Y, which contains 1.3 nm cages, is more active than a catalyst without active sites or one with smaller pores such as H-BEA.

The addition of a heptane solvent further increased selectivity to p-xylene to 76%. The solvent decreases the concentration of DMF in solution and likely reduces Friedel-Crafts type reactions between the highly electrophilic cationic intermediates and DMF, which forms various alkylated and oligomer products. An additional undesired pathway is the reversible hydrolysis of DMF to form the ring-opened 2,5-hexanedione. This reaction proceeds using the water released from the dehydration reaction that forms p-xylene, and thus is difficult to avoid. However, at high DMF conversion 2,5-hexanedione reforms DMF and thereby still contributes to p-xylene production. A more complete reaction pathway for the production of p-xylene from DMF and ethylene, which includes the undesired side-reactions, is included in Figure 6.1.
DFT calculations confirm the uncatalyzed dehydration energy barrier is sufficiently large to prevent reaction. Figure 6.2 shows the calculated gas-phase energy barriers for the Diels-Alder reaction as well as the C-O bond cleavage and two protonation steps associated with the dehydration reaction. The uncatalyzed reaction exhibits an energy barrier of 24.4 kcal/mole for the cycloaddition reaction and 62.8 kcal/mole for dehydration.\textsuperscript{6,123} Therefore, dehydration of the cycloadduct is the rate-limiting step in the uncatalyzed reaction. The addition of a Lewis acid catalyst decreases all energy barriers and maintains the C-O bond cleavage reaction as the rate-limiting step, which requires 35.8 kcal/mole. The addition of a Brønsted acid catalyst has no effect on the cycloaddition reaction, but decreases the energy barrier for C-O bond cleavage to 11.4 kcal/mole. Under these conditions, the rate-limiting step is now cycloaddition, which has the lowest energy barrier (24.4 kcal/mole) of the aforementioned rate-limiting steps.\textsuperscript{123}
Figure 6.2: Energy barriers for the Diels-Alder reaction and dehydration reaction for the overall reaction of DMF and ethylene to form \textit{p-xylene}.\textsuperscript{123}

An investigation of the initial reaction rate for production of Diels-Alder compounds as a function of the concentration of Brønsted acid sites reveals the existence of two distinct kinetic regimes, as depicted in Figure 6.3. At low catalyst loadings, the rate increases with increasing Brønsted of acid site concentration, indicating that Brønsted acid sites are required for the rate-limiting step of the reaction. Meanwhile, at high catalyst loadings the reaction rate is independent of Brønsted acidity. The two different kinetic regimes are present over both H-BEA and H-Y. The activation energy for both regimes was measured over H-BEA and H-Y and confirmed to correspond with DFT calculated energy barriers for dehydration and cycloaddition reactions, as seen in Figure 6.3, Figure 6.4, Figure 6.5, and Table 6.1. This confirms that, at low catalyst loading, the rate-limiting step is dehydration and therefore increasing the number of acid sites increases the reaction rate. At high catalyst loading, the rate-limiting step is
Figure 6.3: Reaction rate for the production of $p$-xylene as a function of Brønsted acid site concentration for the reaction of DMF and ethylene at 250 °C over H-BEA and H-Y.

Figure 6.4: Arrhenius plot for the production of $p$-xylene from DMF and ethylene over (a) 1 mM Brønsted acid sites H-BEA, and (b) 3.5 mM Brønsted acid sites H-BEA.
Figure 6.5: Arrhenius plot for the production of \( p \)-xylene from DMF and ethylene over
(a) 1 mM Brønsted acid sites H-Y, and (b) 3.5 mM Brønsted acid sites H-Y.

Table 6.1: Comparison of DFT theoretical energy barriers and measured activation energies for the production of \( p \)-xylene from DMF and ethylene.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Low Catalyst Loading Energy Barrier (kcal/mole)</th>
<th>High Catalyst Loading Energy Barrier (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DFT</td>
<td>Experiment</td>
</tr>
<tr>
<td>H-BEA</td>
<td>11.3</td>
<td>11.7 ± 3.5</td>
</tr>
<tr>
<td>H-Y</td>
<td>11.3</td>
<td>10.8 ± 2.1</td>
</tr>
</tbody>
</table>

cycloaddition, which is not Brønsted acid catalyzed, and therefore increasing the acid sites has no effect on reaction rate.

What is most fascinating is that the two kinetic regimes are present for a wide variety of catalysts, as seen in Figure 6.6. Despite different structures and different Brønsted and Lewis acid site densities, the DMF/ethylene reaction over these catalysts
transitions from being limited by dehydration to being limited by cycloaddition around the same concentration of Brønsted acid sites. This indicates that reaction rate depends primarily on the number of acid sites, and that catalyst structure does not play a role in determining reaction rate.

Figure 6.6: Reaction rate for the production of Diels-Alder products as a function of concentration of Brønsted acid sites for the reaction of DMF and ethylene at 250 °C.
CHAPTER 7

ULTRA-SELECTIVE CYCLOADDITION OF DIMETHYLFURAN FOR RENEWABLE P-XYLENE WITH H-BEA\(^7\)

The need for sustainable production of everyday materials in addition to market volatility of petroleum-based feedstocks has motivated research into the production of renewable aromatic chemicals from biomass.\(^2,16,124,125,126,127\) Cellulose and hemicellulose comprise a significant fraction of lignocellulosic biomass and provide six-carbon (e.g. glucose) and five-carbon (e.g. xylose) sugars as primary feedstocks for the production of renewable chemicals with six-carbon aromatic ring structures.\(^12\) Specific chemicals of interest include p-xylene, the feedstock for polyethylene terephthalate (PET), and toluene, an important monomer for polyurethane products.\(^128,129,130\) In this work, we reveal a highly selective method (>90% product selectivity and 90% yield for p-xylene formation at 99% conversion of dimethylfuran) for the production of basic monomers from biomass-derived furan feedstocks by combined catalytic cycloaddition/dehydration reactions using H-BEA zeolite.

We have proposed a renewable method of producing renewable p-xylene by cycloaddition of biomass-derived dimethylfuran (DMF) and ethylene,\(^6\) which serves as the last step in a complete process for producing p-xylene from cellulose. Glucose, produced by saccharification of cellulose, can be isomerized with Sn-BEA\(^131\) to fructose, and subsequent acid-catalyzed dehydration produces 5-hydroxymethylfurfural (HMF).\(^132,133\) Hydrogenolysis of HMF over CuRu/C produces DMF,\(^14\) and the final step adds ethylene (which can be derived from ethanol dehydration)\(^134\) to yield p-xylene. Further investigation into the design of this process indicates potential for economic
viability, and a sensitivity analysis of the considered process parameters highlights the need for improved selectivity to \( p \)-xylene in the conversion of DMF.\textsuperscript{135}

Our research on the reaction of DMF and ethylene has revealed the fundamental catalytic chemistry, but the optimal catalytic system converted at least 25\% of feedstock carbon into unusable side products at great cost to overall process viability.\textsuperscript{6} The reaction occurs by symmetry-allowed \([4 + 2]\) Diels–Alder cycloaddition of ethylene and subsequent aromatization by acid-catalyzed dehydration in multiple elementary steps to \( p \)-xylene (Figure 7.1). Addition of ethylene to DMF produces an oxa-norbornene cycloadduct intermediate in a single uncatalyzed step with a barrier of 24.7 kcal mol\(^{-1}\), determined by gas-phase DFT.\textsuperscript{123} In the absence of an acid catalyst, dehydration is inhibited by a large barrier (58.0 kcal mol\(^{-1}\)); however, acid-catalyzed dehydration of 1,4-dimethyl-7-oxabi-cyclo[2.2.1]hept-2-ene occurs readily (19 kcal mol\(^{-1}\)), indicating the

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need for a Brønsted-acid catalyst. While a previous work has observed the cycloadduct intermediate with GC–MS,\textsuperscript{122} it was not measured in this work. Elucidation of the reaction pathways by separation of the reaction mixture and characterization by NMR/GC–MS has revealed three competing side reactions\textsuperscript{122} to the main pathway to p-xylene: (1) hydrolysis of DMF to 2,5-hexanedione, (2) secondary addition of DMF to produce dimers, and (3) secondary reactions of ethylene to alkylated aromatics. From this analysis, further improvement of selectivity to p-xylene can be specifically defined as: (a) elimination of the hydrolysis side reaction or (b) reduction of secondary addition of either the dienophile (e.g. ethylene) or the diene (e.g. DMF).

