Value Added Products From Lignin and Biomass Derivatives

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VALUE ADDED PRODUCTS FROM LIGNIN AND BIOMASS DERIVATIVES

by

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A Dissertation Submitted to the Faculty of
Old Dominion University in Partial Fulfillment of the
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Pyrolysis is one of the traditional lignin and biomass utilization methods. The liquid products bio-oil and solid products bio-char are the main value-added products from lignin pyrolysis. Due to the narrow application and low quality, using the pyrolysis method to produce bio-oil and bio-char cannot bring sufficient economic benefits. In this dissertation, two methods were investigated to improve the quality of lignin bio-products.

Instead of direct pyrolysis, chemical activation (pyrolysis) was introduced in this dissertation. Compared to bio-char, the lignin chemical activation product lignin-activated-carbon has better economic value. With the best activation conditions, the lignin-activated-carbon produced a surface area of around 1117 m²/g, and the yield percentage could reach around 50%. Compared to commercial activated carbon, lignin-activated-carbon had a similar Iodine Number, Methylene Blue Number, BET Surface area, and better yield percentage. The use of ZnCl₂ activated for the carbon method proved to be one of the best ways of utilizing lignin biomass residue.

Bio-oil produced from lignin is a very complex mixture of several organic compounds. However, furfural and acetone are two significant compounds present in bio-oil produced from lignin. An electrochemical hydrogenation method was investigated to upgrade oil and obtain more valuable products, such as isopropanol, Tetrahydrofurfuryl alcohol, and 2-Methyltetrahydrofuran. A novel electrochemical hydrogenation reactor, polymer electrolyte
membrane fuel cell was used in the experiment and results show that target products could be produced in a mild process condition (low temperature and atmospheric pressure) with high current efficiency and high selectivity. The degradation of membranes due to the contamination of the polymer electrolyte membrane fuel cell, the mitigation methods and the effective working hours of the polymer electrolyte membrane fuel cell were investigated.
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This thesis is dedicated to the proposition that the harder you work, the luckier you get.
ACKNOWLEDGMENTS

Right now is the time for me to recall my Ph.D. study journey in Old Dominion University. There are many people who have contributed to the successful completion of this dissertation. First I would like to thank my advisor, Dr. Sandeep Kumar, without his insightful directions on my academic area, I could not have finished this dissertation. His cleverness, wisdom, and personality have huge effects on me as I learned how to be a successful academician in the future.

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I would also like to acknowledge the help and support from my research group members: Ali Teymouri, Caleb Talbot, Adams Kameron, Alexander Asiedu, Ashani Samaratunga, who have made our group as a home for study, for work and for living here as an international student far away from his own country. And I also appreciate the technical assistance from Drs. Can Zhou, Qiang Tang, and Yazdanshenas Elias who help with the experiment set up.

Most importantly, I would like to thank my family, it is your love, understanding, and support encourage me to overcome the difficulties through the Ph.D. study journey, and made the process full of warmth and happiness.
NOMENCLATURE

AC      Activated Carbon
\( C_0 \) Initial concentrations, (mg/L)
\( C_e \) Equilibrium concentrations, (mg/L)
EA      Elemental analysis
ECH     Electrochemical hydrogenation
FA      Furfuryl alcohol
FM      2(3H)-Furanon, 5-methyl-
FTIR    Fourier transform infrared
GV      Gamma-Valerolactone
MB      Methylene Blue
MEA     The membrane electrode assembly
MPK     2-Pentanone
MTHF    2-Methyltetrahydrofuran
\( PEM \) Polymer electrolyte membrane
\( PEMFC \) Polymer electrolyte membrane fuel cell
Qe      Adsorbed amount of unit AC, (mg/g)
\( q_t \) The adsorption amount with regard to adsorption time, (mg/g)
SEM     Scanning electron microscopy
slpm    Standard liter per minute
THFA    Tetrahydrofurfuryl alcohol
TGA     Thermo-gravimetric analyses
UHS     Un-hydrolyzed solid
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<td>V</td>
<td>Volume, (ml)</td>
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CHAPTER 1
INTRODUCTION

Lignin, a valuable resource for chemicals and energy, is a main component of wood, together with cellulose and hemicellulose. It is the second largest source of organic raw material [1], constituting about 4-35 wt% of most biomass, 16-25 wt% of hardwoods and 23-35 wt% of softwoods [2]. As the most abundant natural aromatic polymer [3], lignin has a highly branched three-dimensional phenolic structure (Fig.1) including three main phenylpropane units, namely p-coumaril, coniferyl and sinapyl. Softwood lignin contains relatively few sinapyl units and consists mainly of guaiacyl structures, while hardwood lignin contains guaiacylsyringyl structures.

![Lignin structure diagram](image-url)
As a by-product of the paper industry, lignin is most often used by paper mills as a fuel for the recovery of its energy content. However, due to the very large generated quantities, lignin is increasingly considered as a potential source of chemicals, and studies of its thermal degradation receive much interest. [4]

The structure of lignin suggests that it can be a valuable source of chemicals, particularly phenolics. However, lignin depolymerization with selective bond cleavage is the major challenge for converting it into value-added chemicals. Pyrolysis (thermolysis), gasification, hydrogenolysis, chemical oxidation, and hydrolysis under supercritical conditions are the major thermochemical methods studied with regard to lignin depolymerization. Pyrolytic oil and syngases are the primary products obtained from pyrolysis and gasification.

Figure 1. Partial structure of hardwood lignin[4]

Figure 2. Major Thermochemical lignin conversion processes and their potential products
Lignin bio-oil, lignin bio-char (activated carbon), and lignin depolymerization production are several value-added products from lignin. The objectives of this study are to develop value-added bioproducts from production processes.
1.1 Activated Carbon Production from Lignin Biomass

Activated carbons (ACs) are well known for their high adsorption ability due to their porous structure and large internal surface area, ranging from 500 to 2000 m$^2$/g. These are used in the engineering field as adsorbents for removing inorganic environmental pollutants [5-8] and organic compounds [9-11] from both gas and liquid phases. Therefore, it will be beneficial to develop a production process of ACs from renewable feedstock, which is economical and efficient.

Recently, there has been an abundance of research efforts in developing processes to produce ACs from biomass waste, which contains a high amount of organic constituents such as cellulose, hemicellulose, and lignin [12]. ACs were produced in environmentally friendly ways and economically [13] by thermal conversion processes of pyrolysis and gasification for various biomass wastes such as apricot stone shells [14, 15], bean pods [16], olive stones [17, 18], sugar cane, bagasse, rice, straw, rice hull and pecan shells [19].

ACs production mainly has two steps. The first occurs through carbonization of the biomass under 800°C, followed by either physical or chemical activation of the carbonized product [13]. Compared to a physical activation procedure, chemical activation occurs at a lower temperature and has a better quality of porous structure ACs and lower energy costs [20]. Widely used chemical reagents such as ZnCl$_2$, NaOH, H$_3$PO$_4$, and metal chemicals (e.g., KOH and K$_2$CO$_3$) are reported in the literature as raw precursors of lignocellulosic materials as well as coals [21-25]. Chemical activation is a commonly used method for AC production. The summary of biomass feedstock chemical activation for AC production is shown in Table 7 (Seen in appendices). High surface area (700–2000 m$^2$/g) activated carbon is expected when the biomass waste is used as feedstock and chemical activation is the production method.
1.2 Lignin Bio-oil Derivatives and Upgrading Method

Bio-oil, the liquid product from fast pyrolysis of biomass, is a promising sustainable material for transportation fuel production. However, the raw bio-oil is not ready for end users because of several disadvantages: (1) High water content; (2) High viscosity; (3) High ash content; (4) High oxygen content and low heating value; (5) High corrosiveness. The typical bio-oil composition is shown in Table 1 and Table 2.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Wt%</th>
<th>Composition</th>
<th>Wt%</th>
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<tr>
<td>Formic acid</td>
<td>7.69</td>
<td>H₂O(wt%)</td>
<td>25.2</td>
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<tr>
<td>Hydroxybutyric</td>
<td>2.31</td>
<td>pH</td>
<td>2.8</td>
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<tr>
<td>Furfural</td>
<td>5.00</td>
<td>Density(kg/m³)</td>
<td>1190</td>
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<tr>
<td>Benzoic acid</td>
<td>1.15</td>
<td>Viscosity(mm²/s)</td>
<td>128</td>
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<tr>
<td>2-Cyclopentane-1-one</td>
<td>1.42</td>
<td>LHV(MJ/kg)</td>
<td>17.42</td>
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<tr>
<td>4H-Pyran-4-one</td>
<td>2.15</td>
<td>C(wt%)</td>
<td>41.7</td>
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<tr>
<td>Acetophenone</td>
<td>1.00</td>
<td>H(wt%)</td>
<td>7.7</td>
</tr>
<tr>
<td>2-hydroxyl</td>
<td>1.85</td>
<td>O(wt%)</td>
<td>50.3</td>
</tr>
<tr>
<td>3,5-dimethyl-4-hydroxyl</td>
<td>1.92</td>
<td>N(wt%)</td>
<td>0.3</td>
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<table>
<thead>
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<th>Wt%</th>
<th>Composition</th>
<th>Wt%</th>
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<tr>
<td>Acetic acid</td>
<td>15.33</td>
<td>Other ketones</td>
<td>6.77</td>
</tr>
<tr>
<td>Acetone</td>
<td>5.29</td>
<td>Other aldehydes</td>
<td>8.75</td>
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<tr>
<td>1-hydroxy-2-propanone</td>
<td>14.97</td>
<td>Phenols</td>
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<td>Hydroxyacetaldehyde</td>
<td>10.58</td>
<td>Ethers</td>
<td>0.94</td>
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<tr>
<td>Methanol</td>
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<td>Other Alcohols</td>
<td>6.86</td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>3.94</td>
<td>Others</td>
<td>1.33</td>
</tr>
<tr>
<td>Other acids and esters</td>
<td>10.84</td>
<td></td>
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Due to the presence of unsaturated oxygenates such as aldehydes, ketones, carboxylic acids, acetone, furfural, and phenols, for long-term storage and any further upgrading, bio-oil must first be stabilized in order to minimize downstream coke formation, catalyst deactivation and carbon loss to the gas phase. A central goal of pyrolysis lignin and upgrading lignin bio-oil is to convert
the oxygen-rich, hydrogen-poor, high-molecular-weight lignin into hydrocarbons that are compatible with today’s petroleum-derived fuels or directly used as a high-quality combustion fuel. Popular bio-oil upgrade methods and comparison are shown in Table 8 (Seen in appendices ) [28].

Most popular oil upgrade methods like hydrotreating and hydrocracking usually use supported nickel catalyst, and the reaction is carried out at a high temperature (500°C) with a hydrogen gas pressure in the range of 100–1000psig.

1.3 Electrochemical Hydrogenation Method

Electrochemical hydrogenation (ECH) is considered as an energy saving and environmentally friendly method to upgrade organics, by integrating both the catalytic and the electrochemical methods. The ECH reaction mechanism of organics is suggested as the following equations (1-5) [29-34].

Anode side:
1. Hydrogen or water lost electrons and generate protons;

\[ \text{H}_2 \rightarrow 2(\text{H}^+) + 2\text{e}^- \quad \text{and} \quad \text{H}_2\text{O} \rightarrow 1/2\text{O}_2 + 2(\text{H}^+) + 2\text{e}^- \]

Cathode side:
2. Protons react with electrons and generate \( \text{M(H)}_{\text{ads}} \) (\( \text{M} \) are an adsorption sites);

\[ (\text{H}^+) + \text{e}^- + \text{M} \rightarrow \text{M(H)}_{\text{ads}} + \text{H}_2\text{O} \]

3. Organic molecules \( \text{Y}=\text{Z} \) are adsorbed by adsorption sites \( \text{M} \);

\[ \text{Y} = \text{Z} + \text{M} \rightarrow \text{M(Y=Z)}_{\text{ads}} \]

4. \( \text{M(H)}_{\text{ads}} \) react with the adsorbed organic molecules;

\[ \text{M(Y=Z)}_{\text{ads}} + 2\text{M(H)}_{\text{abs}} \rightarrow \text{M(YH-ZH)}_{\text{abs}} + 2\text{M} \]

5. Hydrogenated products are generated;
M(YH-ZH)_{ads} \rightarrow YH-ZH + M

6. H_2 molecules are reproduced;

2M(H)_{ads} \rightarrow H_2 \text{ (gas)} + 2M \quad \text{M(H)}_{ads} + (H^+) + e^- \rightarrow H_2 \text{ (gas)} + M

In the anode, either hydrogen pumping or water electrolysis lead to the generation of electrons and protons (H^+) (eq. 1). In the cathode, chemisorbed hydrogen M (H)_{ads} is generated in situ on the electrocatalyst surface and reacts with the adsorbed organics (eq. 2). Note that hydrogenation also competes with hydrogen gas evolution (eq. 6), which has a negative influence on the current efficiency and H_2 utilization. ECH allows the reactions (eq.s 3, 4, and 5) to happen at low temperatures and ambient pressure. Compared to conventional hydrogenation methods, the overall ECH process takes place in a mild operating condition (i.e. low temperature and atmospheric pressure) and only uses electrical energy. Therefore, intense thermal energy input is not required in ECH. All of the protons used by ECH are supplied by either water or H_2, which eliminates the need for any reducing agent. ECH can be conducted onsite using fuel cell stacks and renewable power sources to produce hydrogen enriched compounds. This will avoid or minimize the storage and transportation of corrosive and hazardous chemicals.

ECH has been widely investigated to upgrade unsaturated compounds to corresponding saturated chemicals, like soybean oil [35], bio-oil [36], edible oil [37, 38], levulinic acid [39-41], aromatic compounds [34, 42-51], lactic acid [52], lignin [53], furfural [54-60], acetaldehyde [61], ethanol [61], acetylene [62], cyclohexane [30] and glucose [63]. In all those cases, reactions take place under mild conditions with temperatures below 100 °C, atmospheric pressure, and no reducing chemicals. The current efficiency is defined as the efficiency of electrogenerated H_2 addition to unsaturated bonds, and maximum report in those cases is up to 45% [35, 37, 38, 62]. ECH efficiency is determined by the capabilities of catalysts, which is
directly related to all the processes described in equations 1-6. Compared to nickel (Ni), copper (Cu) and lead (Pb), activated carbon fibers supported platinum (Pt) demonstrated the best catalytic activities for upgrading various organics, such as furfural [60] and acetaldehyde [61]. The electrochemical conversion efficiency is affected by many factors, such as the nature of electrodes [64], current density [65], temperature [48, 62, 66, 67], solvent compositions [30, 33, 67], solution pH [30, 43, 54, 66, 68], and chemical potential [35, 36, 66].

H-type cell was commonly used [31, 36, 42, 44, 45, 49, 53-55, 59, 60, 65, 68]. A typical H-type cell consists of two electrode chambers, between which a cation exchange membrane is sandwiched. Compared to the traditional homogenous electrolyte single chamber cell [39, 40, 46, 52, 54, 61], the basic anolyte and the acidic/neutral catholyte H-type cells [42, 54, 66] are proved to improve proton transmission efficiency.

The typical H-type cell is shown in Figure 3, and the typical single chamber cell is shown in Figure 4.
1.4 Polymer Electrolyte Membrane Fuel Cell

A polymer electrolyte membrane fuel cell (PEMFC) is a type of low-temperature fuel cell that takes its name from the ion conductive polymer membrane used as the electrolyte. A typical PEMFC assembly consists of two gas diffusion media (carbon paper), two electrodes made of a carbon layer loaded with catalysts and an ion exchange membrane, which is shown in Figure 5.