In this work we show that selectivity to p-xylene from DMF and ethylene can be significantly enhanced by using the H-BEA catalyst. As shown in Figure 7.2, initial catalytic reaction rates reveal the activity of several solid-acid catalysts at 250 °C in heptane solvent at low conversion (XDMF, the conversion of DMF, <20%). While previous studies using pure DMF reactant at 300 °C have indicated that Y-zeolite is more active than H-BEA,\textsuperscript{6} the reaction with H-BEA (47 mmol (g-cat h)$^{-1}$) in the presence of heptane solvent at 250 °C is at least 50% more active than H-Y zeolite. Additionally, several other catalysts including H-ZSM-5, niobic acid, and γ-Al2O3 are nearly an order of magnitude less active than H-BEA under these conditions.

The initial kinetics of solid-acid catalyzed cycloaddition in heptane solvent support the previously proposed mechanism of p-xylene production, and highlight the importance of H-BEA. As shown in Figure 7.2, the initial reaction rate of p-xylene is independent of the Si/Al ratios within given materials such as BEA, which indicates that the overall reaction rate (at low conversion) is independent of the total number of
Figure 7.2: Initial reaction rates of \( p \)-xylene formation for the reaction of DMF in heptane with ethylene (62 bar) at 250 °C with various catalysts. The Si/Al ratios of catalysts are shown in parentheses. 

Brønsted acid sites for the considered reaction conditions. However, it was shown previously that materials require a Brønsted acid site to exceed the rate of cycloaddition/dehydration occurring within the non-catalyzed system.\(^6\) The necessity for a Brønsted acid site for which site-density does not correlate with activity (at high catalyst loading) is consistent with the proposed mechanism of rate-limiting, non-catalyzed Diels–Alder cycloaddition, described previously.\(^6\) \( \text{H}^+ \) has been shown to exhibit no potential for decrease in the cycloaddition reaction barrier, both experimentally and by DFT.\(^{123, 136}\) With this in mind, the comparison of the activity of H-BEA (\( R_{\text{DMF}} \), the initial reaction rate of DMF is equal to \( 47 \pm 3 \text{ mmol-pX (g-cat h)}^{-1} \)) with those of other non-porous materials such as WOx–ZrO2 (\( R_{\text{DMF}} = 50–55 \text{ mmol-pX (g-cat h)}^{-1} \)) shows comparable reaction activities at the same temperature (250 °C).\(^{53} \)
Figure 7.3: Conversion of DMF as a function of time for the reaction of DMF in heptane with ethylene (62 bar) at 250 °C with various catalysts. The Si/Al ratios of catalysts are shown in parentheses.

The potential of H-BEA for combined cycloaddition/dehydration chemistry relative to other materials is further revealed by long-time experiments examining high conversion of DMF. As shown in Figure 7.3, most catalytic materials at 250 °C in heptane solvent exhibit a similar behavior with significant deactivation after ~10 hours. Niobic acid, γ-Al2O3, H-Y zeolite, and H-ZSM-5 all exhibit only ~50–60% conversion after 30 hours. In contrast, H-BEA exhibits a significantly different catalytic behavior and rapidly achieves a high conversion of ~90% in 10 hours under the same conditions.

The benefit of the high activity of H-BEA relative to other considered materials is a higher selectivity to p-xylene of ~90% on a carbon basis. As shown in Figure 7.4,
Figure 7.4: (a) Selectivity of p-xylene and the concentration of 2,5-hexanedione and (b) the concentration of other products as a function of DMF conversion for the reaction of DMF in heptane with ethylene (62 bar) at 250 °C with H-BEA (Si/Al = 12.5).

23.1

Selectivity to p-xylene increases with DMF conversion. At $X_{\text{DMF}} = 20\%$, selectivity to p-xylene is only 60%, and the hydrolysis product (2,5-hexanedione), alkylated products and oligomers comprise the remaining 40%, within experimental error. However, as $X_{\text{DMF}}$ increases to $>99\%$, selectivity to p-xylene exceeds 90%. This counter-intuitive behavior can be partially explained by the concentration of the hydrolysis side-product, 2,5-hexanedione, as revealed in Figure 7.3.a. For $X_{\text{DMF}} < 60\%$, the concentration of all side products increase in step with DMF conversion. However, while no change in concentration is observed for the alkylated products and oligomers after $X_{\text{DMF}} > 80\%$, the concentration of 2,5-hexanedione decreases from 0.08 M for $X_{\text{DMF}} > 60\%$ and reduces to nearly zero concentration for $X_{\text{DMF}} > 99\%$. This behavior is consistent with the hydrolysis reaction equilibrium between DMF–water and 2,5- hexanedione, as DMF reacts with ethylene, 2,5-hexanedione reforms DMF to maintain equilibrium. p-Xylene
formation is highly favorable thermodynamically,\textsuperscript{6,123} and all reactants including side products in equilibrium will yield \( p \)-xylene at high conversion. This was confirmed by a separate experiment shown in Figure 7.5, which started with 2,5-hexanodione and water in heptane. 2,5-hexanodione undergoes cyclization to DMF, even with the presence of water, during the heating process (point “RT” to time = 0), and the composition did not change significantly over a 4 hour period. Upon the addition of ethylene, the DMF is converted to \( p \)-xylene, which supports the postulation that the decreasing concentration of 2,5-hexanodione seen in Figure 7.3.a is due to the reformation of DMF that then forms \( p \)-xylene.

By the DMF hydrolysis reaction, carbon, which appears lost to the side product 2,5-hexanodione at low conversion, is recovered and results in high selectivity to \( p \)-xylene at high conversion of DMF. The superior performance of H-BEA for selective production of \( p \)-xylene can therefore be attributed to: (a) its resistance to deactivation,

![Graph showing concentration of products as a function of time.](image)

Figure 7.5: Concentration of products as a function of time for the reaction of 2,5-hexanodione, water, and ethylene (62 bar) over H-BEA (Si/Al = 12.5) at 250 °C.
allowing for high conversion of DMF (Figure 7.3), (b) its superior activity relative to other solid-acid materials (Figure 7.2), and (c) its ability to catalyze dehydration of the Diels–Alder cycloadduct without catalyzing important side reactions. \(p\)-Xylene, once formed from DMF, does not readily isomerize to \(o\)- or \(m\)-xylene under the considered reaction conditions, which provides a significant process advantage by eliminating the expensive separation of xylene isomers.

The high activity of H-BEA is more pronounced for the conversion of DMF to \(p\)-xylene than for the reaction of 2-methylfuran (MF)–ethylene to toluene or the reaction of furan–ethylene to benzene. As shown in Figure 7.6.a, the conversion of MF was 93% with H-BEA and 71% with H-Y after 24 hours of reaction under identical conditions to the experiments in Figure 7.2. Similarly, Figure 7.6.b depicts the conversion of furan with ethylene which was 54% with H-BEA and 50% with H-Y after 24 hours. Figure 7.7

![Graphs showing conversion of MF and furan with ethylene over H-BEA and H-Y](image)

Figure 7.6: (a) Conversion of MF and ethylene and (b) furan and ethylene over H-BEA (Si/Al = 12.5) and H-Y (Si/Al = 2.6) at 250 °C.
compares the product selectivities for conversion of DMF and MF at $X_{\text{DMF, MF}} > 90\%$ and furan at $X_{\text{furan}} > 70\%$ at 250 °C. While 90% selectivity to p-xylene is achieved for conversion of DMF, only 46% selectivity to toluene and 35% selectivity to benzene are observed. A significant loss of carbon occurs in the reaction of MF and furan due to increased reactions between the furans forming dimers (e.g. benzofuran) and larger oligomers. The increase in these reactions is likely due to the absence of methyl groups at the furan $\alpha$-carbon positions, which inhibit these side reactions.

The discovery that H-BEA in heptane exhibits high selectivity with high catalytic reaction rate significantly improves the potential for lignocellulosic biomass to serve as a renewable feedstock for aromatic chemicals. Techno-economic analysis of the process to

![Figure 7.7](image.jpg)

Figure 7.7: Product selectivity to (■) p-xylene, toluene, and benzene; (■) alkylated compounds; and (■) oligomer compounds at high conversion (>99% DMF and MF, 70% furan). Reaction conditions: 1 M furanic feedstock in heptane with ethylene (62 bar) at 250 °C with 0.45 ± 0.05 g of catalyst. Error bars were less than 2% for each compound.
convert glucose into HMF and eventually $p$-xylene indicates that the use of H-BEA addresses two of the three most important design parameters for improved economics.\textsuperscript{135,138} First, the high selectivity to $p$-xylene reduces the loss of feedstock carbon, which has been identified as the largest process cost. Second, the ability to utilize the side product, 2,5-hexanedione, by dehydration to DMF allows for the recovery of carbon within the process and raises the value of the ring-opened side product. Future research addressing the design of a continuous flow reaction system (based on a standard engineered slurry reactor and separator) which allows for continuous catalyst replacement and separation of $p$-xylene from 2,5-hexanedione–DMF will allow for the hydrolysis side-product to be recycled until it is completely consumed, thus matching the selective performance of the high conversion batch reactor described here.
CHAPTER 8
THE REACTION NETWORK AND KINETICS FOR THE REACTION OF
2-METHYLFURAN AND ETHYLENE OVER ZEOLITE CATALYSTS

8.1 Introduction

Production of commodity aromatic chemicals from biomass derivatives is a promising approach for replacing current products such as plastics that are currently derived from petroleum.\textsuperscript{2,16,124,125,126,127} These chemicals include BTX, a mixture of benzene, toluene, and xylenes, which are used not only in the fuel industry, but also as precursors for polymers. Specifically, benzene is used in the production of polystyrene, toluene is used to make polyurethane foams,\textsuperscript{128,129,130} and \(p\)-xylene is a precursor for terephthalic acid and polyethylene terephthalate (PET).\textsuperscript{2,3,4} All of these chemicals are critical to the existing infrastructure and require a sustainable method of production.

Production of BTX chemicals from biomass is part of a larger process, shown in Figure 8.1, that initially converts biomass-derived carbohydrates into furan compounds, including: (1) hydrolysis of cellulose and hemicellulose to form glucose and xylose, (2) dehydration of these carbohydrates to form 5-hydroxymethylfurfural (HMF) or furfural, and (3) hydrogenolysis of HMF to 2,5-dimethyfuran (DMF)\textsuperscript{14,15} or the hydrodeoxygenation of furfural to 2-methylfuran (MF)\textsuperscript{23} or furan. Furanic compounds then undergo a symmetry-allowed [4 + 2] Diels–Alder cycloaddition with ethylene, followed by acid-catalyzed dehydration of the cycloadduct intermediate to the targeted aromatic compound.\textsuperscript{6}

Diels-Alder cycloaddition of biomass-derived has significant potential for high yield chemical production of renewable aromatic chemicals. For the reaction of
Figure 8.1: Reaction pathway for the production of 2,5-dimethylfuran and 2-methylfuran from cellulose and hemicellulose, respectively.

DMF and ethylene with H-BEA zeolite catalysts, selectivity to $p$-xylene has been achieved as high as 90% at high conversion. However, Diels-Alder cycloaddition of MF and ethylene, shown in Figure 8.2, has produced only 46% selectivity to toluene at the same reaction conditions. Lower aromatic selectivity was presumably due to a higher occurrence of dimerization reactions as a result of MF having limited functionality (i.e. protecting methyl groups) at the alpha-carbon position.

In this work, the reaction pathways and kinetics of the Diels-Alder addition of MF and ethylene are examined for a fundamental understanding of the active site catalytic chemistry. The existence of two distinct kinetic regimes is revealed, corresponding to a shift in the rate-limiting step between Diels-Alder and dehydration chemistry, the rates of which are controlled by the concentration of Brønsted acid sites. Finally, the long-term, high-yield reaction of MF and ethylene is examined with the goal of optimizing the system for high yield of toluene.
8.2 Results

The reaction network for the Diels-Alder cycloaddition of MF and ethylene over H-BEA was expanded to include the main side-products. The rates of product formation were found to exhibit a dependency on the concentration of Brønsted acid sites, which affected the rate-limiting phenomena. Experiments conducted using a low concentration of Brønsted acid sites exhibited an activation energy similar to the DFT calculated dehydration energy barrier, while experiments with a high concentration of Brønsted acid sites exhibited an activation energy similar to the DFT calculated energy barrier for cycloaddition. Long-term results over H-BEA show that the highest yield of toluene was achieved over a concentration of Brønsted acid sites equivalent to the transition region between the two rate-limiting regimes. The use of Sn-BEA in place of H-BEA changed the product distribution to favor two of the main side products over production of toluene.

8.2.1 Identification of Side-Products

A typical gas chromatogram of the product mixture is included in Figure 8.3, and compound retention times are listed in Table 8.1. Four of the most distinct peaks were identified as n-heptane solvent, MF reactant, tridecane internal standard, and product
Figure 8.3: Typical GC Chromatogram of a 7 hour sample from the reaction of MF and ethylene over 0.5 grams H-BEA at 250 °C.

toluene. Alkylated products include benzene, ortho- and para-toluene, and ortho, meta-, and para-xylene, which form peaks between 1.3 and 10 minutes that are not visible in Figure 8.3. Selectivity to these alkylated products was less than 5%, and their identity was confirmed by comparison with known standards.

Compounds 11 and 12 were identified by GC-MS as 6 member rings containing a methyl group and an epoxide. These two compounds are likely formed from the incomplete dehydration of the MF-ethylene cycloadduct, wherein the C-O bond of the oxygen bridge is cleaved at the methyl group but the oxygen forms an epoxide, rather than leaving as water. Based on the GC-MS fragmentation pattern (see Appendix) and additional results reported herein, it is possible that Compound 12 also undergoes a proton transfer from the epoxide to an alcohol. Compound 13 was identified by GC-MS as a dimer that is formed from the cycloaddition of two MF molecules.
Table 8.1: Identify and retention time of compounds detected via GC.