Feedstocks enter the reactor at the anode and cathode and flow through serpentine flow channels. Between the flow channels is the membrane electrode assembly (MEA), consisting of a hydrogen permeable membrane between two catalyst layers (the anode and the cathode) and gas diffusion layers (carbon cloth or paper upon which the catalyst layer was deposited), which is shown in Figure 6.

The reactor provides temperature control, gas distribution, current collection, water draining and mechanical support of the PEMFC assembly [69]. Compared to one chamber and H-Cell cell
reactor, the PEMFC reactor has a smaller internal resistance, due to its highly conductive and thin membrane electrolyte assembly (MEA), resulting in significantly less electric energy loss [70]. In addition, energy consumption can be further reduced if protons are supplied from hydrogen oxidation, rather than water electrolysis. Furthermore, PEMFCs can be easily scaled up by simply stacking them, and the space-time yield of ECH using PEMFC reactors is superior to the other methods. PEMFC can be easily applied in space limited areas like stationary, transportation, and portable/micro power generation sectors [71].

Figure 6 depicts the concept of the electrocatalytic reduction of biomass-derived oxygenates using a PEM reactor. Water or H₂ is fed into the anode where protons and electrons are produced. The protons migrate through the PEM to the cathode, where they reduce the biomass-derived molecules. The reaction procedure is shown in the last chapter (Eq. 1 to Eq. 6)

Organic compounds ECH by PEMFC reactors were also reported by many researchers [35, 37, 38, 51, 58]. Green et al. reported that the main products from ECH of furfural were furfural alcohol (54-100% selectivity) and tetrahydrofurfuryl alcohol (0-26% selectivity). The better production rate was achieved by feeding pure hydrogen gas rather than from water electrolysis [58]. Alfonso et al. hydrogenated acetophenone and found that the selectivity of 1-phenylethanol was around 90% with only methylbenzene and hydrogen as by-products [51]. Pintauro et al. and An et al. both studied ECH of soybean oil in a PEMFC reactor at 60-90°C and atmospheric pressure. Pintauro et al. proved that a bimetallic cathode (Pd/Co or Pd/Fe) could increase the yield rate of the ECH process [35]. An et al. proved Pd-black cathode worked significantly better than Pt and the best current efficiency could reach 41% [37, 38].
Figure 5. Scheme of Polymer Electrolyte Membrane Electrochemical Reactor [51].

Figure 6. Schematic of the electrocatalytic PEM reactor for the reduction of acetone to isopropanol [72].

1.5 Method and Procedure
Pyrolysis is a traditional lignin biomass utilization method. The liquid products bio-oil and solid products bio-char [73-76] are the main value-added products from lignin pyrolysis [77-79]. Due to the narrow application and low quality, using the pyrolysis method to produce bio-oil and bio-char cannot bring sufficient economic benefits [26, 27, 80-84].

Three lignin value added processes are designed in this paper, as shown in Figure 7.

![Figure 7](image)

Therefore, two methods were designed to improve the quality of lignin bio-products. Instead of direct pyrolysis, chemical activation (pyrolysis) was introduced in this dissertation. Compared to bio-char, the lignin chemical activation product lignin-activated-carbon is usually believed to be a more extensive application. Three different control parameters were selected to optimize the activation process: activation temperature, activation time, and heating rate. The activation effect of ZnCl₂ and H₃PO₄ were compared. Iodine No., Methylene Blue No, Surface area, Yield percentage, and Ash percentage were selected to evaluate the qualities of products.
Furfural and acetone are believed to be two main compounds of lignin-bio-oil[26, 27]. The electrochemical hydrogenation method was investigated in this dissertation to upgrade oil and obtain more valuable products, such as isopropanol, Tetrahydrofurfuryl alcohol, and 2-Methyltetrahydrofuran. A novel electrochemical hydrogenation reactor, a polymer electrolyte membrane fuel cell was applied in the experiment. Four different control parameters, including RH, operating temperature, input current density, and input voltage, were assessed to identify the optimized operating conditions for ECH of acetone. The degradation of membranes due to contamination of the polymer electrolyte membrane fuel cell, the mitigation methods and the effective working life of the polymer electrolyte membrane fuel cell were also investigated.

The objectives of this study are: (1) find effective ways to improve the value of lignin bio-products; (2) explore the best chemical activation condition of lignin biomass, and compare the activation effects by using the different activation chemicals ZnCl₂ and H₃PO₄; (3) pursue the optimized ECH condition of furfural and acetone; (4) evaluate the degradation of FEMFC membranes, estimate FEMFC effective working life and recommend methods to mitigate membrane pollution.
CHAPTER 2

PREPARATION OF ACTIVATED CARBON FROM UN-HYDROLYZED BIOMASS RESIDUE (LIGNIN)

In this chapter, un-hydrolyzed (UHS) biomass residue generated from enzymatic hydrolysis of corn stover was used for activated carbon production. Activated carbons were prepared by a high-temperature chemical activation method, with phosphoric acid and Zinc chloride (ZnCl$_2$) as the activation agents. A factorial design was used to optimize the activation process and five different parameters (pretreatment methods, impregnation ratio, activation time, activation temperature, and temperature increasing rate) were analyzed with respect to their influence on BET surface area and pore volume. At the optimized activation condition (i.e., co-precipitation pretreatment method, impregnation ratio 1.5, activation time 60 min, activation temperature 500°C and heating rate 60°C/min), activated carbon is obtained with surface areas and pore volumes approaching 1117 m$^2$/g and 0.12 cm$^3$/g, respectively. The capacity of methylene blue adsorption from aqueous solutions could reach 279 mg/g and adsorption isotherm fits the Langmuir model. Iodine number of the prepared activated carbon was comparable to that of commercially available material. The prepared activated carbon was characterized using SEM, XRD, FT-IR, TGA, and EDS.
2.1 Background

In this study, we used un-hydrolyzed solids (UHS) for ACs production. Bioethanol from lignocellulosic biomass is a promising alternative fuel source [85]. During the production of bioethanol, about one-third of biomass is recovered as un-hydrolyzed solids (UHS). The UHS resulting from enzymatic hydrolysis are difficult to convert into useful chemicals due to high moisture content, aromatic content, and bioactivity. However, it is a carbon-rich residue which mainly consists of lignin and unconverted sugars, depending upon the types of biomass pretreatment used in the earlier stages [86]. The production of cellulosic biofuel is estimated to increase more than five times, from the years 2015 to 2022. Therefore, the UHS residue generation will also increase. For example, a ton of lignocellulosic biomass generates approximately 60 gals of bioethanol, and 250 kg UHS residue during the production of cellulosic ethanol or butanol from biomass. According to the US Energy Independence and Security Act of 2007 (EISA), 36 billion gallons per year (BGY) of biofuels will be mandated to be produced by 2022, whereby 16 BGY will form lignocellulosic biomass [87]. Thus, the approximate generation of UHS will be 67.2 million tonnes per year, by 2022. The carbohydrate composition of UHS is introduced in Table 3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Glucan, wt%</th>
<th>Xylan, wt%</th>
<th>Arabinan, wt%</th>
<th>Lignin, wt%</th>
<th>Ash, wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHS</td>
<td>13.90</td>
<td>5.79</td>
<td>1.05</td>
<td>52.49</td>
<td>12.32</td>
</tr>
<tr>
<td>RSD</td>
<td>&lt;1.5</td>
<td>&lt;1.2</td>
<td>&lt;1.0</td>
<td>&lt;2.0</td>
<td>&lt;2.0</td>
</tr>
</tbody>
</table>

At present, several biochemical and thermochemical methods are being developed and have proved to efficiently produce lignocellulosic biofuels [88]. The bioethanol production from lignocellulosic biomass has already been demonstrated at pilot/demo-scale but cost-effectiveness
is still significantly below the EISA envisioned requirement [89]. Thus, the efficient utilization of UHS has a positive impact on making biofuels cost competitive.

Ammonia Fiber Explosion (AFEX) is a physiochemical process used for the pretreatment of corn stover under moderate temperatures (60-100 °C) and high pressure (250-300 psi) for 5 minutes with liquid anhydrous ammonia, followed by released pressure. During this procedure the conversion of cellulose and hemicellulose to fermentable sugars is completed. AFEX treatment offers unique advantages than other biomass treatments, such as almost all the ammonia could be restored and recycled through the procedure, there is no liquid stream produced and cellulose and hemicellulose are well preserved without much degradation during the process [90-92].

The objectives of the present study are to (1) find an efficient method of making activated carbon from UHS, (2) optimize the process conditions to achieve the maximum BET surface area, (3) compare the activation effects by using different activation chemicals, ZnCl₂ and H₃PO₄, and (4) characterize ACs for its physio-chemical properties.

2.2 Materials and Methods

2.2.1 Material

Un-hydrolyzed biomass supplied by Biomass Conversion Research Laboratory at Michigan State University is solid residue remaining after the enzymatic hydrolysis of pretreated corn stover for bioethanol production. The Ammonia Fiber Explosion (AFEX) process was used for the pretreatment of corn stover. UHS was produced using a high-pressure stainless steel vessel. The element composition of UHS is shown in Table 2.

2.2.2 Activation Method
Activated carbon was produced by a typical one-step activation process. Prior to activation, the UHS was dried at 65°C for 48 hours and then ground to obtain a powder. H\textsubscript{3}PO\textsubscript{4}-UHS feedstock was prepared by soaking the UHS powder in H\textsubscript{3}PO\textsubscript{4} 85 wt% at 80°C for 15 minutes and then drying in an oven at approximately 80°C for 14 hours. ZnCl\textsubscript{2} and UHS feedstock was prepared by mixing the ZnCl\textsubscript{2} solution with UHS at 80°C for 7 hours. The resulting mixture's suspension that was directly dried at 110°C for 48 h was labeled co-precipitation ZnCl\textsubscript{2} and UHS feedstock. The suspension that was dried after filtration was labeled filtration ZnCl\textsubscript{2} and UHS feedstock.

The impregnation ratio of ZnCl\textsubscript{2} and H\textsubscript{3}PO\textsubscript{4} was calculated by the following equation:

$$\text{Impregnation ratio} = \frac{\text{weight of mixture after impregnation} - \text{weight of UHS}}{\text{weight of UHS}}$$

(1)

The impregnation ratio in this study ranged from 0.09 to 3.

The dried feedstock was activated in a quartz tube reactor (Diameter 2.7 cm; Length 56 cm). Three different control parameters were selected to optimize the activation process: activation temperature, activation time, and heating rate. The ranges of these parameters are from 400 to 600°C, 60 to 90 minutes, and 7 to 125°C/min, respectively. The activation process was taken under an N\textsubscript{2} flow condition. The experimental setup is shown in Figure 8.
After activation, the reactor with the primary products was cooled down to room temperature. The final product was obtained after washing once with 100 mL hot acid (20 minutes, 1:6 HCl) and four times with 1 L deionized water (25 minutes).

The entire activation step is shown in Figure 9.
2.3 Products Analysis

2.3.1 Elemental analysis

The component percentages of C, H, and N were measured by combustion analyzer and the amount of other elements were measured by energy-dispersive spectrometry (EDS).

2.3.2 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) images were recorded on a JEOL JSM-6060LV microscope, and accelerating voltage was kept at 15.0 kV. The dry powdered samples were coated with gold to increase electrical conductivity.

2.3.3 Bulk density, moisture content, ash content, and Particle size

Bulk density was determined by the volume weight method; moisture and ash content was determined by the gravimetric method. Particle size was estimated from SEM images. Triplicated measurements were taken to measure Bulk density, moisture content, ash content, and the results show the average value.

2.3.4 Iodine number

Iodine number was determined following the standard test (ASTM Standard D4607-94). Instead of potassium iodate, potassium permanganate was selected to titrate sodium thiosulfate standard solution. The ratio of sample to adsorption solution was changed from 1g activated carbon with 1 L of 0.1 N iodine solution to 50 mg product with 40 mL of 0.03 N iodine solution. Triplicated measurements were taken and the result shows the average value.

2.3.5 Surface area and pore volume

Surface area was analyzed with a nova 2000e device. Before adsorption experiments, products were degassed under dynamic vacuum condition at 65°C for 12 hours. The adsorption
and desorption of $\text{N}_2$ were performed at temperature 77.3 K. The Brunauer–Emmett–Teller (BET) model was selected to determine specific surface areas of the sample with relative pressures of $P/P_0 = 0.01 - 0.3$. The total pore volume ($V_t$) was determined from the uptake at $p/p_0=0.99$ by using the Barrett-joner-halenda method. Surface Area Analyzer with 5% accuracy, only the $R^2 > 0.99$ the value of surface area will be adopted. A duplicated experiment was taken for BET measurement, using the average value drawing graph and raw data also was shown in the graph.

### 2.3.6 Thermo-gravimetric analyses (TGA)

Thermo-gravimetric analyses (TGA) were carried out by the instrument Q5000 v3.6 build 253. The samples were contained in alumina pans. The mass was recorded with temperature increasing, with 20 mL/min of $\text{N}_2$ flow condition. The temperature increasing rate was 10ºC/min with a range from 20ºC to 900ºC.

### 2.3.7 Fourier transform infrared (FTIR) spectra

Fourier transform infrared (FTIR) spectra measurement was acquired by using Nicolet 6700 at room temperature. Before analysis, the sample was dried in a vacuum oven at 80ºC. Spectra were collected at a resolution of 4 cm$^{-1}$, and a range of 390-4000 cm$^{-1}$.

### 2.3.8 X-Ray Diffraction analyzer

XRD is used for identifying the atomic and molecular structure (usually for crystal), in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. A 5$^{\text{th}}$ generation Miniflex x-ray diffractometer was used for X-ray analyses, 20 was selected from 0º to 45º.

### 2.3.9 Acid surface group
Acid surface groups were determined by the Boehm titration method. Three allots of 100 mg samples were suspended in a 25 mL aqueous solution with 0.02 mol/L base. The bases used here were NaOH, NaHCO₃, and Na₂CO₃. After 24 h of agitation, solids were filtered off and elutes were titrated with 0.02 N HCl. The amount of acidic functional groups was determined according to the consumption of the base.

2.3.10 Methylene Blue (MB) dye adsorption

MB is one kind of heterocyclic dye compound, which is widely used in the textile industry. The molecular size of MB is around 1.6 nm × 0.7 nm. It is used to indicate the sorbent’s ability to function as activated carbon for removing mesoporous molecules or large molecules from aqueous solutions [93].

Referring to the ASTM C837 method, Methylene Blue (MB) dye adsorption experiment was designed to determine the impact of initial MB concentration, pH, and adsorption time, with regard to adsorption equilibrium capacity.

For the experiment with varying initial MB concentrations, 20 mg of selected products were mixed with 20 mL aqueous MB solutions at varying initial concentrations (C₀) to get suspensions. The suspensions were placed on a platform shaker for 24 h to ensure adsorption equilibrium. After the allotted time, solids were filtered off, and the eluate was collected for analyses. Equilibrium concentrations of MB were determined by ultraviolet-visible (UV-vis) spectrophotometry at a wavelength 665 nm. The calibration curve was obtained by standard solutions of MB. The adsorbed amount of MB at equilibrium (Qₑ, mg/g) was calculated by the following equation:

\[ Q_e = \frac{(C_0 - C_e)V}{W} \]

(2)
where \( C_0 \) and \( C_e \) are the initial and equilibrium concentrations [mg/L], respectively. \( V \) is the volume of the solution [L], and \( W \) is the weight of products used [g].

Adsorption capacity with respect to time was tested to study adsorption kinetics of MB. For each experiment, 20 mg of selected products were mixed with 20 mL aqueous MB solutions, with 400 mg/L initial concentration. The amount of MB adsorption with regard to adsorption time (\( q_t, \text{mg/g} \)) was calculated by the following formula:

\[
q_t = \frac{V(C_0 - C_t)}{W}
\]

where \( C_t \) is the concentration of MB at a specific time [mg/L].