<table>
<thead>
<tr>
<th>Peak #</th>
<th>Retention Time (Min)</th>
<th>Compound Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.7</td>
<td>Heptane</td>
</tr>
<tr>
<td>2</td>
<td>1.3</td>
<td>2-Methylfuran (MF)</td>
</tr>
<tr>
<td>3</td>
<td>1.77</td>
<td>benzene</td>
</tr>
<tr>
<td>4</td>
<td>3.2</td>
<td>Toluene</td>
</tr>
<tr>
<td>5</td>
<td>4.93</td>
<td>p-xylene</td>
</tr>
<tr>
<td>6</td>
<td>5.07</td>
<td>m-xylene</td>
</tr>
<tr>
<td>7</td>
<td>6.07</td>
<td>o-xylene</td>
</tr>
<tr>
<td>8</td>
<td>7.02</td>
<td>4-ethyltoluene</td>
</tr>
<tr>
<td>9</td>
<td>8.09</td>
<td>2-ethyltoluene</td>
</tr>
<tr>
<td>10</td>
<td>10.02</td>
<td>Tridecane</td>
</tr>
<tr>
<td>11</td>
<td>13.26</td>
<td>Incomplete Dehydration (ID) Isomer 1</td>
</tr>
<tr>
<td>12</td>
<td>13.55</td>
<td>Incomplete Dehydration (ID) Isomer 2</td>
</tr>
<tr>
<td>13</td>
<td>15.99</td>
<td>MF Dimer</td>
</tr>
<tr>
<td>14</td>
<td>19.86</td>
<td>MF Trimer</td>
</tr>
</tbody>
</table>

Compound 14 represents the MF trimer 5,5-bisylvyl-2-pentanone, which is formed by the hydrolysis of MF to form 4-oxopentanal followed by alkylation with two additional MF molecules.\textsuperscript{139,140,141}

The formation of 4-oxopentanal can also undergo the reverse reaction reproducing water and MF. For this work, 5,5-bisylvyl-2-pentanone was synthesized using a mixture of MF and water with sulfuric acid as a catalyst. The identity of the MF trimer was confirmed by GC-MS, which matched the parent ion and fragmentation pattern (See Appendix). Comparison of the gas chromatogram containing the trimer with the chromatogram derived from the MF/ethylene product mixture identified peak 14 as the
MF trimer.

An expanded reaction scheme is shown in Figure 8.44, which includes: (1) the formation of toluene from MF and ethylene, (2) the formation of the MF trimer, (3) the formation of the MF dimer, (4) the formation of the incomplete dehydration isomers, (5) alkylation products formed from the cycloadduct intermediate or toluene, and (6) polymer products formed from the cycloadduct, MF, and/or toluene.

Figure 8.4: Reaction scheme for the reaction of MF and ethylene over a zeolite catalyst to form: (1) toluene, (2) a MF trimer, (3) a MF dimer, (4) Incomplete Dehydration Isomers, (5) alkylated products, and (6) polymer products.
8.2.2 Kinetic Regimes: Dehydration-limited and Cycloaddition-limited Reactions

Investigation of the initial kinetics for the production of toluene from MF and ethylene at low conversion (<15%) reveals two distinct kinetic regimes with respect to concentration of Brønsted acid sites. The transition is apparent for both H-BEA (Si/Al = 12.5, 0.7 moles Brønsted acid sites per gram catalyst) and H-Y (Si/Al = 2.6, 0.36 moles Brønsted acid sites per gram catalyst), as seen in Figure 8.5. At less than 0.7 mmoles of Brønsted acid site per liter of reaction solution, there is a direct relationship between rate of toluene production and the concentration of Brønsted acid sites. This indicates that the rate-limiting step for this regime is dehydration, which is Brønsted acid catalyzed. At greater than 2 mM of Brønsted acid sites, the reaction rate is independent of Brønsted acid site concentration. This indicates that the rate-limiting step for this kinetic regime is likely non-Brønsted acid catalyzed cycloaddition.

Figure 8.5: Rate of toluene production as a function of Brønsted acid site concentration for the reaction of MF and ethylene at 250 °C over H-BEA (Si/Al = 12.5) and H-Y (Si/Al = 2.6).
Activation energies for the dehydration and cycloaddition limited regimes were experimentally measured at conditions identified in Figure 8.5 (0.11 mM Brønsted acid sites for the dehydration kinetic regime, and 3.5 mM for the Diels-Alder cycloaddition kinetic regime) using H-BEA catalyst. The low catalyst loading kinetic regime

![Graphs showing Arrhenius plots for the production of toluene from MF and ethylene over H-BEA catalyst.](image)

Figure 8.6: Arrhenius plots for the production of toluene from MF and ethylene over (a) 3.5 mM Brønsted acid sites H-BEA and (b) 0.112 mM Brønsted acid sites H-BEA.

Table 8.2: Comparison of DFT calculated energy barriers with measured activation energies for the reaction of MF and ethylene over H-BEA.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Dehydration Energy Barrier (kcal/mole)</th>
<th>Cycloaddition Energy Barrier (kcal/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT</td>
<td>13.7</td>
<td>23.4</td>
</tr>
<tr>
<td>Experiment</td>
<td>9.7 ± 1.0</td>
<td>20.4 ± 0.6</td>
</tr>
</tbody>
</table>
(dehydration) exhibits a kinetic energy barrier of 20.4 ± 0.64 kcal/mol, while the high catalyst loading kinetic regime (cycloaddition limited) exhibits a kinetic energy barrier of 9.72 ± 1.02 kcal/mol, as seen in Figure 8.6. These values were found to correspond with energy barriers calculated using Density Functional Theory (DFT) for the dehydration and cycloaddition limited regimes (Table 8.2).

Figure 8.7 shows the rate of production of the MF trimer, MF dimer, incomplete dehydration isomers, and toluene as a function of Brønsted acid site concentration. The rates of production of the incomplete dehydration (ID) isomers are comparable to that of toluene, and also exhibit two kinetic regimes. The rate of ID Isomer 2 follows the same trend as the rate of toluene when fewer than 2 mM Brønsted acid sites are present, and then decreases with increasing acid site concentration above 2 mM. However, the rate of ID Isomer 1 is higher than all other products until >1.5 mM Brønsted acid sites, and is seen to decrease after 0.5 mM.

Figure 8.7: Rate of production of the side products as a function of Brønsted acid site concentration for the reaction of MF and ethylene at 250 °C over H-BEA.
The rates of production of the MF trimer and the MF dimer increase with increasing Brønsted acid site concentration as shown in Figure 8.7, which indicates that both are catalyzed by Brønsted acidity. The MF trimer rate appears to level off at concentrations of Brønsted acid sites >1.5 mM. The rate of production of the MF dimer does not exhibit a plateau for the range of catalyst loadings tested.

When the reaction temperature was decreased to 200 °C, the rate of production of toluene and the identified side products decreased, as expected. However, Figure 8.8 shows that cycloaddition is the rate limiting reaction step for toluene production for all measured concentrations of Brønsted acid site; a second kinetic regime was not observed. Similar to Figure 8.7, the rate of production of the ID isomers is comparable to toluene production, but with production of ID Isomer 1 slightly higher at low catalyst loading. The rate of production of the MF dimer is again lower than the other side-products, and it increases with increasing catalyst loading. At 250 °C the trimer rate was significantly

![Figure 8.8: The rate of toluene and side-product production as a function of Brønsted acid site concentration for the reaction of MF and ethylene at 200 °C over H-BEA.](image-url)
lower than toluene; however, at 200 °C the rate of trimer production surpasses the rate of toluene at high catalyst loading. This indicates that the reaction can be tuned to selectively make the MF trimer at lower temperatures and higher catalyst loadings.

8.2.3 Determination of Kinetic Parameters

Reaction orders with respect to ethylene, MF, and Brønsted acid sites were analyzed at both low and high catalyst loadings for all products and are reported in Figure 8.9 and Table 8.3. Experiments evaluated reaction orders at low conversion by varying the concentration of MF, ethylene, or Brønsted acid sites while holding the concentration of the other two components constant. In the dehydration-limited regime, the ID Isomer 2, MF trimer, and MF dimer all exhibit reactions orders of approximately one with respect to acid sites while this reaction order is fractional for toluene and the ID Isomer 1. The reaction order with respect to acid sites for the MF dimer does not change in the cycloaddition-limited regime; however, the reaction orders for all other products decrease. Both toluene and the MF trimer have reaction orders of approximately zero, while the ID isomers exhibit negative reaction orders with respect to acid site concentration. These changes in reaction orders highlight the importance of catalyst loading for this reaction system.

Toluene and the ID Isomers have similar reaction pathways and thus it is expected that they will have similar reaction orders with respect to MF and ethylene. This is the case in the cycloaddition-limited regime, where the reaction orders with respect to MF and ethylene are approximately one for all three products. In the dehydration-limited regime, the reaction orders with respect to MF for the formation of these products are
Figure 8.9: Arrhenius plot for the formation of toluene over H-BEA as a function of (a) ethylene concentration and 3.5 mM Brønsted acid sites, (b) ethylene concentration and 0.122 mM Brønsted acid sites, (c) MF concentration and 3.5 mM Brønsted acid sites, and (d) MF concentration and 0.112 mM Brønsted acid sites.
Table 8.3: Reaction orders for MF, ethylene, and acid sites at low and high loadings of H-BEA at 250 °C for the formation of toluene, the ID isomers, and MF polymers.

<table>
<thead>
<tr>
<th>Product</th>
<th>Toluene</th>
<th>ID Isomer 1</th>
<th>ID Isomer 2</th>
<th>MF Trimer</th>
<th>MF Dimer</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF</td>
<td>0.53 ± 0.04</td>
<td>0.76 ± 0.03</td>
<td>0.41 ± 0.05</td>
<td>1.34 ± 0.13</td>
<td>0.64 ± 0.10</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>0.68 ± 0.02</td>
<td>0.97 ± 0.08</td>
<td>1.06 ± 0.11</td>
<td>0.19 ± 0.14</td>
<td>0.41 ± 0.04</td>
</tr>
<tr>
<td>Acid Sites</td>
<td>0.61 ± 0.04</td>
<td>0.70 ± 0.08</td>
<td>1.18 ± 0.01</td>
<td>0.95 ± 0.20</td>
<td>0.96 ± 0.04</td>
</tr>
<tr>
<td>MF</td>
<td>0.95 ± 0.04</td>
<td>1.16 ± 0.06</td>
<td>1.12 ± 0.04</td>
<td>2.26 ± 0.30</td>
<td>0.09 ± 0.04</td>
</tr>
<tr>
<td>C₂H₄</td>
<td>0.81 ± 0.05</td>
<td>0.86 ± 0.06</td>
<td>0.85 ± 0.07</td>
<td>0 ± 0.13</td>
<td>0 ± 0.02</td>
</tr>
<tr>
<td>Acid Sites</td>
<td>0.03 ± 0.06</td>
<td>-0.40 ± 0.03</td>
<td>-0.26 ± 0.03</td>
<td>0.12 ± 0.22</td>
<td>0.96 ± 0.04</td>
</tr>
</tbody>
</table>

mainly fractional (0.53 ± 0.04, 0.76 ± 0.03, and 0.41 ± 0.05 for toluene, ID Isomer 1, and ID Isomer 2, respectively). The reaction order with respect to ethylene is approximately one for both ID Isomers, but is 0.68 ± 0.02 for formation of toluene.

Reaction orders for the formation of the MF trimer and dimer are difficult to determine due to low concentration. The reaction order with respect to ethylene for both of these products in both regimes is low, as neither product includes this reactant. The reaction orders with respect to MF for the MF dimer are 0.64 ± 0.10 and 0.09 ± 0.04 in the dehydration and cycloaddition limited regimes, respectively. The reaction orders with respect to MF for the MF trimer are 1.34 ± 0.13 and 2.26 ± 0.30 in the dehydration and cycloaddition limited regimes, respectively.

8.2.4 Long Term Results

Figure 8.10 shows the concentration profiles of toluene and side products at 275 °C with 0.3 grams H-BEA as a function of reaction time for the first 30 hours of reaction.
Figure 8.10: Concentration of MF and products as a function of reaction time for the reaction of MF and ethylene over 0.3 grams of H-BEA at 275 °C.

MF conversion is ~91% at the end of 7 hours of reaction time and ~100% after 24 hours. The concentration of both toluene and unidentified polymers increases for the first 10 hours of reaction before leveling off. The concentrations of the ID isomers reaches a maximum around 3.5 hrs, and the profile suggests that the isomers are intermediates for other products at long reaction time. These products could be toluene, larger polymers, or solid residue that remains on the catalyst surface. The MF trimer was observed at < 7 hr reaction time; however, its concentration decreased throughout the reaction, and it appeared that its formation occurred mainly during the heating process for the reaction. Concentrations of the MF dimer and alkylated products increased for the 30 hours of reaction time but did not exceed 0.02M.
8.2.5 Effects of Lewis Acidity.

The long-term reaction of MF and ethylene was conducted over 100% Lewis acid sites with Sn-BEA (1 mM Lewis acid sites) and a physical mixture of 10:1 Lewis acid sites (Sn-BEA, 1 mM acid sites) to Brønsted acid sites (H-BEA (0.11 mM acid sites) to analyze the effects of a solid Lewis acid catalyst on the reaction network. It has previously been shown that, for the Diels-Alder cycloaddition of Dimethylfuran and ethylene, Lewis acidity will catalyze the dehydration reaction to a lesser extent than Brønsted acidity. Additionally, Lewis acidity is known to catalyze the Diels-Alder cycloaddition step, which is not catalyzed by Brønsted acidity. The reaction over Sn-BEA produced higher concentrations of the ID Isomers than over H-BEA, as shown in Figure 8.11. The rate of production of Isomer 1 was also higher at 6.26 ± 0.35 mmoles/hr and 6.04 ± 0.45 mmoles/hr over Sn-BEA and 10:1 Sn-BEA:H-BEA, respectively, compared to 2.91 ± 0.23 mmoles/hr over H-BEA. Concentrations of toluene and the MF dimer were lower over Sn-BEA, while no change was observed for concentration of the MF trimer. The production rate of ID Isomer 2 was lower over Sn-BEA, 1.06 ± 0.07 mmoles/hr, and 10:1 Sn-BEA:H-BEA, 1.87 ± 0.25 mmoles/hr, as compared to H-BEA, 2.39 ± 0.22 mmoles/hr. The same trend was observed for production of toluene with rates of 1.56 ± 0.31 mmoles/hr over Sn-BEA, 1.69 ± 0.20 mmoles/hr and over 10:1 Sn-BEA:H-BEA, and 2.40 ± 0.36 mmoles/hr over H-BEA.
Figure 8.11: Concentration profiles for (a) ID Isomer 1, (b) ID Isomer 2, (c) Toluene, and (d) MF dimer as a function of reaction time for the reaction of MF and ethylene over 1 mM Sn-BEA (Lewis Acid – LA), a physical mixture of 1 mM Sn-BEA and 0.122 M H-BEA, and 1 mM H-BEA (Brønsted acid – BA) at 250 °C.
8.3 Discussion

The Diels-Alder cycloaddition of MF and ethylene is a potential route for renewable toluene produced from biomass resources. The lack of a protecting methyl group on the alpha carbon of the furan ring increases the number of possible side reactions, as compared to the Diels-Alder cycloaddition of Dimethylfuran and ethylene. The main side products have been identified as a MF dimer, a MF trimer, and two isomers of incomplete dehydration of the cycloadduct. The MF dimer is formed from the cycloaddition of two MF molecules. The rate of its formation is significantly lower than other products, as was shown in Figure 8.7, and depends on the concentration of Brønsted acid sites for the range examined, which indicates that the reaction is always limited by dehydration. The reaction order of one with respect to acid sites (Table 8.3) signifies that only one of the MF molecules may be absorbed on the catalyst for this reaction. The fractional orders with respect to MF are unexpected as the reaction requires two MF molecules. It is possible that the concentration of this product is sufficiently low that the reaction order cannot be decoupled from the other products.