The adsorption of MB was studied under different pH conditions. For each experiment, 20 mg of selected product was mixed with 20 mL aqueous MB solution with 400 mg/L initial concentration 400 mg/L. \( \text{Na}_2\text{CO}_3 \), \( \text{NaHCO}_3 \), and HCL solutions were used to adjust different pH values. The suspensions were placed on a platform shaker for 24 hours to ensure reaching adsorption equilibrium. The concentration of MB (\( C_e \)) was determined by UV-vis spectrophotometry.

Every ultraviolet-visible (UV-vis) spectro-photometry measurement was duplicated, using the averaged value drawing graph and raw data also was shown in the graph.

All the experiments are shown in Table 9 (Seen in appendices).

2.4 Results and discussion

The surface and particle features of UHS and representative activated carbon were examined by SEM measurement and the results are shown in Figure 10. UHS particles show high heterogeneity in both size and the shape (Figure 10a and 10b). The visually observed particle size ranges from tens to hundreds of micrometers. If zoomed in to the surface of the particle, we
could clearly see that the UHS particle has a very smooth surface with low porosity (Figure 10c). After chemical activation with ZnCl₂ and H₃PO₄, the morphology characteristics have changed significantly. The result shows a relatively homogeneous particle size distribution with an average of around 70 µm (Figure 10d). Highly porous structures were successfully obtained on the activated carbon through the chemical activation reaction. The micro-scale pore size was visually estimated to be approximately 20µm through SEM imaging (Figure 10e and 10f).
Figure 10. Scanning electron microscopy (SEM) images of UHS (a, b, c), ZnCl₂-AC (d, e) and H₃PO₄-AC (f) prepared from UHS. ZnCl₂ activation at 500°C, 2.5 impregnation ratio, 1 h activation time 62.5 °C/min heating rate and H₃PO₄-AC prepared from UHS, H₃PO₄ activation at 500 °C, 1.7 impregnation ratio, 1 h activation time, 52.8 °C/min heating rate.

Table 4 presents the elemental components and ash content result of activated carbon and UHS. By comparison with the UHS components, the activated carbon produced by a chemical agent of H₃PO₄ retains similar element composition, except that P is present in the product of activated carbon during the chemical activation process. In contrast, the ZnCl₂ activation process obviously increases the C amount from 53.70% to 75.67%, while reducing the O component from 38.79% to 18.14%. This indicates that the ZnCl₂ chemical activation procedure was more distinctly reacted and Zn was totally removed by a hot acid rinse, followed by hot water wash. The effect of this reaction is also reflected in the SEM images which show that the carbon produced by ZnCl₂ activation has a better porous structure than that by H₃PO₄ (Figure 10e and 10f).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Moisture wt%</th>
<th>Ash wt%</th>
<th>Bulk Density (g/mL)</th>
<th>C wt%</th>
<th>H wt%</th>
<th>O wt%</th>
<th>N wt%</th>
<th>Cl wt%</th>
<th>Zn wt%</th>
<th>P wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHS</td>
<td>6.9</td>
<td>13.0</td>
<td>0.64</td>
<td>53.70</td>
<td>4.04</td>
<td>38.79</td>
<td>2.44</td>
<td>0.39</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>UHS-ZnCl₂ AC</td>
<td>10.6</td>
<td>27.6</td>
<td>0.21</td>
<td>75.67</td>
<td>0.77</td>
<td>18.14</td>
<td>2.55</td>
<td>0.62</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>UHS-H₃PO₄ AC</td>
<td>6.3</td>
<td>19.4</td>
<td>0.53</td>
<td>49.41</td>
<td>-</td>
<td>35.52</td>
<td>1.35</td>
<td>-</td>
<td>-</td>
<td>9.53</td>
</tr>
</tbody>
</table>
ZnCl$_2$-AC prepared from UHS, ZnCl$_2$ activation at 500°C, 1.5 impregnation ratio, 1 h activation time, 62.5°C/min heating rate; H$_3$PO$_4$-AC prepared from UHS, H$_3$PO$_4$ activation at 500°C, 1.7 impregnation ratio, 1 h activation time, 52.8°C/min heating rate.

Activation temperature is a very important parameter for the development of porous structures in activated carbon, and the response curve could indirectly indicate the activation temperature. TGA of feed stocks (Figure 11) shows the response of weight change with increasing temperature. From 20°C to 180°C, the weight loss is due to the moisture release. The results show that the water content in the three samples is less than 10% of the total weight. From 180°C to 400°C, the weight loss is due to the process of lignin releasing volatiles: ether group, carboxyl, and carbonyl group convert to CO, CO$_2$, and CH$_4$. Significant weight loss was observed in temperatures from 400°C to 600°C, especially for the case of ZnCl$_2$ and UHS 2:1 mixture. This range has the highest decreasing rate of weight loss (more than 50%) and suggests that the best activation temperature should be in this region. According to research by Macedo et al. (2008) [94], fused ZnCl$_2$ volatile in this region. Also, Macedo et al. believe that activation chemicals like ZnCl$_2$ could promote the release of water molecules from organic compounds and formation of less volatilized aromatic compounds. Compared to the ZnCl$_2$-UHS mixture, the H$_3$PO$_4$-UHS mixture does not show any drastic weight lost region. According to Rubner et al. (2014)[95], lignocellulose constituent degradation could be deformed and be “dragged-out” over a wide temperature range when using H$_3$PO$_4$ as activation chemical agent.
Total weight loss for chemical and UHS mixture samples was approximately 75% at temperatures above 650ºC. This implies that the yield percentage should reach a very high number.

The yield percentage measurement could indicate the output efficiency of activated carbon. It could be calculated by the following equation:

$$\text{Yield percentage(%) = } \frac{\text{Yield weight of AC}}{\text{Input weight of UHS}} \times 100\%$$  \hspace{1cm} (4)

The yield percentage is affected by reaction time, heating rate, reaction temperature, and impregnation ratio (shown in Figure 12). Specifically, with temperature increases from 400ºC to 600ºC, the yield percentage first decreases and the lowest amount happens at temperature 500ºC and then increases back, but the highest yield percentage is at 400ºC (Figure 12a).

The yield percentage is shown to be not proportional to the change of the impregnation ratio, and the results show that when the impregnation ratio is bigger than 1, the yield percentage has no big changes (Figure 12b).
The yield percentage is inversely proportional to the change with heating rate (Figure 12c) and not very sensitive to the change of reaction time. The yield percentage could be stabilized at a certain impregnation ratio, temperature, and heating rate with 1 h (Figure 12d).
Figure 12. The yield percentage relationship with reaction time, heating rate, reaction temperature, and impregnation ratio:
(a) Yield percentage as a function of activation temperature: activation time is 60 mins, the heating rate is around 60 mins/°C, the impregnation ratio is around 2, and activation chemical agent is ZnCl₂; (b) Yield percentage as a function of impregnation ratio: heating rate is around 10 min/°C, temperature is around 500 °C, activation time is 60 mins, and activation chemical agent is ZnCl₂; (c) Yield percentage as a function of heating rate: activation time is 90 mins, temperature is around 500 °C, impregnation ratio is around 2, and activation chemical agent is ZnCl₂; (d) Yield percentage as a function of reaction time: heating rate is around 10 min/°C, temperature is around 500 °C, impregnation ratio is around 0.175, and activation chemical agent is ZnCl₂.

Porous volume and surface area of activated carbons determine their adsorption quality. The results from the yield percentage investigation experiment show that the optimum reaction conditions when using ZnCl₂ as the activation chemical agent are activation temperature of
500°C, impregnation ratio of 1.5-2, a heating rate of 60°C/min, and reaction time between 60 to 75 minutes. Activation temperature and impregnation ratio have a more significant impact on the surface area than temperature increasing rate and reaction time.

The surface area of the representative UHS-ZnCl$_2$ activated carbon sample was up to 1117 m$^2$/g under the reaction conditions of 60 minutes activation time, approximately 60 mins/°C heating rate, and an impregnation ratio of 1.5. The pore volume of a representative UHS-ZnCl$_2$ activated carbon sample was as high as 0.52 cc/g under the conditions of 60 minutes activation time, approximately 60 mins/°C heating rate, and around 3 impregnation ratio.

Comparing with ZnCl$_2$, the activation chemical agent with H$_3$PO$_4$ shows relatively little effect on the surface area and pore volume activated carbon off. For instance, the surface area and pore volume just reach 365.1 m$^2$/g and 0.0479 ccs/g respectively, under activation time of 60 minutes, approximately 50 mins/°C heating rate, and an impregnation ratio of 1.7.

According to the experimental results, ZnCl$_2$ is a better activation chemical than H$_3$PO$_4$ for UHS activation.
Figure 13. The surface area and pore volume relationship with Temperature, Impregnation, Heating rate and reaction time.
(a) Surface area and pore volume as a function of activation temperature: activation time is 60 mins, the heating rate is around 60 mins/°C and impregnation ratio is 2; (b) Surface area and pore volume as a function of impregnation ratio: activation time is 60 mins, the heating rate is around 60 mins/°C and activation temperature is 500°C; (c) Surface area and pore volume as a function of heating rate. Activation time is 90 mins, the temperature is around 500°C and impregnation ratio is around 2; (d) Surface area and pore volume as a function of reaction time: heating rate is around 10min/°C, the temperature is around 500°C and impregnation ratio is around 0.175.

Yield surface area could show the combined effect between yield and surface area; it could be calculated by the following equation:

\[
\text{Yield Surface Area} = \text{yield percentage} \times \text{surface area}
\]  

\hspace{1cm} (5)

Yield Surface area VS activation temperature is shown in Figure 14.
When the temperature reaches 450ºC, the yield surface area has the maximum value of 459m²/g, the decrease is slow. The uptake of MB was studied on the activated carbon with a surface area of 1077 m²/g. The observed methylene blue adsorption results show that there is a good affinity for MB on to UHS-ZnCl₂ activated carbons. Qₑ could reach 186 mg/g at the initial pH of 4.8, while Qₑ is 279 mg/g at the pH value of 10. The isotherm was measured by subjecting the samples to aqueous solutions of MB, with different initial concentrations, at room temperature and an equilibration time of 7 hours.

Figure 15 shows the experimental isotherm of MB on UHS-ZnCl₂ activated carbon. To some extent, the result moderately fits with the Freundlich model. The expression of the Freundlich model is $Q_e = 101.9C_e^{0.1143}$ with $R^2=0.988$ to get K and N numbers.

The kinetics of MB adsorption are presented in Figure 16. From the change of $C_i$ with uptake time, the equilibrium time of MB adsorption between 3 to 4.5 hours.
Figure 17 shows the significance of the effect of pH on the adsorption capacity of UHS-ZnCl₂ activated carbon. When pH value was below 7, Qₑ was stable around 175 mg/g. The Qₑ is proportional to the change of pH value once the pH exceeds 7.

Deng et al. have explained this phenomenon by the zero charge pH theory. There is a very special pH point for activated carbon called the point zero charge (PZC). At this special pH point, there is no charge on the surface of activated carbon. When pH < pH_PZC, both H⁺ and MB are adsorbed, which means the capacity to MB adsorption was reduced. Once pH > pH_PZC, the surface of the activated carbon is negatively charged, which increases the adsorption capacity of positively charged MB molecules [96].

Figure 15. Qₑ changes with Cₑ. Adsorption time=7h, pH=4.8, activated carbon was prepared at 500°C, 62.5°C/mins heating rate, 2 impregnation ratio, and 60 min reaction time.
Figure 16. Cₜ changes with uptaking time. pH=4.8, initial MB concentration=400mg/L, activated carbon was prepared at 500°C, 62.5 °C/mins heating rate, 2 impregnation ratio, and 60 min reaction time.

Figure 17. Qₑ change with pH of UHS-ZnCl₂. Adsorption time=7h, initial MB concentration =400mg/L, activated carbon was prepared at 500°C, 62.5 °C/mins heating rate, 2 impregnation ratio, and 60 min reaction time.

Table 5 shows that the UHS-ZnCl₂ activated carbon contained 0.7 cmol/L acid groups, most of which were relatively strong acids (e.g., phosphoric, lactonic, and carboxylic). Compared with
physical activation for commercial activated carbon (Norit, GAC 1240), chemical activation with 
ZnCl₂ introduced fewer acid groups on the interfaces of the activated carbons.

Table 5. Surface functional group comparison from UHS-ZnCl₂ and commercial AC
(UHS-ZnCl₂ AC prepared from UHS at 500°C with impregnation ratio 1.5 at heating rate 60°C/min and activation time 1h)

<table>
<thead>
<tr>
<th>Type</th>
<th>Phenolic (cmol/L)</th>
<th>Lactonic (cmol/L)</th>
<th>Carboxylic (cmol/L)</th>
<th>Total (cmol/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UHS-ZnCl₂ AC</td>
<td>0.1</td>
<td>0.2</td>
<td>0.4</td>
<td>0.7</td>
</tr>
<tr>
<td>Coal AC (Norit, GAC 1240)</td>
<td>0.3</td>
<td>0.5</td>
<td>0.2</td>
<td>1.0</td>
</tr>
</tbody>
</table>

FT-IR analysis was used to determine the functional groups of activated carbon and to estimate the compositions. Commercial activated carbon used as a control in FT-IR responses is Aqua Nuchar. The activation condition for UHS-ZnCl₂ AC used in FT-IR analyses is impregnation ratio of 2, 500°C activation temperature, 52.6°C/min heating rate, and a 90 minute reaction time. Activation conditions for UHS-H₃PO₄ AC are impregnation ratio of 8, activation temperature of 600°C, 52.1°C/min heating rate, and a 90 minute reaction time.

As shown in Figure 18, UHS, UHS-ZnCl₂ AC, UHS-H₃PO₄ AC, and commercial AC have very similar FT-IR curves. Peaks at 1600 cm⁻¹ and between 1000 and 1300 cm⁻¹ are from the aromatic ring C=C band and C-H band and all the four curves have these two peaks. Peaks at 3300 cm⁻¹ and 1315 cm⁻¹ probably are from the phenolic hydroxyl (Ar)O-H, which is observed from UHS. The peak at 1690 cm⁻¹, which is present in UHS-ZnCl₂ AC and commercial AC samples, implies that carboxyl (C=O) may exist. The peak at 680-900 cm⁻¹ is from the substituted aromatic ring which is shown in all four curves. The wide peak between 1000-1300 cm⁻¹ in UHS-H₃PO₄ AC curve may due to C=P and C-P band stretching vibrations. Alcoholic hydroxyl (O-H) peak at 1410 cm⁻¹ is only observed in the UHS curve. In summary, this indicates that chemical activation does not destroy the aromatic structure, while it only removes phenolic hydroxyl (Ar) O-H. The results also indicate that alcoholic hydroxyl (O-H)
may be converted to carboxyl (C=O). The percentage of both H and O was reduced due to these conversions.

Figure 18. FT-IR spectra of activated samples, commercial activated carbon, and UHS

X-Ray diffraction (XRD) analyses were used to determine molecular structure (usually for crystal), in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. XRD was used in this study to estimate the composition of UHS and activated carbon samples.

Activation conditions for UHS-ZnCl₂ AC used in XRD analyses are impregnation ratio of 2, the activation temperature of 500°C, a heating rate of 52.6 °C/min, and a reaction time of 90 minutes. Activation conditions for UHS-H₃PO₄ AC are impregnation ratio of 8, the activation temperature of 600°C, a heating rate of 52.1 °C/min and a reaction time of 90 minutes.

The results show a broad diffraction peak corresponding to the graphitic ordering in molecular planes near 26° in ZnCl₂ activated carbon, which is more compared to H₃PO₄ sample[97]. And there is a SiO₂ peak observed on all the three samples due to residual materials
after carbonization and activation processes at the used temperatures. There is 4.67 wt% Si in UHS; SiO\textsubscript{2} is generated by the activation process. SiP\textsubscript{2}O\textsubscript{7} and H\textsubscript{3}PO\textsubscript{4} peaks were observed in UHS-H\textsubscript{3}PO\textsubscript{4} AC curve, which indicates that P was introduced to the activated carbon produced by the addition of activation chemical agent, H\textsubscript{3}PO\textsubscript{4}.