The MF trimer is formed from the hydrolysis of MF to form 4-oxopentanal followed by alkylation with two additional MF molecules. 4-oxopentanal can reversibly react to form MF and water, similar to the equilibrium between DMF and 2,5-hexanediione. However, the 2,5-hexanediione does not react with additional DMF molecules, likely due to the protecting methyl groups on the furan ring. Figure 8.7 showed that the rate of formation of the MF trimer exhibits two kinetic regimes with respect to acid site concentration. At high catalyst loading, the rate does not change and the reaction order with respect to acid sites, reported in Table 8.3, is approximately zero.
This may be due to a lack of water production (derived from cycloadduct dehydration), which is required for MF trimer formation, as the rate of toluene production does not increase in the cycloaddition-limited regime. At low catalyst loading, where the rate of trimer formation increases linearly with catalyst loading, the reaction order with respect to acid sites is approximately one. The fractional reaction orders with respect to MF signify that the low concentration of the trimer may hinder the ability to measure these parameters.

A potential reaction scheme for the production of the ID isomers is included in Figure 8.12. The cycloadduct intermediate undergoes a C-O bond cleavage at the methyl group, which results in an epoxide that is likely ID Isomer 1. This compound could then undergo a proton transfer to form an alcohol, which is potentially ID Isomer 2. This structure has the same molecular weight as the epoxide, but has undergone an additional acid-catalyzed step towards complete dehydration. This could explain why ID Isomer 1 exhibits a high reaction rate at low catalyst loading, while ID Isomer 2 has rates similar to toluene. This is further supported by the increased rate of production and concentration of ID Isomer 1, but not ID Isomer 2 or toluene, over Sn-BEA as compared to H-BEA. The Lewis acid catalyst should produce a higher amount of the cycloadduct intermediate, due to the Lewis acid catalyzed pathway for cycloaddition. However, the Lewis acid catalyzed dehydration pathway is likely higher in energy than the Brønsted acid catalyzed pathway, as was shown for the DMF/ethylene system, and thus a lower rate of dehydration should be measured over Sn-BEA. The result would therefore be an increased amount of ID Isomer 1 and a decrease in the amount of ID Isomer 2 and toluene as was found experimentally. In general, the high rates of formation of the ID
isomers indicates that a significant amount of the cycloadduct intermediate is desorbing from acid sites prior to completing dehydration, and thereby forming the ID isomers instead of toluene. The decrease in the rate of production of the ID isomers at high catalyst loadings may indicate that sufficient Brønsted acid sites are now present for the ID isomers to complete dehydration to toluene prior to desorbing from the catalyst surface. However, the decreasing rate of ID production does not coincide with an increase in toluene production. Therefore it is possible that the increase in acid sites results in the formation of larger polymers.

Figure 8.13 depicts the ratio of the rate of formation of the main side products to the rate of formation of toluene over H-BEA for the dehydration-limited regime (0.37 mM acid sites), the transition region (2.12 mM acid sites), and the cycloaddition limited regime (5.41 mM acid sites). The data indicates that a high catalyst loading may produce the greatest amount of toluene, due to the low ratio of ID isomer formation rate (i.e. the main side products) to toluene formation rate. Figure 8.13a shows that the ratio of the rate of formation of the ID isomers to the rate of formation of toluene decreases with increasing catalyst loading. This result is expected, as the rates of formation are highest when the system is limited by the dehydration reaction and lowest when the system is
limited by cycloaddition. Additionally, the rate of formation of ID Isomer 1 is significantly greater than toluene or Isomer 2 in the dehydration limited regime, which again supports that this isomer more closely resembles the cycloadduct while isomer 2 more closely resembles toluene. Although the ratio of the rate of formation of the trimer and dimer increase with increasing catalyst loading (Figure 8.13b), these side products are present in significantly lower concentrations than toluene and do not consume a significant portion of the MF.

Figure 8.13: Ratio of the formation rate of (a) the ID Isomers and (b) the MF trimer and dimer to the rate of formation of toluene from MF and ethylene over H-BEA at 250 °C.

Figure 8.14 depicts the concentration profile of toluene as a function of reaction time for several catalyst loadings and temperatures, and shows that the highest concentration of toluene was actually measured at a catalyst loading near the transition
point between the two kinetic regimes. At a given catalyst loading, increasing the temperature increases the rate of formation of toluene, but ultimately achieves the same final concentration. At a given temperature, the concentration of toluene increased with decreasing catalyst loading within the cycloaddition limited regime. As shown in Figure 8.15a and 8.15b, decreasing catalyst loading within the cycloaddition limited regime also increased the maximum concentration of both ID isomers. This may be because a high catalyst loading results in the formation of larger polymers. Figure 8.15c shows that high temperatures and high catalyst loadings are favorable for formation of the MF dimer. However, the concentration of the MF trimer, shown in Figure 8.15d, decreases drastically with increasing temperature and does not exhibit a strong dependence on catalyst loading. The highest concentration of the MF trimer was achieved at 200 °C over 5.4 mM, as was expected from the 200 °C regime plot shown in Figure 8.8. Selectivity towards the trimer at these conditions was ~ 52 ± 5% at < 3 hrs of reaction time.

Figure 8.14: Concentration of toluene as a function of reaction time for the reaction of MF and ethylene over H-BEA at 200 - 275 °C over 0.3 – 0.77 grams H-BEA.
Figure 8.15: Concentration profiles for (a) ID Isomer 1, (b) ID Isomer 2, (c) MF dimer, and (d) MF trimer as a function of reaction time for the reaction of MF and ethylene over H-BEA at 200 - 275 °C over 0.3 – 0.77 grams H-BEA.
The hydrodeoxygenation of the MF trimer has been shown to be an important reaction in the production of renewable diesel fuel.\textsuperscript{139,140,141}

Previously, a selectivity of $46 \pm 2\%$ towards toluene was measured at $250^\circ \text{C}$ and 0.5 grams of H-BEA.\textsuperscript{7} Although this work examined the formation of toluene at several different reaction conditions, the average selectivity towards toluene at 99\% MF conversion over 0.3 – 0.77 grams H-BEA and $250 – 275^\circ \text{C}$ was still $44 \pm 2\%$. Increasing the catalyst loading shifted the product distribution away from ID isomers and towards larger polymers, which are unidentified. Increasing the reaction temperature increased the reaction rate for all components, except the MF trimer, and did not affect product selectivity. It has been shown that the ID isomers consume a large quantity of the MF, and these reactions must either be pushed towards complete dehydration or avoided if selectivity to toluene is to be increased.

\textbf{8.4 Conclusion}

The reaction network for the reaction of MF and ethylene over H-BEA has been expanded to include products such as incomplete dehydration isomers, a MF dimer, and a MF timer that are not detected or present in low quantities in the similar DMF/ethylene system. The prevalence of these side reactions is due to the unprotected alpha carbon on the furan ring for MF. The existence of two distinct kinetic regimes with respect to the concentration of Brønsted acid sites was discovered, with each regime corresponding to a different rate-limiting step. These regimes also exist for the ID isomers, and the ratio of the rates of the products supports the proposed structures. The highest concentration of toluene was measured at a catalyst loading equal to the transition region between the two
regimes, but selectivity to toluene never exceeded 45%. Regarding this reaction network, it is necessary to find a catalyst that can fully dehydrate the cycloadduct intermediate to toluene if selectivity is to be increased. Specifically, a catalyst is required with sufficiently strong acid sites that the cycloadduct remains absorbed to the surface for the duration of dehydration. These results provide a deeper understanding of the more general Diels-Alder cycloaddition of furan-based feedstocks and olefins, and will facilitate optimization of the production of additional important biomass-derived aromatic chemicals.
CHAPTER 9

FURAN REACTIONS OVER ZEOLITE CATALYSTS

9.1 Formation of Benzene from Furan and Ethylene over H-BEA

Furan is an important biomass derived compound that is often used as a surrogate for biofuel. The Diels-Alder cycloaddition of furan and ethylene produces a cycloadduct intermediate subsequently dehydrates to form benzene. When this reaction is conducted in a heptane solvent at 250 °C, selectivity to benzene was 33%. This is significantly lower than the selectivity to p-xylene from the reaction of DMF and ethylene, and slightly lower than the selectivity to toluene from the reaction of toluene and ethylene. The lower selectivity is likely due to an increased number of side-reactions that occur because the alpha carbons on the furan ring are not protected by methyl groups. The regime plot for the rate of benzene production as a function of acid site concentration is depicted in Figure 9.1. Unlike the regime plots for DMF and MF, the furan plot only

![Figure 9.1 Reaction rate for the production of benzene as a function of Brønsted acid site concentration for the reaction of Furan and ethylene at 250 °C over H-BEA.](image-url)
shows one regime where the rate is dependent on the number of acid sites. This indicates that the production of benzene is limited by the dehydration reaction at all concentrations of acid sites that were examined. Figure 9.2 plots the Arrhenius relationship between reaction rate and temperature, and confirms that the reaction displays an activation energy of $11.6 \pm 1$ kcal/mole, which is similar to the dehydration energy barrier for both MF and DMF.

![Arrhenius plot for the production of benzene from Furan and ethylene over 3.5 mM Brønsted acid sites HBEA.](image)

**Figure 9.2**

**9.2 Formation of Benzofuran from Furan over H-ZSM5**

Another important reaction is the formation of benzofuran from two furan molecules. This occurs as a side-reaction in the formation of benzene, but is also a key reaction in the pyrolysis of biomass to form aromatic chemicals. Catalytic fast pyrolysis of biomass, involving rapid heating of biomass in the presence of nanoporous zeolite catalysts such as HZSM-5,\textsuperscript{142} has proven to be a promising route for converting a variety
of biomass sources into aromatic-range biofuels.\textsuperscript{58} While this is an attractive approach, only a fraction of the biomass carbon ends up in the resulting fuel (in effect increasing the price of this cellulosic biofuel), largely because of the tendency to form solid carbonaceous materials (i.e., “coke”) in the process. Optimization of this technology has been hampered by a lack of fundamental understanding of the catalytic mechanisms at play. Previous experimental studies\textsuperscript{126,143} have shown that furan is a good proxy for vapors that arise during cellulose pyrolysis, and that benzofuran is made in HZSM-5 nanopores as an intermediate on the way to making aromatic-range biofuels (Figure 9.3). However, there is no information on the mechanism by which benzofuran is made, nor is there substantial evidence that the process from furan to benzofuran occurs via Diels-Alder cycloaddition, which has been assumed in the literature.\textsuperscript{143} To address this issue, we performed experiments and calculations to obtain fundamental insights into this key step in catalytic fast pyrolysis.\textsuperscript{144}

![Potential chemical reactions during furan pyrolysis at 600 °C. The colored box highlights the key step that is investigated in the present work.](image-url)

Figure 9.3 Potential chemical reactions during furan pyrolysis at 600 °C. The colored box highlights the key step that is investigated in the present work.
Figure 9.4 shows the geometry-optimized structures of stable intermediates in the HZSM5 zeolitic pathway following a ring-opening route. The two branches, I and II, correspond either the protonation of the furan ring at the C2 atom or protonation at the oxygen, respectively. The first step in the process is the adsorption of furan in the zeolite (Figure 9.4.A). In the minimum energy configuration, one furan is hydrogen bonded to the zeolite acid site, at a distance of roughly 3.4 Å from the second furan molecule. Thus, there are two reacting furan molecules per acid site, consistent with the experimental observation that furan adsorbs in HZSM-5 at a furan-to-aluminum molar ratio of 1.73.\textsuperscript{143}

In branch I, the zeolitic proton is transferred to the furan at the C2 position (Figure 9.4.A), followed by the ring-opening of the protonated furan into an alkoxy species covalently bonded to the zeolite framework (Figure 9.4.C). In branch II, the

![Geometry optimized structures of the stable intermediates in the zeolite-catalyzed, minimum energy pathway. In the zeolite, only the acid site and adjacent atoms are displayed.](image-url)
zeolitic proton is transferred to the O atom of the furan, but this protonated furan derivative is not a stable intermediate. It is instead a transition state on the proton hopping path between the central O atom of the zeolite cluster, and one of the other zeolite O atoms adjacent to the Al atom. The transiently protonated furan ring opens to a species that is hydrogen bonded to the zeolite framework (Figure 9.4.D). At the next step branches I and II merge, and the ring-opened species alkylate the second furan molecule (Figure 9.4.E). Deprotonation (Figure 9.4.F), ring-closing (Figure 9.4.G), and dehydration (Figure 9.4.H) steps lead to benzofuran (Figure 9.4.I) with the loss of a water molecule.

We note that this mechanism is also a potential source of the larger polycyclic compounds, that is, coke, that can clog the pores of the zeolite and deactivate it. Similar to the ring-opening of the protonated furan discussed above, the positively charged, alkylated furan derivative (Figure 9.4.E) can ring open and alkylate a third furan molecule. This process will result in species that are too big to diffuse out of the pores of HZSM-5, leading to the accumulation of carbon deposits and subsequent deactivation of the catalyst.

We next consider the geometry optimized structures of the stable intermediates for the Diels-Alder route to benzofuran inside the zeolite cavity, shown in Figure 9.5.. As with the indirect process discussed above, the first step in the direct route is the adsorption of two furans per zeolite acid site (Figure 9.5.A). In the next step, the two furans undergo a Diels-Alder cycloaddition. In its lowest energy configuration, the cycloadduct is hydrogen bonded to the acid site at the furanic O atom. However, the adduct cannot be stably protonated at the furanic O atom and is, therefore, an off-pathway
dead end. In the lowest energy, on-pathway configuration (Figure 9.5.B), the cycloadduct is hydrogen bonded to the acid site at the bridge O atom. Subsequently, the adduct is protonated at the bridge O atom (Figure 9.5.C), following which, deprotonation (Figure 9.5.D) and dehydration (Figure 9.5.E) reactions lead to benzofuran (Figure 9.5.F) with the loss of a water molecule.

Figure 9.5: Geometry-optimized structures of the stable intermediates in the zeolite-catalyzed, Diels-Alder pathway.