![Figure 19. XRD spectra of activated samples and UHS](image)

Compared to commercial AC (Table 6), UHS- ZnCl\textsubscript{2} AC has similar Iodine number, Methylene Blue number, and surface area, but a better yield percentage. This indicates that high-temperature ZnCl\textsubscript{2} activated carbon method is a possible way of utilizing UHS residue. Relatively high ash content, higher bulb density, oxygen percentage, and relatively lower carbon element, pore volume are the main shortage of UHS-ZnCl\textsubscript{2} AC.

| Table 6. Commercial AC and UHS-ZnCl\textsubscript{2} AC Comparison |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Iodine No. (mg/g) | Methylene Blue No. (mg/g) | Surface area (m\textsuperscript{2}/g) | Yield percentage (%) | Ash content (%) | Bulb density (g/mL) | Oxygen Percentage (wt%) | Carbon Percentage (wt%) | Pore Volume (cm\textsuperscript{3}/g) |
| ZnCl\textsubscript{2}-AC | 939.5 | 187.5 | 1117 | 42-57 | 27.6 | 0.21 | 12-18 | 73-81 | 0.12-0.52 |
| Commercial AC | 900~ | 135~ | 800~ | 20-40 | 2~4 | 0.48~ | 3~7 | 90-94 | 0.2-0.7 |
| H\textsubscript{3}PO\textsubscript{4}-AC | 1050 | 210 | 2000 | 82 | 19.4 | 0.53 | 35.5 | 49.4 | 0.05 |
2.5 Conclusions

Un-hydrolyzed solid from biomass was applied to prepare good quality activated carbons through a single stage chemical activation process. ZnCl$_2$ and H$_3$PO$_4$ were used as impregnating agents and ZnCl$_2$ was tested to most effectively produce ACs. The optimal experimental condition is that when the activation time is 60 minutes, the impregnation ration is between 1.5 to 2, the heating rate is 60 ºC/mins, and an activation temperature around 500ºC. With the best activation conditions, the carbons produced have a surface area of around 1117 m$^2$/g, and the yield percentage could reach around 50%. Comparing to Commercial AC, UHS-ZnCl$_2$ AC has similar Iodine No., Methylene Blue No, Surface area, better Yield percentage, which makes high-temperature ZnCl$_2$ activated carbon method is a possible way of utilizing un-hydrolyze biomass residue. In addition, the Zinc residues could be totally removed through the acid wash and water wash which increased the purity of the activated carbon produced. In comparison, the activated carbon produced by the H$_3$PO$_4$ agent has a relatively low surface area and a high amount of phosphorus residue.
CHAPTER 3
ELECTROCHEMICAL HYDROGENATION OF ACETONE TO PRODUCE ISOPROPONAL

Electrochemical hydrogenation (ECH) of acetone is a relatively new method to produce isopropanol. It provides an alternative way of upgrading bio-fuels with less energy consumption and chemical waste as compared to conventional methods. In this chapter, a Polymer Electrolyte Membrane Fuel Cell (PEMFC) hardware was used as an electrochemical reactor to hydrogenate acetone to produce isopropanol and diisopropyl ether as a byproduct. High current efficiency (59.7%) and selectivity (>90%) were achieved, while ECH was carried out in mild conditions (65ºC and atmospheric pressure). Various operating parameters were evaluated to determine their effects on the yield of acetone and the overall efficiency of ECH. The results show that an increase in humidity increased the yield of propanol and the efficiency of ECH. The operating temperature and power supply, however, have less effect. The degradation of membranes due to contamination of PEMFC and the mitigation methods were also investigated.
3.1 Background

Propanol is an important organic raw material in chemical production, two isomers 1-propanol and isopropanol are widely used in the paint, medicine and pesticide industries [98]. Compared to 1-propanol, isopropanol has more extensive and important applications. Along with ethanol, n-butanol, and methanol, isopropanol belongs to the group of alcohol solvents, about 6.4 million tons of which were utilized worldwide in 2011 [99]. Isopropanol is primarily produced by combining water and propene in a hydration reaction, through either an indirect or direct process. In an indirect process, propene reacts with sulfuric acid and forms a mixture of sulfate esters. Subsequent hydrolysis of those esters by steam produces isopropanol. In a direct hydration process propene reacts with water or steam at high pressure (200 to 300 atm) and high temperatures (230 to 270 °C), in the presence of solid or supported acidic catalysts [100, 101]. Isopropanol is produced by a direct combination of propene and water. Both processes require intensive energy input and use of corrosive chemicals.

Thermal hydrogenation of acetone is a relatively new and more advanced method to produce isopropanol, where acetone is hydrogenated either in the liquid or gas phase over a Raney nickel or copper and chromium oxide mixture[102]. Compared to the aforementioned conventional methods, thermal hydrogenation can be carried out at a lower temperature (75 °C) with up to 35% yield rate. However, an elevated temperature (350 to 400°C) is still required to enable fully activated catalysts. In addition, handling corrosive chemicals remains a problem [103].

Electrochemical hydrogenation (ECH) provides a more energy efficient and environment-friendly method of upgrading organics, by integrating both the electrochemical and catalytic methods [42]. In this chapter, ECH of acetone to produce isopropanol was demonstrated using a PEMFC reactor at ambient pressure. Various factors that impact the yield of propanol were
investigated, including current density, temperature, relative humidity (RH), and membrane
degradation. The main objective of this work was to evaluate the appropriate pathways of ECH
of bio-oil components using a PEMFC reactor.

3.2 Materials and Method

3.2.1 Material and experimental setup

The experiments were performed using a standard PEMFC hardware (Scribner Associates
Inc., USA) with an active area of 25 cm². Such standard PEMFC hardware has been widely used
for PEMFC evaluation tests [51, 104]. Commercially available MEAs were purchased from Ion
Power Inc., USA. The MEAs consist of Nafion® 117 membranes sandwiched with porous
carbon-based electrodes, each of which has a Pt loading of 0.3 mg/cm². Micro-porous carbon
papers (SIGRACET® 10BC) were trimmed and used as gas diffusion layers (GDLs) for both
electrodes. Teflon gaskets were used to seal the assembly. A pair of graphite bipolar plates with
flow patterns was used to distribute flows and enclose the assembly. All the temperatures were
acquired via K-type thermocouples (OMEGA, USA). A fuel cell test station (850e, Scribner
Associates Inc., USA) was used to control temperatures, flow rates, and humidity. It was also
used for data acquisition.

Ultra-high purity (99.999%) N₂ (Airgas, USA), and filtered shop air were connected to the
fuel cell test station and supplied to the PEMFC through the purge line. They were used for
purging the system and making current and voltage curve, respectively, and were cut off while
the ECH experiment was running. The ultra-high purity (99.999%) H₂ (Airgas, USA) and
Deionized (DI) water tanks were purged through the anode side of the reactor, using the fuel cell
test station. H₂ was the electrons donator and deionized (DI) water tank was used for adding
humidity to H₂. Acetone (Fisher Scientific, Certified ACS Reagent Grade) was injected into the
cathode side of the reactor by a syringe pump (MTI Corporation, EQ-300sp-LD). A direct current (DC) power supply (Tektronix, PWS 4205) was used to supply DC power for ECH. The positive probe was connected to the anode, while the negative probe was connected to the cathode. While ECH was running, electrons were deprived of H₂ and transferred to the cathode through the DC power supply. Acetone was the electron acceptor and reacted with the produced protons. The products from the cathode outlet were collected by airbags (Tedlar®), which were held by the water bath. The room temperature water bath was used for condensing the unreacted acetone and products. The cell temperature was controlled by the fuel cell test station. The exhaust gases and byproducts from the anode were condensed in a knock-out bottle prior to venting out. The schematic diagram of the whole experimental setup is shown in Figure 20.

Figure 20. Schematic diagram of the experimental setup
3.2.2. Electrochemical hydrogenation and characterization

All the PEMFCs were assembled in accordance with the standard assembly procedure of fuel cell hardware[105]. Prior to each ECH experiment, a new membrane was conditioned based on the standard protocol [105] for at least 24 hours, until it reached a fully functional state. Current-voltage (I-V) sweeps were performed to establish the baseline data for the following ECH experiments.

In each ECH experiment the acetone and H₂ flow rates were controlled at 6 ml/hr and 0.25 slpm, respectively. The voltage was consistent for each reaction; the current was recorded every five minutes. Four different factors, including cell temperature, RH, supplied voltage, and membrane degradation, were investigated to identify the optimized operating conditions. The operating conditions were in the range of 55 °C to 80 °C, 0.01 V to 0.02V, and 35 % to 90 %, respectively. I-V scans were conducted before and after ECH to characterize the membrane degradation.
The flow chart of the ECH experimental operation is shown in Figure 21. Initially, three collection methods, including the dead end, were partially confined and an open end was evaluated to identify the best means for accurate collection of products. In the partially confined method, products were collected by airbags with pressure relief valves, which prevents pressure buildup while trapping the products. In the other two collection methods, although the products were condensed by room temperature water bath, dead-end still resulted in too much back pressure accumulation, whereas open end failed to collect enough products for analysis. Therefore, partially confined airbags were used for all the experiments. The pressure differential of two electrodes can be controlled by airbags confined extent. Green et al. proved that a suitable pressure differential between the anode and cathode could decrease cross-over and increase conversion [72]. Dadda et al. believed that water transport in the membrane of a PEMFC is influenced by a convective force, resulting from a pressure gradient [106]. Many researchers also point out the importance of flow pressure [107].
The collected samples were analyzed by a gas chromatography-mass spectroscopy (Shimadzu, GC-MS-QP2010 SE), using a Shimadzu (SH-Rxi-5Sii) MS column (length: 30 m, inner diameter: 0.25 mm). Volume quantitative analysis was conducted by another gas chromatograph (SRI Instrument, 8610C), using a Restek (MXT-WAX) column (length: 30 m, inner diameter: 0.53 mm). Helium was used as a carrier gas for both gas chromatographs.

3.3 Results and Discussion

3.3.1 Product characterization

Both the liquid and gaseous products were analyzed by GC-MS. Unreacted acetone (C₃H₆O), isopropanol (C₃H₈O), and diisopropyl ether (C₆H₁₄O) were detected in the liquid products. Unreacted acetone, diisopropyl ether, and isopropanol were found in the gaseous and liquid products.

The reactions on both electrodes are catalyzed by Pt. While applying a DC voltage, protons formed at the anode are electrochemically pumped to the cathode. The protons then react with acetone to produce isopropanol and diisopropyl ether. The most feasible reaction pathways at the cathode are shown below:

\[ 2H^+ + 2e^- \xrightarrow{\text{Pt}} 2H_{\text{ads}} (a) \]

\[ \text{Acetone} + 2H_{\text{ads}} \xrightarrow{\text{Pt}} \text{Isopropanol} \]
Electrosorbed hydrogen is formed on Pt surface by reduction of H+ (eq.(a), where H$_{ads}$ is the electrosorbed hydrogen). Hydrogenation of the C=O bond then proceeds as in catalytic hydrogenation through the reaction of the acetone with the electyrosorbed hydrogen (eq(b)). As a result, isopropanol, which is the main product generated. Two isopropanol molecules may also combine together and free one water, generating diisoproply ether as a byproduct is formed (eq. (c)). Note that hydrogen gas can also be regenerated, which is an unfavorable electrochemical reaction during ECH. Hydrogen regeneration reduces the efficiency by electrochemically pumping useless hydrogen through the MEA, resulting in a reduction of the yield rate of products.

Each MEA had undergone at least three ECH experiments before replacement. In order to minimize the impacts of MEA degradation on ECH experiments, the results of the I-V scans, which were carried out prior to the experiments, were compared to the baseline performance of each MEA. If the I-V curve demonstrated an obvious deflection from the baseline performance, then the MEA needs to be replaced. The components detected in the products were isopropanol, diisopropyl ether, acetone, and water, with their volumetric percentages ranging from 12% to 16%, 1% to 2%, 69% to 75%, and 11% to 14%, respectively. Note that abundant acetone was supplied to the cathode to prevent fuel starvation. As a result, the maximum conversion rate of acetone to isopropanol was 23%. The selectivity of isopropanol was calculated more than 90%. Acetone was also detected in the anode due to crossover and will be discussed later. The produced isopropanol can be easily separated from the mixture using extraction and distillation,
which are two widely adopted methods in the industry [108] and therefore not discussed in detail here.

Three different control parameters, including RH, operating temperature, and input voltage, were assessed to identify the optimized operating conditions for ECH of acetone. All the operating parameters used in the experiments are shown in Table 10 (seen in the appendices).

RH is a very important parameter that affects the performance of PEMFCs [107, 109-113]. Figure 22a shows a typical impact of RH on the product yield during ECH of acetone. It was obviously evidenced that higher humidity promoted a higher yield of isopropanol. The composition of isopropanol in the products increased from 4.9% to 16.1%, while RH climbed from 35% to 90%. Humidity had such a significant impact because the MEA usually uses a perfluorosulfonic acid membrane (e.g. Nafion®) as the electrolyte. A high or nearly saturated humidity (RH >80%) is usually required to obtain practical performance because the conductivity of perfluorosulfonic acid membrane membranes depends on the water content. Higher humidity means higher conductivity, resulting in better performance [114-117]. Water management is critical for PEMFC operation. Sufficient water must be absorbed into the membrane to ionize the acid groups, whereas excess water can cause flooding issues and thus diminish the performance [72]. The inlet RH of the electrodes must be controlled to prevent both membrane dry out and electrode flooding. Although better performance is usually obtained by increasing RH, excess moisture may result in water flooding that hinders gas transport [118].

In the present experiments, RH was maintained between 35% and 90% to prevent either water starvation or over saturation. In fact, many researchers have investigated the mechanism of humidity influence. It is generally believed that RH can impact electro-osmotic drag, water diffusion, membrane ionic conductivity, and water back diffusion flux in the MEAs, which
consequently influence the performance [119, 120]. Elevated RH can greatly improve the PEMFC performance, through increasing the membrane conductivity [121, 122], the catalyst activities [121, 123], the electrode kinetics [124, 125], and the mass transfer rates [126, 127].

Figure 22. Isopropanol yield (percentage) change as a result of (a) RH and (b) temperatures. H₂ and acetone flow rates were 0.25 L/min and 6 ml/hr, respectively.
(a) The ECH experiments were conducted for 5 times at 65 °C. Each ECH experiment was repeated twice; (b) The ECH experiments were conducted for 4 times at 80% RH.
Operating temperature is the second factor that was assessed in this study. Generally, the temperature was found to have a slightly positive impact on the product yield. As shown in Figure 22b, the isopropanol yield percentage of products varied between 9.3% and 14.3%, when the temperature increased from 55ºC to 80 ºC. However, the temperature seemed to have minimal effect on the total efficiency.

The results agreed with the findings from the literature. Singh et al. [47] investigated ECH of phenol by Pt accordance with increasing temperature. It was believed that dehydrogenated phenol adsorbents easily block the active sites of Pt at higher temperatures. The ECH efficiency was claimed to be directly correlated with the adsorption properties of acetone, hydrogen, and propanol onto the Pt/C catalyst. Murillo and Chen [128] used temperature programmed desorption (TPD) to monitor the desorption and decomposition property of propanol in a wide temperature range on the Pt surface. According to their research, propanol decomposition peaked at 65 ºC and 117 ºC. In the present research, the operating temperature ranged from 55ºC to 80 ºC, between which propanol decomposition could happen at a higher temperature (above 80 ºC). Decomposition of propanol was believed to cause the decrease of its yield. Therefore, increasing the operating temperature in the range does not necessarily result in an increase in the product yield.