The likelihood of which mechanism occurs can be determined by comparing the energetics of the ring-opening and Diels-Alder zeolite-catalyzed processes in HZSM-5. The solid red and dotted blue lines in Figure 9.6 show the energies of the intermediates in branches I and II of the ring opening route, respectively. The highest energy intermediate of the ring-opening pathway is roughly 50 KJ/mole. The solid black line depicts the energies of the intermediates of the Diels-Alder pathway, and the dashed black line is the lowest energy configuration of the cycloadduct in the zeolite, which likely leads to coke.
Figure 9.6: Energies of the intermediates for the ring-opening and Diels-Alder pathways in HZSM5. The ring-opening pathways are shown in the solid red (branch I) and dotted blue (branch II) lines. The solid black line shows the energies of intermediates in the zeolite-catalyzed Diels-Alder route.

Meanwhile, the highest energy intermediate of the Diels-Alder pathway is around 200 KJ/mole.

Figure 9.7 shows an Arrhenius plot of initial rates of benzofuran production measured from the liquid phase reaction of furan in heptane over HZSM5. The good linear fit is consistent with a single, dominant mechanism in the temperature range 270-300 °C. The slope corresponds to an apparent activation energy of 72 ± 3 kJ/mol for the HZSM-5 catalyzed process. This apparent activation energy is inclusive of the following physical processes: diffusion, adsorption- desorption from the zeolite catalyst, and of course, chemical reaction. As such, this measured apparent activation energy is likely an upper bound for the activation energy of the rate- determining chemical reaction in benzofuran production. The intermediate energy of the ring-opening pathway, 50 kJ/mol,
Figure 9.7: Arrhenius plot for the production of benzofuran from 1M furan in heptane over HZSM5.

fits nicely into the “energy budget” determined by our experimentally determined apparent activation energy. The rate of production of benzofuran also exhibits only one kinetic regime with respect to the concentration of Brønsted acid sites, as shown in Figure 9.8.

The computational results, taken together with the experiments reported herein, provide strong evidence that the HZSM-5 catalyzed conversion of furan to benzofuran proceeds by a ring-opening pathway involving open ring intermediates, rather than the Diels-Alder route. The stable intermediates along the Diels-Alder pathway are seen to be higher in energy than the experimentally measured apparent activation energy. Hence, we can rule out the Diels-Alder route to benzofuran in HZSM-5, even without locating transition states along any of the pathways.
While this analysis applies to the formation of benzofuran from furan in HZSM-5, it is important to note that these results do not necessarily apply to other potential Diels-Alder reactions such as furan condensation with olefins. Specific reaction mechanisms depend on the reactant species, catalyst type, and reactant, intermediate, and product energetics. The results of this study serve to highlight the importance of examining individual key steps in biomass conversion to determine which mechanisms are favorable for a given system.

Figure 9.8: Reaction rate for the production of benzofuran as a function of Brønsted acid site concentration for the reaction of Furan in heptane at 250 °C over HZSM5.
CHAPTER 10

CONCLUSION

This body of work has explored the feasibility of producing important fuels and chemicals from biomass-derivatives, and shown that it can be accomplished. The continuous electrocatalytic membrane reactor was able to produce measurable quantities of furfuryl alcohol, tetrahydrofurfuryl alcohol, 2-methylfuran, and 2-methyltetrahydrofuran from furfural and water. Additionally, this technology was able to influence the product selectivity via controlling the applied voltage. The economic potential of this technology was discussed in Chapter 4, and is closely tied to the cost of electricity, hydrogen gas, and the precious metals used as the catalyst. Using the continuous electrocatalytic reactor in a location that is close to a renewable energy source and far from a hydrogen gas pipeline would enhance its economic viability. The greatest improvement for both efficiency and economics will likely come from the replacement of the precious metal catalyst. It was shown that platinum and palladium were the most active for furfural hydrogenation; however, bimetallic catalysts could also be explored as well as other supports that may enhance the activity. Additionally, different reactor designs could be explored that either combine the electrocatalytic reactor with conventional catalysis, or that combine multiple electrocatalytic reactors to enhance conversion and selectivity. Finally, the oxidation of a biomass-derived compound at the anode of the reactor could be coupled with the hydrogenation of a different biomass-derived compound at the cathode of the reactor, such that multiple desired fuels/chemicals could be produced from the same system.
The investigation of the Diels-Alder cycloaddition of furans and ethylene has produced \( p \)-xylene at high selectivity, expanded the reaction network for MF and ethylene, and confirmed that the formation of benzofuran from furan occurs via a ring-opening pathway. H-BEA was found to have superior catalytic activity at a given catalyst loading; however, it was discovered that the concentration of Brønsted acid sites is the most important factor for determining rate. The rate-limiting step of the reaction actually changes from dehydration to cycloaddition based on the concentration of Brønsted acid sites. A selectivity of 90% to \( p \)-xylene was achieved using the H-BEA catalyst, with 46% and 33% selectivity for toluene and benzene, respectively. This difference was attributed to the presence of fewer protecting methyl groups on the furan ring. Indeed, the loss of one methyl group when replacing DMF with MF results in the formation of a MF trimer, not seen in the DMF system, and a measurable increase in dimer and incomplete dehydration products. Changing the system parameters affected the product distribution; however, the highest selectivity to toluene was still only 45%. To increase the selectivity to toluene it is necessary to either complete the dehydration of the incomplete dehydration side products, or avoid their formation. This could be accomplished with a catalyst that has strong enough absorption of the cycloadduct such that dehydration is completed prior to desorption. It is also possible that a biphasic or two-step system would provide additional acid sites to fully catalyze dehydration of these products. The optimization of the Dimethylfuran/ethylene system and the examination of the methylfuran/ethylene system can be applied to the more general Diels-Alder cycloaddition of furan-based feedstocks and olefins, to improve the production of numerous aromatics.
APPENDIX

MASS SPECTROMETRY FRAGMENTATION PATTERNS

Mass spectrometry fragmentation patterns were collected using both electron ionization and chemical ionization. Figure A.1 shows that both isomers of incomplete dehydration present the same parent ion of 110.9 in the chemical ionization (CI) fragmentation pattern. This is expected based on the molecular weight of 110 grams/mole and the addition of a H\(^+\) ion.

Figure A.2 depicts the EI fragmentation pattern for the two isomers of incomplete dehydration. The loss of the epoxide with three hydrogen atoms from the predicted structure of Isomer 1 would result in fragment with molecular weights of 43 grams/mole and 67 grams/mole, as in seen in Figure A.2.a. The fragmentation pattern in Figure A.2.b shows that a main fragment has the molecular weight of 82 grams/mole. This could be the loss of both the methyl group and the alcohol from Isomer 2, accompanied by the addition of two protons.

Figure A.3 depicts the fragmentation pattern of the methylfuran dimer and the NIST predicted structure. The structure is similar to the methylfuran dimer, except that one of the methyl groups is shown on the 6-carbon ring rather than on the furan ring. Loss of both methyl groups would result in the main fragment peak at 115 grams/mole.

The fragmentation pattern in Figure A.4 represents the methylfuran trimer. The parent ion has a molecular weight of 246 grams/mole, which is the same as the methylfuran trimer. Main fragment peaks occur at 189 grams/mole, 175 grams/mole, and 165 grams/mole, which represent the loss of C\(_3\)H\(_5\)O, C\(_4\)H\(_7\)O, and C\(_5\)H\(_5\)O (methyl furan ring), respectively.
Figure A.1: CI fragmentation patterns of (a) isomer 1 and (b) isomer 2 of the incomplete dehydration (ID) side product.

Figure A.2: EI fragmentation pattern for (a) isomer 1 and (b) isomer 2 of the incomplete dehydration side product.
Figure A.3: (a) EI fragmentation pattern of the methylfuran dimer and (b) the NIST database predicted structure and fragmentation pattern.

Figure A.4: (a) EI and (b) fragmentation patterns of the methylfuran trimer.
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