Finally, the influence of applied voltage on the product yield was also investigated. Generally, the input voltage has no obvious impact on the product yield. In the experiments, the voltage ranged from 10 mV to 20 mV, with 5 mV increments. At 10 mV and 15 mV, the yield of isopropanol was 15.9% and 17.0%, respectively. Diisopropyl ether was not detected in both cases. However, when the input voltage was increased to 0.02V, the volumetric percentage of isopropanol produced was up to 16% and about 1% diisopropyl ether was detected.
3.3.2 System analysis

Selectivity, H$_2$ utilization, and current efficiency are selected to evaluate the hydrogenation efficiency. Selectivity represents the yield of desirable products. As the major product, higher isopropanol selectivity was pursued. The selectivity is calculated based on the following equation [54, 60], where acetone unreacted is excluded:

\[
\text{Selectivity} = \frac{\text{Moles of Desired Product}}{\text{Total Moles of Product}} \times 100\% \quad (1)
\]

In the present research, H$_2$ was supplied to the anode to produce protons for ECH reactions on the cathode. Due to gas diffusion resistance, gas crossover, and hydrogen regeneration on the cathode, some H$_2$ was wasted. The H$_2$ utilization is directly related to the overall ECH efficiency. Higher H$_2$ utilization percentage is desired since more hydrogen will be actually involved in the ECH process. The actual amount of H$_2$ used to produce isopropanol can be derived from the amount of product. The H$_2$ utilization is calculated by the following equation:

\[
\text{H}_2 \text{ Utilization} = \frac{\text{Atomic Hydrogen Used for Faraday Current}}{\text{Total Atomic Hydrogen Supplied}} \times 100\% \quad (2)
\]

During the ECH process, acetone reacts with M(H)$_{ads}$ to produce isopropanol and byproducts on the cathode. Concurrently, H$_2$ regeneration happens and is an unfavorable process simply because it wastes energy. The H$_2$ regeneration reaction is affected by supplied voltage, temperature, humidity, and catalyst. Hereby, current efficiency (shown below) is used as an important parameter to determine how efficient H$_2$ is used for the ECH process [54, 60].

\[
\text{Current Efficiency} = \frac{\text{Current used for the ECH process}}{\text{Total Faraday current}} \times 100\% \quad (3)
\]
The total efficiency is defined by the H$_2$ utilization multiplying the current efficiency, as shown in the following equation:

\[ \text{Total Efficiency} = \text{H}_2 \text{ Utilization} \times \text{Current Efficiency} \]  

Figure 23a shows the impact of temperature on H+ utilization, current efficiency, and total efficiency in a typical set of experiments. As the operating temperature increased from 50 °C to 80 °C, H+ utilization increased from 1.5% to 6.0%, whereas current efficiency decreased from 28% to 18.5%. Temperature affects H+ utilization and current efficiency differently. Higher ionic mobility and catalytic activities are achieved with higher operating temperatures, resulting in higher H$_2$ utilization. Consequently, the electrochemical conversion and reaction rates increase with elevated temperatures [72]. However, Figure 4a indicates that although elevated operating temperature enabled more hydrogen being involved in reactions, yet the yield of products did not increase or even decreased. That resulted in a loss of current efficiency, which means most extra protons produced were somehow wasted. The conclusion can also be evidenced by the curve of the total efficiency, which remained almost flat. Note that the total efficiency was low because abundant H$_2$ was supplied to the system to minimize the impact of fuel starvation and gas diffusion resistance. Practically, stoichiometric flow can be fed to the system based upon the actual current. In their experiments of ECH of acetone, Sara et al. observed that the current efficiency increased while the cell temperature increased from 25 °C to 50 °C, which seems to contradict our results [72]. However, in the present research, PEMFCs were operated in a recommended range between 50 °C and 80 °C to achieve the best performance. The reduction of current efficiency is believed mainly due to propanol decomposition, as mentioned in 3.1. Another minor reason was acetone vaporization, since the boiling point of acetone is 56 °C.
Acetone gasification might have a negative impact on the hydrogenation reactions on the cathode, due to increased pressure and thus higher diffusion resistance.

Figure 23. H$_2$ Utilization, Current Efficiency, and Total efficiency calculated at different (a) temperatures and (b) RH. H$_2$ and acetone flow rates were 0.25 L/min and 6 ml/hr, respectively. (a) The ECH experiments were conducted for 5 times at 80% RH; (b) The ECH experiments were conducted for 5 times at 65 °C. Each ECH experiment was repeated twice.
Figure 23b shows the impact of RH on H\textsubscript{2} utilization, current efficiency, and total efficiency. The operating temperature was set at 65 °C, and the RH was controlled by setting the humidifier’s temperature. It is seen that higher RH resulted in better efficiencies. As the RH ranged from 35% to 90%, the H\textsubscript{2} utilization increased from 0.9% to 2.8%, and the total efficiency increased from 0.4% to 1.5%. A sudden hike of the current efficiency was observed when ramping the RH from 80% up to 91%. It can be concluded that higher RH is favorable for ECH of acetone and will result in a higher yield of products. It has been proved that higher ionic conductivity can be achieved when MEAs become more hydrated [121-123, 129-132]. Practically, high RH is required to maintain the best fuel cell performance. The higher water content in the Nafion membrane will ease proton transport, i.e. less ionic resistance. As a result, more protons can be created and transported to the cathode for ECH. Typically >80% RH is recommended [114-117, 133], which explains that a hike in the current efficiency was observed when the RH surpassed 80%.

The present research shows that the performance of ECH of acetone is correlated with RH, input voltage, and temperature, in which RH has the most obvious effect. It is suggested that the optimized operating conditions are RH of 80% or more, the input voltage of 0.02 V or less, and temperature of between 50 °C and 55 °C. The obtained maximum H\textsubscript{2} utilization and maximum current efficiency achieved in the present experiments were 5.9% and 59.7%, respectively. To further increase those efficiencies, stoichiometric flow control is strongly recommended.

3.3.3 MEA degradation

Long-term durability is one important factor that affects the practical applications of ECH using PEMFC reactors. Nowadays, commercial MEAs are fairly durable for their common roles as power sources. The ECH process, however, involves organics that may contaminate MEAs
and thus shorten their lifetime. To our best knowledge, very limited research has been conducted to evaluate the impacts of contaminants on the durability of ECH. In the past decade, extensive research has been carried out on mitigating contamination of PEMFCs from impurities, including CO, CO$_2$, H$_2$S, NO$_x$, SO$_x$, and hydrocarbons [134, 135]. Impurities may contaminate one or more components of the MEA, resulting in performance degradation. Three major contamination effects were identified as the poisoning of the electrode catalysts, a decrease of the ionic conductivity, and an increase of the mass transfer resistance.

Additionally, the crossover is another factor that negatively impacts the PEMFC performance. Crossover of organic compounds during hydrogenation using PEMFCs has been reported [136, 137]. One immediate drawback is the loss of fuel and/or products, which decreases the efficiency. Furthermore, contaminants not only poison just one electrode but also may crossover and further poison the catalyst on the other electrode [33].

To investigate the impacts of MEA degradation on the present hydrogenation tests, polarization scans (V-I sweeps) were performed after each test [56]. The black curves in Figure 5 were the baseline data recorded for the fresh MEAs prior to ECH tests. After each test, pure N$_2$ was purged for at least 10 hours to remove all the temporary contaminants. The effects of RH and temperature on the MEA degradation were also evaluated.
Figure 24. V-I scans performed during three sets of ECH experiments. (a) The ECH experiments were conducted for 5 times at 65 °C and 80% RH; (b) The ECH experiments were conducted for 4 times at 65 °C but different RH. The RH of the four reactions are 65%, 65%, 50%, and 50%, respectively; (c) The ECH experiments were conducted 5 times at 80% RH but different temperatures. The temperature of four reactions are 80 °C, 73 °C, 57 °C, and 50 °C, respectively; The black curves were the baseline data recorded for the fresh MEAs prior to ECH tests. After each test, pure N₂ was purged for at least 10 hours to remove all the temporary contaminants.

Figure 24a shows the results of five sets of V-I measurements performed on a PEMFC, which underwent five 10-hour long ECH experiments. Both the ECH experiments and V-I measurements shown in Figure 26a were conducted at 65 °C with 80% RH. It clearly shows that the MEA performance degraded as more ECH tests were conducted, especially after the third ECH experiment. The open circuit voltage (OCV) dropped a lot starting from the 4th V-I scan, which indicates that crossover became significant. It implied that pinholes might form due to degradation.

Figure 24b shows the effect of RH on MEA degradation during ECH. For the ECH experiments conducted in Figure 24b, RH was reduced to 65% for the 1st and 2nd tests and was further reduced to 50% for the 3rd and 4th tests. Note that in order to compare with the same baseline data (the black curve in Figure 24b), all the V-I scans were performed using the same operating conditions that have been used for the baseline scan. The results illustrate that reducing RH was able to mitigate the degradation to some extent. It is believed that less RH resulted in less mass transport via the MEA, which eventually extended the lifetime of the catalysts. However, permanent damage to the MEA still existed, as seen from the general trend of the V-I scan. Similar to what was observed in Figure 24a, purging with pure N₂ could not remove permanent contaminants.

Last but not least, the effect of operating temperature on the MEA degradation was investigated, as shown in Figure 24c. For the ECH experiments conducted in Figure 5c, the operating temperatures were 80 °C, 73 °C, 57 °C, and 50 °C, while maintaining the same RH.
Again, all the V-I scans were performed using the same operating conditions as those used for the baseline scan (black curve in Figure 24c). The results show that temperature variation has no observable impact on MEA degradation. In other words, changing the operating temperature did not mitigate degradation.

Figure 25 shows the trends of current efficiency, H₂ utilization, and total efficiency using the same MEA for several ECH experiments. Figure 25 shows that as the MEA degraded, current efficiency, H₂ utilization, and total efficiency all decreased. Until a method of contamination mitigation is found, it is acceptable to use one MEA three times.

![Figure 25. H₂ Utilization, Current Efficiency and Total efficiency as a function of ECH experiment times. The ECH experiments were conducted for 4 times at 65 °C and 80% RH. H₂ and acetone flow rates were 0.25 L/min and 6 ml/hr, respectively. After each test, pure N₂ was purged for at least 10 hours to remove all the temporary contaminants. Each ECH experiment was repeated twice.](image)

Usually, the lifespan of a PEMFC under steady-state operation can be very long, up to thousands of hours [138-143]. However, catalyst contamination is the major factor that diminishes the PEMFC performance and very likely results in significant degradation [144-146]. In fact, many organic compounds are able to contaminate the MEA. Those compounds include acetaldehyde, toluene, propane, vinyl acetate, methyl methacrylate, acetonitrile,
dichloromethane, acetylene, chlorobenzene, formic acid, methanol, ethanol, phenol, butane, acetone, and naphthalene [147-149], and the list is expanding. The main reason that so many contaminants were found is that the catalysts used in common MEAs are Pt-based. Pt is a premium catalyst, but also sensitive to so many contaminants. The MEAs used in the present research contain pure Pt as the catalyst. Although developing a non-Pt catalyst is beyond the scope of the present research, in order to further conduct durable ECH experiments, MEAs with contamination tolerant catalysts need to be used.

Reactant and product crossing over is another possible reason that caused the MEA degradation. Liquids that contained mainly acetone were detected at the anode side during the ECH experiments. Those liquids not only decrease the fuel utilization but also further contaminate the anode catalyst. Feasible solutions to this issue include adopting thicker MEAs, feeding gaseous feedstock instead of liquid, and using non-Pt catalyst [150].

In summary, to minimize the MEA contamination using the current setup, keeping low RH is suggested. To solve the problem essentially, novel non-Pt catalysts need to be developed, such as Pd and Ni-based catalysts [151, 152]. Despite the fact that a wide range of metals can be used as electrocatalysts at the cathode, those with the strong capability of hydrogen absorption are desired.

3.4 Conclusions

Electrochemical hydrogenation of acetone using a PEMFC reactor was successfully demonstrated in the present research. The results proved that ECH can be a feasible way of hydrogenating acetone to produce isopropanol in mild conditions. In the experiments, the main product obtained was isopropanol with a selectivity of approximately 90%. A small amount (about 1%) of diisopropyl ether was also obtained as a byproduct. The mild operation conditions,
including low temperature and ambient pressure, are the greatest advantages of the proposed ECH method. The present research suggests that the optimized conditions for ECH of acetone using a PEMFC reactor include an operating temperature around 65 °C and relative high RH.

Contamination impact using the PEMFC reactor during ECH was also investigated. It was concluded that organic compounds are able to contaminate the MEAs, resulting in serious degradation. However, the methods to mitigate contamination are limited. The present research only demonstrated that lower RH could help reduce contamination. Eventually, novel non-Pt catalysts need to be developed for durable ECH process.
CHAPTER 4

HYDROGENATION OF FURFURAL USING A POLYMER ELECTROLYTE MEMBRANE REACTOR

The electrochemical hydrogenation of biomass-derived compounds in a polymer electrolyte membrane reactor presents a promising method that minimizes energy consumption and chemical waste as compared to conventional methods. In this paper, a Polymer Electrolyte Membrane Fuel Cell (PEMFC) hardware was used as an electrochemical reactor to hydrogenate aqueous solutions of furfural into furfuryl alcohol (FA, 6-15% selectivity), tetrahydrofurfuryl alcohol (THFA, 0-2% selectivity), 2-Methyltetrahydrofuran (MTHF, 12-31% selectivity), 1-Pentanol(10-33%, selectivity), 2-Pentanone(MPK, 1-15% selectivity) and (S)-(+)2-Pentanol (2-Pentanol, 15-44% selectivity). High current efficiency (85.27%) was achieved. Various operating parameters were evaluated to determine their effects on the yield of products and the overall efficiency of ECH. The results show that an increase in humidity of anode increased the yield of products and H₂ utilization. High current density significantly increased the H₂ utilization while having less effect on the product’s yield. Cell temperature between 50 °C and 80 °C had a negative effect on furfural conversion. The degradation of membranes due to contamination of PEMFC and the mitigation methods were also investigated.
4.1 Background

Furfural is a versatile compound in the fragrance industry and is produced from the acid-catalyzed dehydration of xylan contained in lignocellulose. Many different lignocellulosic residues could be used for furfural production, like corncob, sugarcane bagasse, rice husk, olive stones and wheat bran [153, 154].

Furfural is already produced with an amount of more than 200 000 tons per annum from lignocellulosic biomass and is the most common industrial chemical derived from renewable resources [155, 156].

Furfural cannot be used directly as a fuel due to its tendency to polymerize at room temperatures [157]. However, Furfural is believed as one of the platform chemicals which can be used as a starting reagent to produce other high value-added products, like vapor phase hydrogenation of furfural is commonly used to produce 2-Methyltetrahydrofuran and furfuryl alcohol [158, 159]. Through the hydrogenation and acid–base catalyzed reactions, furfural could be upgraded to biofuels. The complete value chain of furanic biofuels is shown in Figure 26 [160].
Furfural derivatives are prepared traditionally by the catalytic hydrogenation method. For instance, there are two ways to produce furfuryl alcohol (FA) by hydrogenation of furfural: vapor-phase hydrogenation and liquid-phase hydrogenation. In vapor-phase hydrogenation, the experiment could be carried out atmospheric, while high temperature (170°C -300°C) is required. Depending on the type of catalyst used, hydrogenation of furfural can give, besides furfuryl alcohol, a variety of products such as 2-methylfuran, 2-pentanol, 2-methyltetrahydrofurran(MTHF), 2-pentanone(MPK), 1,5-pentanediol, and tetrahydrofurfuryl alcohol (THFA) [161, 162]. Hydrogenation of furfural in liquid phase requires high pressures (0.1-2MPa) and temperatures (170°C -350°C). Ring-opening products like 1-pentanone, 2-pentanone, 1-pentanol, 1-pentanol, 1,2-pentanediol and 1,5-pentanediol are formed [163, 164]. Catalyst residues are the main drawback of this method [165]. Overall, both processes require intensive energy input and use corrosive chemicals.
Furfuryl alcohol is an important fine chemical for the polymer industry. It is mainly used for the production of dark thermostatic resins resistant to acids, bases and various solvents; liquid resins for galvanic bath-tube, and resins used for strengthening ceramics. It is also widely used as a solvent, e.g. phenolic resins or pigments of low solubility [158, 162, 166-169].

2-methyl-retrahyfrofuran is an important intermediate in fine chemical industrial practices, which is mainly used for the synthesis of crysanthenemate pesticides, perfume intermediates and chloroquine lateral chains in medical intermediates [162, 170, 171]. The potential of 2-methylfuran as biofuels has been corroborated by Langue et al. [160]. 2-methyl furan is also used as a gasoline blend[172]. Pentanol can be used as a solvent for coating CDs and DVDs. Pentanol has all the properties necessary to replace gasoline as an internal combustion fuel, and used as fuel blend [173-176].

Electrochemical hydrogenation (ECH) is believed to be a more energy saving and environmentally-friendly method to upgrade organics, by integrating both the catalytic and the electrochemical methods. In this paper, ECH of furfural to produce furfuryl alcohol (FA), tetrahydrofurfuryl alcohol (THFA,), 2-Methyltetrahydrofuran (MTHF), 1-Pentanol, 2-Pentanone (MPK) and (S)-(+-)2-Pentanol (2-Pentanol) was demonstrated using a PEMFC reactor at ambient pressure. 2(3H)-Furanon,5-methyl-(FM) and Gamma-Valerolactone(GV) were also identified in the products, which were probably from the hydrogenation of furfural impurity, 2-Acetylfuran, and 2-Methyl-2-furaldehyde(MF). Various factors that impact the yield of propanol were investigated, including current density, temperature, relative humidity (RH), reaction time and membrane degradation. The main objective of this work was to evaluate the appropriate alternative pathway of furfural hydrogenation to conventional hydrogenation techniques using a PEMFC reactor.
4.2 Material and Method

4.2.1 Material and experimental setup

The experiments were performed using a standard PEMFC hardware (Scribner Associates Inc., USA) with an active area of 25 cm$^2$. Such standard PEMFC hardware has been widely used for PEMFC evaluation tests [51, 104]. Commercially available MEAs were purchased from Ion Power Inc., USA. The MEAs consist of Nafion® 117 membranes sandwiched with porous carbon-based electrodes, each of which had a Pt loading of 0.3 mg/cm$^2$. Micro-porous carbon papers (SIGRACET® 10BC) were trimmed and used as gas diffusion layers (GDLs) for both electrodes. Teflon gaskets were used to seal around the assembly. A pair of graphite bipolar plates with flow patterns was used to distribute flows and enclose the assembly. All the temperatures were acquired via K-type thermocouples (OMEGA, USA). A fuel cell test station (850e, Scribner Associates Inc., USA) was used to control temperatures, flow rates, and humidity. It was also used for data acquisition.

Ultra-high purity (99.999%) N$_2$ (Airgas, USA), and filtered shop air were connected to the fuel cell test station and supplied to the PEMFC through the purge line. They were used for purging the system and making current and voltage curve, respectively, and were cut off while the ECH experiment was running. The ultra-high purity (99.999%) H$_2$ (Airgas, USA) and Deionized (DI) water tanks were purged through the anode side of the reactor, using the fuel cell test station. H$_2$ was the electrons donator and deionized (DI) water tank was used for adding humidity to H$_2$. Furfural (98+, Fisher Scientific, Acros Organics, USA) was injected into the cathode side of the reactor by a syringe pump (MTI Corporation, EQ-300sp-LD). A direct current (DC) power supply (Tektronix, PWS 4205) was used to supply DC power for ECH. The positive probe was connected to the anode, while the negative probe was connected to the
cathode. While ECH was running, electrons were deprived of H₂ and transferred to the cathode through the DC power supply. Furfural was the electron acceptor and reacted with the produced protons. The products from the cathode outlet were collected by airbags (Tedlar®), which were held by the water bath. Room temperature water bath was used for condensing the unreacted furfural and products. The cell temperature was controlled by the fuel cell test station. The exhaust gases and byproducts from the anode were condensed in a knock-out bottle prior to venting out. The schematic diagram of the whole experimental setup is shown in Figure 27.

Figure 27. Schematic diagram of the experimental setup.

4.2.2 Experimental characterization

All the PEMFCs were assembled in accordance with the standard assembly procedure of fuel cell hardware [56]. Prior to each ECH experiment, a new membrane was conditioned based on the standard protocol [56] for at least 24 hours, until it reached a fully functional state.
Current-voltage (I-V) sweeps were performed to establish the baseline data for the following ECH experiments.

In each ECH experiment, the 5% furfural solution and H₂ flow rates were controlled at 12 ml/hr and 0.15 slpm or 0.25 slpm, respectively. The voltage was consistent for each reaction; the current was recorded every one minute. Four different factors, including cell temperature, RH, current density, reaction time and membrane degradation, were investigated to identify the optimized operating conditions. The operating conditions were in the range of 55 °C to 80 °C, 40 % to 100 %, 20mA/cm² to 200mA/cm² and 60 minutes to 220 minutes, respectively. I-V scans were conducted before and after ECH to characterize the membrane degradation.

After each experiment, the system was washed by water and air for 24 hours, respectively. A 5% HCl solution also was tested to wash the system. Products were collected by airbags with pressure relief valves. The airbag was immersed into room temperature water bath. The pressure differential of two electrodes can be controlled by airbags confined extent. Green et al. proved that a suitable pressure differential between the anode and cathode could decrease cross-over and increase conversion [72]. Dadda et al. believed that water transport in the membrane of a PEMFC is influenced by a convective force, resulting from a pressure gradient [106]. Many researchers also point out the importance of the flow pressure [107].

The product volume and weight were recorded after the reaction. The collected samples were extracted by 3 to 5 ml methylene dichloride (DCM). The extracted samples were quantitatively and qualitatively analyzed by a gas chromatography-mass spectroscopy (Shimadzu, GC-MS-QP2010 SE), using a (Restek, Rxi-1ms) MS column (length: 30 m, inner diameter: 0.25 mm). Helium was used as a carrier gas for gas chromatography. The standard curves of products were made by GC-MS using MTHF (99+%, Fisher Scientific, Fisher
Scientific, Acros Organics, USA), 2-Acetyluran (99%, Fisher Scientific, Acros Organics, USA), MPK(99+%, Fisher Scientific, Acros Organics, USA), FA(98%, Sigma Aldrich, Alfa Aesar, USA), 1-pentanol(99+%, Fisher Scientific, Acros Organics, USA), GV(98+%, Sigma Aldrich, Alfa Aesar, USA), (s)-(+)2-pentanol(97+%, Fisher Scientific, Acros Organics, USA), THFA(99+%, Fisher Scientific, Acros Organics, USA), MF(98+%, Fisher Scientific, Acros Organics, USA) and FM(98%, Sigma Aldrich, Alfa Aesar, USA).

The flow chart of the ECH experimental operation is shown in Figure 28.

4.3 Results and Discussion

4.3.1 Product characterization

Both furfural and the liquid products were analyzed by GC-MS. Two impurities of 5-Methyl-2-furaldehyde (MF, C₆H₆O₂) and 2-Acetylfuran (C₆H₆O₂) were detected in the initial
furfural sample. Except furfural and the impurities, eight products of furfuryl alcohol (FA, C₅H₆O₂, 6%-15% selectivity), tetrahydrofurfuryl alcohol (THFA, C₅H₁₀O₂, 0%-2% selectivity), 2-Methyltetrahydrofuran (MTHF, C₅H₁₀O₂, 12%-31% selectivity), 1-Pentanol (C₅H₁₂O, 10%-33%, selectivity), 2-Pentanone (MPK, C₅H₁₀O, 1%-15% selectivity), (S)-(+) 2-Pentanol (2-Pentanol, C₅H₁₂O, 15%-44% selectivity), 2(3H)-Furanon,5-methyl-(FM, C₅H₆O₂, 0%-2% selectivity) and Gamma-Valerolactone (GV, C₅H₈O₂, 0%-3% selectivity) were found in the liquid.

The reactions on both electrodes were catalyzed by Pt. while applying a DC voltage protons formed at the anode were electrochemically pumped to the cathode. The protons then reacted with furfural to produce products. The most feasible reaction pathways at the cathode are shown in Figure 29.

![Figure 29. Furfural hydrogenation pathway](image)

Electrosorbed hydrogen (Hₐds) was formed on Pt surface by reduction of H⁺, and then Hₐds reacts with furfural and intermediate products. The first reaction was the hydrogenation of the
furful C=O bond with the product of FA (Rea.1), then the FA C=C bond was hydrogenated with the corresponding saturated chemicals THFA generation (Rea.2). THFA converted to MTHF through dehydration reaction (Rea.3). The carbon ring-opening of MTHF was the ultimate hydrogenation process, and the final products are 1-pentanol, 2-pentanol, and 2-pentanone (Rea 4, 5, 6). Although FM and GV are detected in products, they cannot be confirmed as furfural hydrogenation products (Rea 7, 8). The most possible source of them was furfural impurity hydrogenation (Rea 9, 10). The reason will be explained in the following chapters.

According to the various product concentrations (Figure 30), 2-pentanol, 1-pentanol, and MTHF were the main products, others are by-products. The yield of products is determined by the catalyst type. Green et al. reported that the Pt/C catalyst has a higher electrochemically active surface area and lower overpotential than Pd/C. Furfural hydrogenation over Pd/C could produce four products of FA, THFA, MF, and MTHF, compared to the only product of FA by Pt/C [58]. Platinum has long been known as a furfural hydrogenation catalyst [158, 177, 178] and favors the side and consecutive reactions such as hydrogenolysis of the C-O bond and ring-opening [179]. In this paper, Pt was used as the catalyst for all the experiments.

The electrocatalytic hydrogenation of aqueous solutions of 5 wt% furfural in a continuous PEMFC reactor was investigated, as shown in Figure 30. Three different control parameters, including RH, temperature and current density were assessed to identify the optimized operating conditions for ECH furfural. All the operating parameters used in the experiments are shown in Table 11 (seen in the appendices).

RH is a very important parameter that affects the performance of PEMFCs [107, 109-113]. Figure 30a shows a typical impact of RH on the product yield during ECH of furfural. It was
obviously evidenced that higher humidity slightly promoted the yield of 2-pentanol (100 ppm to 150 ppm), 1-pentanol (55 ppm to 110 ppm), FM (4 ppm to 23 ppm) and MTHF (83 ppm to 115 ppm), while FA, GV, MPK, and THFA concentration were constant or slightly descended. Compared to C=O and C=C hydrogenation, the higher temperature contributed more to the ring-opening reaction, since the selectively of ring-opening product 1-pentanol increased from 16% to 24% with the RH increasing from 40% to 100%. The reason why humidity had such an impact is that the MEA usually uses a perfluorosulfonic acid membrane (e.g. Nafion®) as the electrolyte. A high or nearly saturated humidity (RH >80%) is usually required to obtain practical performance because the conductivity of perfluorosulfonic acid membrane membranes depends on the water content. Higher humidity means higher conductivity, resulting in better performance [114-117]. Water management is critical for PEMFC operation. Sufficient water must be absorbed into the membrane to ionize the acid groups, whereas excess water can cause flooding issues and thus diminish the performance [72]. The inlet RH of the electrodes must be controlled to prevent both membrane drying out and electrode flooding. Although better performance is usually obtained by increasing RH, excess moisture may result in water flooding that hinders gas transport [118]. In the present experiments, cathode side water was from furfural solution, while anode water was supplied by RH and cathode water crossing over. RH selection should be determined by target products and reaction time. According to Figure 5a, if the preferred product was FA, less than 50% RH should be selected. Correspondingly, more than 80% RH could favor the yield of preferred product 2-pentanol and 1-pentanol. The amount of crossing over water was easily accumulated, with the extension of reaction time. To prevent either water starvation or over saturation, RH could be adjusted with time.
Nowadays, the mechanism of humidity influence has been investigated by many researchers. It is generally believed that RH can impact electro-osmotic drag, water diffusion, membrane ionic conductivity, and water back diffusion flux in the MEAs, which consequently influence the performance [119, 120]. Elevated RH can greatly improve the PEMFC performance, through increasing the membrane conductivity [121, 122], the catalyst activities [121, 123], the electrode kinetics [124, 125], and the mass transfer rates [126, 127].
Figure 30. Products change as a result of (a) current, (b) RH and (c) (d) temperatures. 
H2 and furfural solution flow rates were 0.25 L/min and 12 ml/hr, respectively. Products concentration were identified three times. (a) The current ECH experiments were conducted for 6 times at 65 °C; (b) The ECH experiments were conducted for 5 times at 65 °C and 80% RH; (c) (d) The ECH experiments were conducted for 5 times at 80% RH.

Operating current density was the second factor assessed in this study. Figure 30b shows the influence of current density on the product yield during ECH of furfural. The concentrations for all the main products of 2-pentanol, 1-pentanol, FA and MTHF were more than 200ppm. Correspondingly, the by-product’s concentration was less than 30ppm. Therefore, the yield of the main products was maximized. It is also proved that an increase of current density had an
obviously positive influence on the yield of 2-pentanol (240ppm to 644ppm) and 1-pentanol (130ppm to 468ppm), while other products’ concentrations were almost constant. At the maximum current density of 200mA/cm², 2-pentanol and 1-pentanol achieved their maximum selectivity, 44%, and 32%, respectively. In temperature and RH experiments, the cell current density changed with time by fixing voltage at 0.02V. Different from them, the current density was constant in this set, while the input voltage changed with time (Figure 31). In these experiments, the operating temperature, RH, H₂ flow rates and furfural solution flow rates were set at 80%, 65 °C, 0.25 L/min and 12 ml/hr. Figure 31 shows the input voltage was determined by the required current density. 0.05V to 0.27V voltage was required to maintain 200mA/cm² (black line), while the voltage number decreased to 0.01 with 20mA/cm² current density (green line). In addition, due to the decrease of PEMFC membrane performance, the input voltage was elevated with the extension of reaction time. Green et al. found that higher applied voltage was favorable for current density elevation and also demonstrated that the input voltage significantly impacted on the type of products, due to the difference of standard cell potentials required by each reaction, such as THFA was only present at a power input of 0.3 W [58]. This experiment proved that when the input voltage was below 0.27V, the yield of products is impacted by current density, rather than determined by the input voltage.
Operating temperature was another factor assessed in this study and is shown in Figure 30c and 30d. Generally, the temperature was found to have a significantly negative impact on the yield of MTHF, FA, 2-pentanol, and 1-pentanol, while a slightly negative influence on MPK, THFA, and MF was also evidenced. The only exception was GV, for which the maximum concentration appeared at 73 °C. The maximum decrease was from 1-pentanol, whose concentration declined from 920 ppm to 20 ppm when the temperature increased from 55°C to 80 °C. At 80 °C, meanwhile, 1-pentanol reached the minimized selectivity of 26%. Therefore, the optimized temperature seemed to be room temperature. The results agreed with some findings from the literature. Singh et al. [47] investigated the ECH of phenol by Pt accordance with increasing temperature. It was believed that dehydrogenated phenol adsorbents easily block the active sites of Pt at higher temperatures. Li et al. investigated ECH of bio-oil and the results show that the electrochemical efficiency for guaiacol reduction decreased from 17% at 50 °C to 10% at 80 °C [66]. Green et al. investigated the ECH of furfural by Pt/C catalyst with increasing temperature. The results indicate that the increase in temperature promotes water electrolysis of
hydrogen gas but not furfural hydrogenation [58]. Room temperature ECH was also recommended by many researchers [34, 50, 51, 57, 58].

In sum, room temperature, high current density, and high RH are recommended to optimize the yield of products, especially for ring-opening products.

### 4.3.2 System analysis

Selectivity, \( \text{H}_2 \) utilization, and current efficiency are selected to evaluate the hydrogenation efficiency. Selectivity represents the yield of products. The selectivity is calculated based on the following equation [54, 60], where furfural unreacted is excluded:

\[
\text{Selectivity} = \frac{\text{Moles of Desired Product}}{\text{Total Moles of Product}} \times 100\% \quad (1)
\]

In the present research, \( \text{H}_2 \) was supplied to the anode to produce protons for ECH reactions on the cathode. Due to gas diffusion resistance, gas crossover, and hydrogen regeneration on the cathode, some \( \text{H}_2 \) was wasted. The \( \text{H}_2 \) utilization is directly related to the overall ECH efficiency. Higher \( \text{H}_2 \) utilization percentage is desired since more hydrogen will be actually involved in the ECH process. The actual amount of \( \text{H}_2 \) used to produce products can be derived from the amount of product. The \( \text{H}_2 \) utilization is calculated by the following equation:

\[
\text{H}_2 \text{ Utilization} = \frac{\text{Atomic Hydrogen Used for Faraday Current}}{\text{Total Atomic Hydrogen Supplied}} \times 100\% \quad (2)
\]

During the ECH process, furfural reacts with \( \text{M(H)}_{\text{ads}} \) on the cathode. Concurrently, \( \text{H}_2 \) regeneration happens and is an unfavorable process simply because it wastes energy. The \( \text{H}_2 \) regeneration reaction is affected by current density, temperature, humidity, and catalyst. Hereby, current efficiency (shown below) is used as an important parameter to determine how efficient \( \text{H}_2 \) is used for the ECH process [54, 60].
Current Efficiency = \frac{\text{Current used for the ECH process}}{\text{Total Faraday current}} \times 100\% \quad (3)

The total efficiency is defined by the \( \text{H}_2 \) utilization multiplying the current efficiency, as shown in the following equation:

\[
\text{Total Efficiency} = \text{H}_2 \text{ Utilization} \times \text{Current Efficiency} \quad (4)
\]

Figure 32a shows the impact of temperature on \( \text{H}_2 \) utilization, current efficiency, and total efficiency in a typical set of experiments. As the operating temperature decreased from 50 °C to 80 °C, \( \text{H}_2 \) utilization decreased from 3.3% to 1.1%, current efficiency decreased from 11.7% to 2.5%. Temperature negatively affected \( \text{H}_2 \) utilization and current efficiency. Figure 32a indicates that with elevated operating temperature, less hydrogen being involved in reactions and more current electrons wasted. Note that the total efficiency was low because abundant \( \text{H}_2 \) was supplied to the system to minimize the impact of fuel starvation and gas diffusion resistance. Practically stoichiometric flow can be fed to the system based upon the actual current. It used to believe that higher ionic mobility and catalytic activities are achieved with elevated operating temperatures, resulting in higher \( \text{H}_2 \) utilization, better current efficiency, more electrochemical conversion, and faster reaction rates \([42, 43, 180]\). Actually, the temperature influence on ECH reaction is controversial. It is claimed to be correlated with properties of reactants. Singh et al. believed that dehydrogenated phenol adsorbents easily block the active sites of Pt at higher temperatures, according to his ECH of phenol result\([47]\). Green et al. electrocatalytically hydrogenated acetone and furfural in the same proton-exchange-membrane (PEM) reactor at the same catalysts. The results demonstrated the different influence of temperature on ECH efficiency. The acetone conversion, reaction rate, and current efficiency increased with
increasing temperature. However, the ECH furfural results indicated that the increase in temperature cannot improve furfural hydrogenation [58, 72].
Figure 32. H₂ Utilization, Current Efficiency, and Total efficiency calculated at different (a) temperatures, (b) RH and (c) Current. H₂ and furfural flow rates were 0.25 L/min and 12 ml/hr, respectively. Products concentrations were identified three times. (a) The ECH experiments were conducted for 5 times at 80% RH; (b) The ECH experiments were conducted for 5 times at 65 °C; (c) The current ECH experiments were conducted for 6 times at 65 °C and 80% RH.

Figure 32b shows the influence of RH on H₂ utilization, current efficiency, and total efficiency. The operating temperature was set at 65 °C, and the RH was controlled by setting the humidifier’s temperature. It was seen that higher RH resulted in worse current efficiencies and better H₂ utilization. As the RH ranged from 40% to 100%, the H₂ utilization increased from 0.4% to 3.1%, and the current efficiency decreased from 20% to 1.9%. A sudden descent of current efficiency from 17.3% to 5.6% was observed when ramping the RH from 50% up to 63%; meanwhile, the H₂ utilization hiked slightly. In this experiment, anode water was supplied by RH and cathode water crossing over. It has been proved that higher ionic conductivity can be achieved when MEAs become more hydrated [121-123, 129-132]. With the ionic conductivity increasing, it is favorable for anode H₂ to protonate and generate current electrons, which is expressed as the increase of H₂ utilization. After sufficient hydration of MEAs, elevating RH cannot improve H₂ utilization, which was shown in the range of RH 63% to 100%. Different
from the anode side, sufficient water was supplied to cathode side by furfural solution. Therefore, the change of RH cannot bring directly impact on cathode reaction. It was also demonstrated that higher RH resulted in a slightly higher yield of products, which was shown in Figure 30a. This phenomenon of H₂ utilization and products increasing with current efficiency decreasing in the same time was due to higher RH generating more current electrons, but the increased current elections were only partially utilized by cathode side organics. With the HR increasing, total efficiency was improved significantly, which increased from 0.02% to 0.06%. Practically, high RH is required to maintain the best fuel cell performance. The higher water content in the Nafion membrane will ease proton transport, i.e. less ionic resistance. As a result, more protons can be created and transported to the cathode for ECH. Typically >80% RH is recommended by many researchers [114-117, 133]. Accordingly, although the current efficiency is not optimized, >80% RH is still suggested.

Figure 32c shows the influence of current density on H₂ utilization, current efficiency, and total efficiency. The operating temperature and RH were set at 65 °C and 80%, the current density was constant and controlled by current (DC) power supply. The changing trend of input voltage with reaction time was shown in Figure 31. It has been seen that the higher current density required a higher input voltage to maintain. In Figure 32c, H₂ utilization was proportional to the fixed current and achieved the top 25% at 200 mA/cm², which was the maximum affordable current of the PEMFC system. The current efficiency was significantly descended at the current density between 20 mA/cm² and 40 mA/cm² and then maintained at 0.9%. Higher current density means more electrons were deprived from H₂, which corresponded to H₂ utilization elevation. However, not all the increasing electrons could be utilized by organics, which resulted in the stagnant or even decreasing current efficiency. Because total efficiency
significantly increased from 0.08% to 0.19% over the range of 20 mA/cm² to 200 mA/cm², high current density is commended with ignoring the operation lifetime of the reactor. Some researchers reported the influence of current density on furfural electrochemical hydrogenation. Niles et al. investigated the electrochemical conversion of furfural to 2-methylfuran and of 5-hydroxymethylfurfural to 2,5-dimethylfuran. It indicated that the furfural conversion rate corresponded to the current density and suggested increasing the electrode surface area to improve current efficiency [59]. Green et al. used a continuous-flow electrocatalytic membrane reactor for the reduction of aqueous solutions of furfural into furfuryl alcohol, tetrahydrofurfuryl alcohol, 2-methylfuran, and 2-methyl tetrahydrofuran and found that higher applied voltage was favorable for current density elevation [58]. Li et al. studied electrocatalytic hydrogenation of furfural to furfuryl alcohol and 2-methylfuran. It indicated that the current density also strongly affected the product yield and electrochemical efficiency [54].
Figure 33. The change of voltage and current with time (a), the comparison of products (c), H₂ utilization (b), current efficiency (b), and total efficiency (b) between different voltage and current. A constant current was 180 mA/cm², at first 60 min. A constant current was 1.2 V, at between 60 min to 350 min. Product was collected time times, at 60 min, 150 min, and 350 min, and then were identified three times. The ECH experiments were conducted at 65 °C, 80% RH, 12 ml/hr furfural flow rates and 0.15 L/min H₂ flow rate.

The comparison between the current fixed ECH method and input voltage fixed method was investigated, and the result was shown in Figure 33. The experiment was conducted at 65 °C, 80% RH, 12 ml/hr furfural flow rates and 0.15 L/min H₂ flow rate. Products were collected at 60 minutes, 120 minutes, and 350 minutes. At the first hour, to keep current density constant at 200 mA/cm², which was the maximum affordable current density of the system, the voltage was elevated from 0.5 V to 1.2 V. between 60 minutes and 350 minutes, the current density cannot be maintained at 180 mA/cm², though voltage was still 1.2 V. This trend was shown in Figure 8a. It indicated that due to the degradation of MEAs with time, which will be discussed in the next chapter, high current density maintenance required more input voltage, in another words, more energy. It is corresponding to Figure 6. similar phenomenon was observed by other researchers [60]. As shown in Figure 33b and 33c, all the parameters including product concentration, H₂ utilization, current efficiency, and total efficiency behaved much better in the first hour than at any other time periods. The results from Figure 30b were reconfirmed by the data in Figure 33c, which demonstrated that high current results in better product yield. No new products were detected even when the input voltage was increased up to 1.2 V. Accordingly, the current fixed ECH method is recommended.

In summary, the present research shows that the performance of ECH of furfural is correlated with RH, input current density, and temperature. Specifically, temperature and input current density have a more obvious effect than the rest of the parameters. The obtained maximum H₂ utilization and maximum current efficiency achieved in the present experiments was 25% and 21%, respectively. It is suggested that the optimized operating conditions are RH
of 80% or more, the input current of 200 mA/cm$^2$ or more, and room temperature. To further increase those efficiencies, stoichiometric flow control is strongly suggested.

4.3.3. MEA degradation

Long-term durability is one important factor that affects the practical applications of ECH using PEMFC reactors. Nowadays, commercial MEAs are fairly durable for their common roles as power sources. The ECH process, however, involves organics that may contaminate MEAs and thus shorten their lifetime. To our best knowledge, very limited research has been conducted to evaluate the impacts of contaminants on the durability of ECH. In the past decade, extensive research has been carried out on mitigating contamination of PEMFCs from impurities, including CO, CO$_2$, H$_2$S, NO$_x$, SO$_x$, and hydrocarbons [134, 135]. Impurities may contaminate one or more components of the MEA, resulting in performance degradation. Three major contamination effects were identified as the poisoning of the electrode catalysts, a decrease of the ionic conductivity, and an increase of the mass transfer resistance.

Additionally, the crossover is another factor that negatively impacts the PEMFC performance. Crossover of organic compounds during hydrogenation using PEMFCs has been reported [136, 137]. One immediate drawback is the loss of fuel and/or products, which decreases efficiency. Furthermore, contaminants not only poison just one electrode but also may crossover and further poison the catalyst on the other electrode [33].

To investigate the impacts of MEA degradation on the present hydrogenation tests, polarization scans (V-I sweeps) were performed after each test [56], which is shown in Figure 34. The black curves in Figure 34a, 34b-1 and 34c-1 were the baseline data recorded for the fresh MEAs prior to ECH tests. Figure 34b-2 and 34c-2 were the current VS time curve of the tests, corresponding to the reaction mentioned in Figure 34b and 34c. After each test, pure N$_2$ and
water were purged for at least 24 hours to remove all the temporary contaminants. An HCl solution was also tested in the experiment. The effects of RH, temperature and time on the MEA degradation were also evaluated.
Figure 34. V-I scans (a) (b-1) (c-1) and current (b-2) (c-2) performed during three sets of ECH experiments. (a) The ECH experiments were conducted for 6 times at 65 °C and 80% RH. The current of five reactions are 200 mA/cm², 160 mA/cm², 120 mA/cm², 80 mA/cm², 40 mA/cm² and 20 mA/cm²; (b) The ECH experiments were conducted for 4 times at 65 °C but different RH. The RH of the four reactions are 100%, 63%, 50%, and 38%, respectively; (c) The ECH experiments were conducted 5 times at 80% RH but different temperatures. The temperature of five reactions is 50 ºC, 58 ºC, 65 ºC, 73 ºC, and 80 ºC, respectively. Products concentrations were identified three times. H₂ and furfural flow rates were 0.25 L/min and 12 ml/hr, respectively. The black curves were the baseline data recorded for the fresh MEAs prior to ECH tests. After each test, pure N₂ and water were purged for at least 24 hours, respectively, to remove all the temporary contaminants.

Figure 34a shows the results of five sets of V-I measurements performed on a PEMFC, which underwent five 1-hour long ECH experiments. Both the ECH experiments and V-I measurements shown in Figure 34a were conducted at 65 °C with 80% RH. Note that in order to compare with the same baseline data (the black curve in Figure 34a), all the V-I scans were conducted using the same operating conditions that have been used for the baseline scan. It clearly shows that the MEA performance degraded as more ECH tests were conducted, especially after the fifth ECH experiment. The open circuit voltage (OCV) dropped a lot starting at the 1st V-I scan, and then the dropping trend is not obvious until the 6th ECH V-I scan which indicates that crossover became significant. It implied that pinholes might form due to degradation.

The effect of RH on MEA degradation was investigated, as shown in Figure 34b. For the ECH experiments conducted in Figure 33, the operating RH were 100%, 63%, 50%, and 38%, while maintaining the same temperature at 65 °C for 4 hours. Again, all the V-I scans were performed using the same operating conditions as those used for the baseline scan (black curve in Figure 33b-1). Figure 34b-1 shows that the drop of V-I scans negatively correlated to the reaction RH. The current number of V-I scans at 0.5V decreased by 259 mA/cm², 112 mA/cm², 58mA/cm² and 24 mA/cm², at 100%, 63%, 50% and 38% RH, respectively. It indicated that the variation of RH from 100% to 38% has a positive impact on MEA degradation. Figure 34b-2 gave the demonstration that less RH resulted in less reaction current, leading to less mass
transport via the MEA, which eventually prolonged the lifetime of the catalysts. However, permanent damage to the MEA still existed, as seen from the general trend of the V-I scan. Similar to what was observed in Figure 34a, purging with pure N₂ and water could not remove permanent contaminants.

Figure 34c shows the effect of temperature on MEA degradation during ECH. For the ECH, five 2 hours long experiments conducted in Figure 33c, Temperature was reduced from 80 ºC to 50 ºC, at 80% HR. The temperature of five reactions was 50 ºC, 58 ºC, 65 ºC, 73 ºC, and 80 ºC, respectively. The strongest drop of the open circuit voltage (OCV) happened at the 1st V-I scan, which was performed after the minimum 50 ºC, and then the decrease became slight. The 4th V-I scan and the 5th V-I scan were most coincided, which means the population of MEA was maximized. Again, all the V-I scans were performed using the same operating conditions as those used for the baseline scan (black curve in Figure 33c-1). The results illustrate that the most significant inefficiency of MEAs appeared at a minimum temperature of 50 ºC. Figure 34c-2 demonstrated the current of each test, which was extremely correlated to the drop of OCV. For instance, the 1st reaction current curve was obviously higher than other, which corresponded to the strongest drop of the OCV happened at the 1st V-I scan. Accordingly, increasing temperature was recommended to mitigate the degradation to some extent. permanent damage to the MEA still existed, which was similar to temperature and current tests.
Figure 35. Product (a), current efficiency (b), H\textsubscript{2} utilization (b) and total efficiency (b) as a function of ECH experiment time. The ECH experiments were conducted for 220 min. The corresponding current vs time curve was shown in Figure (c). The ECH experiments were conducted at 65 °C, 80% RH, 0.02V input voltage, 12 ml/hr furfural flow rates and 0.25 L/min H\textsubscript{2} flow rate. Products were collected at 60 min, 120min, and 220 min and were identified three times.

Figure 35 shows that the trends of product, current efficiency, H\textsubscript{2} utilization and total efficiency using one MEA for 220 minutes. Products were collected at 60 min, 120min, and 220 minutes. Figure 10b shows a typical impact of reaction time on the product yield during ECH of furfural. Most of the main products of 2-pentanol, 1-pentanol and MTHF were produced at the first 60min, and then extremely descended at the time between 60 minutes and 120 minutes, eventually tended to be constant in the range of 120 minutes to 220 minutes. For instance, the yield of 2-pentanol at first 60 minutes was 268ppm and then dropped to 47ppm and 21ppm, at 120 minutes and 220 minutes, respectively. Different from the main products, by-products of GV and MPK slightly descended at the time between 60 minutes and 120 minutes. Very few mounts of MF were detected in this experiment. Figure 35a shows that the trend of current efficiency and H\textsubscript{2} utilization with time were totally opposite, H\textsubscript{2} utilization was negatively impacted by reaction time, while current efficiency was positively affected. Ultimately, 85% H\textsubscript{2} utilization was achieved at 220 minutes. Figure 35c exhibited that the current changed with time and proved that most of the current electrons were produced at the first hour. The Pt catalyst was commonly applied in fuel cells and proved to be an effective catalyst of depriving electrons from hydrogen [181, 182]. Although Pt has long been known as a furfural hydrogenation catalyst [158, 177, 178], the initial activity of Pt for furfural ECH by PEM reactor is not as good as Pd, Ni and Ru [41] Pt catalyst deactivation with time brings more serious influence on proton formation than the organic reduction. The deactivation of the Pt catalyst prevented anode H\textsubscript{2} protonation and current electrons generation, which was expressed as the decrease of H\textsubscript{2}
utilization. Because the impact of deactivation of Pt on cathode organic reduction was not as serious as the current generation, the current efficiency was elevated with the decrease of current density.
Figure 36. Current efficiency (a), H\textsubscript{2} utilization (b), total efficiency (c), products (d) (e) (f) (g) (h) (i) (j) (k) and impurity(l) (m) as a function of ECH experiment time. The ECH experiments were conducted for 120 min, and the products were collected twice at 60 min and 120 min. The ECH experiments were conducted at 80% RH, 0.02V input voltage, 12 ml/hr furfural flow rates and 0.25 L/min H\textsubscript{2} flow rate. Products were identified three times.

Figure 36 shows the impact of temperature and reaction time on H\textsubscript{2} utilization, current efficiency, total efficiency and products in a typical set of experiments. Each experiment was conducted for 120 minutes, and with the products collected twice at 60 minutes and 120 minutes. Black curves in each figure expressed 1-hour collection, with red one standing for 2-hour collection. As we have already discussed the negative effects of temperature, on H\textsubscript{2} utilization,
current efficiency total efficiency and products previously, the discussion here will focus on the comparison of the different reaction time curve. Figure 36a, 36b, and 36c demonstrates that comparing with the current efficiency, H\textsubscript{2} utilization and total efficiency had a more significant drop between the 1st-hour curve and the 2nd-hour curve, which means H\textsubscript{2} utilization and total efficiency declined faster than current efficiency at the same operating time. It could be explained by the fact that the deactivation of Pt with time bringing more a negative effect on anode H\textsubscript{2} protonation than cathode organic reduction. This has been discussed in the last chapter. Compared with the first hour curve of Figure 36d, 36e, 36f and 36g, the second hour curve in these figures also took a huge descent, and it was more obvious at a lower temperature. For instance, the decrease of 1-pentanol between the first and the second-hour curve at 50°C was from 1484ppm to 345ppm, and the corresponding number was from 32ppm to 2ppm at 80°C. Obviously, with the same reaction time, at a lower temperature, furfural conversion rate was much higher, which resulted in the faster degradation of MEAs. This was why the low temperature gap between the two lines is bigger than the high temperature one. It concluded that these products of 2-pentanol, MTHF, 1-pentanol, and FA were centrally produced in the first hours and 1 hour operating time is recommended to ECH of furfural.

Compared to the main products, the by-product concentration of THFA and MPK in the ultimate product is fairly low, which is shown in Figure 36h and 36i. Especially for THFA, the maximum detected concentration was less than 3 ppm, which means the concentration change cannot be as significant as others. However, the gap between the two lines was still observable. It demonstrated that the yield of by-products decreased with reaction time extension, not as obvious as the main products.
A completely different changing trend of 1 hours curve and 2 hours curve were demonstrated in Figure 36j and 36k. The two lines of FM almost overlapped. The gaps of GV 2 lines just appeared at a temperature between 57°C and 73°C. Different from the structure of furfural, one extra –CH₃ is bonded to the O-C ring of FM and GV. Although traditional methods could produce FM and GV form furfural [157, 183], there was no evidence to prove that –CH₃ could be added to furfural and generate FM and GV by the ECH method [54-59, 184]. MF and 2-cetylfuran were detected in the initial furfural sample and determined to be an impurity. FM was very likely to form the C=C double bond hydrogenation of MF, which has a similar structure, and then FM C=C bond was hydrogenated with the corresponding saturated chemicals GV generation. Since the possibility that FM and GV transformed from furfural cannot be ruled out, the yield of FM and GV was still reported in the present research.

The concentration of MF and 2-cetylfuran with temperature and reacted hours is also shown in Figure 36l and 36m. Both the 1-hour curve and 2-hour curve are not constant, which means MF and 2-cetylfuran joined in the hydrogenation. Different from other figures, the 2-hour curve of MF and 2-cetylfuran is higher than the 1-hour curve, which means more MF and 2-cetylfuran were consumed in the first hour.

Usually, the lifespan of a PEMFC under steady-state operation can be very long, up to thousands of hours [138-143]. However, catalyst contamination is the major factor that diminishes the PEMFC performance and very likely results in significant degradation [144-146]. In fact, many organic compounds are able to contaminate the MEA. Those compounds include acetaldehyde, toluene, propane, vinyl acetate, methyl methacrylate, acetonitrile, dichloromethane, acetylene, chlorobenzene, formic acid, methanol, ethanol, phenol, butane, acetone, and naphthalene [147-149], and the list is expanding. The main reason for the discovery
of so many contaminants is that the catalysts used in common MEAs are Pt-based. Pt is a premium catalyst, but also sensitive to so many contaminants. The MEAs used in the present research contain pure Pt as the catalyst. Although developing non-Pt catalyst is beyond the scope of the present research, in order to further conduct durable ECH experiments, MEAs with contamination tolerant catalysts need to be used.

Reactant and product crossing over is another possible reason that caused the MEA degradation. Liquids that contained mainly furfural and some products were detected at the anode side during the ECH experiments. Those liquids not only decrease the fuel utilization but also further contaminate the anode catalyst. Feasible solutions to this issue include adopting thicker MEAs, feeding gaseous feedstock instead of liquid, and using a non-Pt catalyst [150].

In sum, 1 reaction hour is strongly recommended for furfural ECH to maintain the conversion rate, and then MEAs degradation should be mitigated. Some simple methods proved to be effective, such as water wash, air wash and acid wash, which is shown in Figure 37. At 0.5 V, after air wash, water wash and acid wash, the current density increased by 40 mA/cm², 23 mA/cm² and 27 mA/cm², respectively.
Current density control was certified as a better method than input voltage control, by which MEA could be reused five times. Low operating temperature and high reaction humidity accelerated MEA’s degradation. Nevertheless, it cannot be avoided, since high furfural conversation rate was also required. To solve the problem essentially, novel non-Pt catalysts need to be developed, such as Pd and Ni-based catalysts [60, 151, 152]. Despite the fact that a wide range of metals can be used as electrocatalysts at the cathode, those with the strong capability of hydrogen absorption are desired.

4.4 Conclusions

Electrochemical hydrogenation of furfural using a PEMFC reactor was successfully demonstrated in the present research. The results proved that ECH can be a feasible way of hydrogenating furfural in mild conditions (room temperature and atmosphere). The main products include 2-pentanol, 1-pentanol, FA and MTHF, while THFA and MPK are by-products. Temperature negatively impacts the product’s yield, while humidity brings positive influence. Maintaining high current density by the applied voltage is a good method to increase the product’s yield and accelerate furfural conversion. The mild operation conditions, including low temperature and ambient pressure, are the greatest advantages of the proposed ECH method. The present research suggests that the optimized conditions for ECH of furfural using a PEMFC reactor include room temperature, relative high RH around 80\% and high current density.

Contamination impact using the PEMFC reactor during ECH was also investigated. It was concluded that organic compounds are able to contaminate the MEAs, resulting in serious degradation. However, the methods to mitigate contamination are limited. The present research demonstrated that lower RH could help reduce contamination; a high-efficiency work hour of
MEAs is 1 hour, and then simple wash is necessary to remove the temporary contamination.

Eventually, novel non-Pt catalysts need to be developed for a durable ECH process.
CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The following five conclusions can be deduced from this dissertation.

(1) Chemical activation is a feasible method to produce AC from lignin biomass, ECH of lignin bio-oil compounds e.g., furfural and acetone to produce a value added product, such as FA and isopropanol by using PEMFC reactor is an effective way to improve economic benefits from lignin utilization.

(2) In comparison, the activated carbon produced by the H₃PO₄ agent has a relatively low surface area and a high amount of phosphorus residue. ZnCl₂ proved to be a better impregnating agent. The optimal experimental condition is that when the activation time is 60 minutes, the impregnation ration is between 1.5 to 2, the heating rate is 60ºC/mins, and an activation temperature around 500ºC. With the best activation conditions, the carbons produced have a surface area of around 1117 m²/g, and the yield percentage could reach around 50%. Compared to Commercial AC, UHS-ZnCl₂ AC has similar Iodine No., Methylene Blue No, Surface area, better Yield percentage, which makes the high-temperature ZnCl₂ activated carbon method a possible way of utilizing lignin biomass residue. In addition, the Zinc residues could be totally removed through the acid wash and water wash which increased the purity of the activated carbon produced.

(3) Electrochemical hydrogenation of acetone using a PEMFC reactor was successfully demonstrated in the present research. The results proved that ECH can be a feasible way of hydrogenating acetone to produce isopropanol in mild conditions. In the experiments, the main product obtained was isopropanol with a selectivity of approximately 90%. A small amount
(about 1%) of diisopropyl ether was also obtained as a byproduct. Temperature had no impact on the isopropanol yield, while humidity brings a positive influence. The mild operation conditions, including low temperature and ambient pressure, are the greatest advantages of the proposed ECH acetone method.

(4) ECH can be a feasible way of hydrogenating furfural in mild conditions (room temperature and atmosphere). The main products include 2-pentanol, 1-pentanol, FA and MTHF, while THFA and MPK were by-products. Temperature negatively impacts the product’s yield, while humidity brings a positive influence. Maintaining high current density by applied voltage was a good method to increase the product’s yield and accelerate furfural conversion. The mild operation conditions, including room temperature and ambient pressure, are the greatest advantages of the proposed ECH furfural method.

(5) High operating RH and input current density of PEMFC significantly accelerated the degradation of MEAs, while relatively low temperature had a slightly negative influence on the degradation. In sum, the degradation speed of MEAs was proportional to the product’s yield rate.

5.2 Recommendations

(1) Relatively high ash content, higher bulb density, oxygen percentage, and relatively lower carbon element, pore volume are the main shortage of UHS-ZnCl₂ AC. Especially for the high ash content, it easily causes the corrosion of equipment and blockage of pipes, and also is harmful to the regeneration of AC. Pretreatment is a good option for lignin like UHS before chemical activation, especially to remove Si.

(2) To increase the product yield and rate, the operating conditions for ECH of acetone using a PEMFC reactor including an operating temperature around 65 ℃ and relative high RH above 80% is recommended.
(3) room temperature and relative high RH above 80% are recommended for ECH furfural using a PEMFC reactor.

(4) The effective working life of PEMFC membrane was around 30 hours. After each 1 hour of operating time, a simple method like water wash, acid wash, and air wash is recommended to mitigate the degradation. Reducing the concentration of reactants is another way to mitigate degradation.

(5) To solve the MEA contamination problem, novel non-Pt catalysts need to be developed, such as Pd and Ni-based catalysts. Despite the fact that a wide range of metals can be tested as electrocatalysts at the cathode, for now Pt is still believed to be the strongest capability of hydrogen absorption.
REFERENCES


## APPENDIXES

Table 7. Summary of biomass feedstock chemical activation for ACs production

<table>
<thead>
<tr>
<th>Feed stock</th>
<th>Temp.(°C)</th>
<th>Reaction Time(min)</th>
<th>Activation chemicals</th>
<th>Surface area(m²/g)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wood</td>
<td>850</td>
<td>60</td>
<td>H₃PO₄</td>
<td>1708</td>
<td>[185]</td>
</tr>
<tr>
<td>Plum stones</td>
<td>500</td>
<td>60</td>
<td>KOH</td>
<td>2174–3228</td>
<td>[186]</td>
</tr>
<tr>
<td>Coconut shell</td>
<td>800</td>
<td>-</td>
<td>Strong base</td>
<td>931</td>
<td>[187]</td>
</tr>
<tr>
<td>Corn cob</td>
<td>500</td>
<td>30–240</td>
<td>ZnCl₂</td>
<td>400–1410</td>
<td>[188]</td>
</tr>
<tr>
<td>Olive-seed</td>
<td>800</td>
<td>60</td>
<td>KOH</td>
<td>1339</td>
<td>[189]</td>
</tr>
<tr>
<td>Pecan shell</td>
<td>--</td>
<td>-</td>
<td>H₃PO₄</td>
<td>682</td>
<td>[190]</td>
</tr>
<tr>
<td>Cassava peel</td>
<td>750</td>
<td>180</td>
<td>KOH</td>
<td>1378</td>
<td>[191]</td>
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<tr>
<td>Bean pods</td>
<td>700</td>
<td>60</td>
<td>K₂CO₃</td>
<td>1580</td>
<td>[16]</td>
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<tr>
<td>Apricot stone shells</td>
<td>800</td>
<td>120</td>
<td>ZnCl₂</td>
<td>783</td>
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<td>Almond shell</td>
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<td>120</td>
<td>ZnCl₂</td>
<td>736</td>
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<td>120</td>
<td>ZnCl₂</td>
<td>793</td>
<td>[18]</td>
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<td>120</td>
<td>ZnCl₂</td>
<td>774</td>
<td></td>
</tr>
<tr>
<td>olive stones</td>
<td>850</td>
<td>120</td>
<td>-</td>
<td>677</td>
<td>[18]</td>
</tr>
<tr>
<td>olive stones</td>
<td>650</td>
<td>120</td>
<td>ZnCl₂</td>
<td>790</td>
<td>[17]</td>
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<tr>
<td>Pecan Shell</td>
<td>450</td>
<td>60</td>
<td>-</td>
<td>&gt;800</td>
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<td>Jackfruit peel</td>
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<td>30</td>
<td>H₃PO₄</td>
<td>907–1260</td>
<td>[20]</td>
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<td>Rice husk</td>
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<td>ZnCl₂</td>
<td>750</td>
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<td>Bagsse</td>
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<td>30</td>
<td>ZnCl₂</td>
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<tr>
<td>Palm shell</td>
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<td>120</td>
<td>K₂CO₃</td>
<td>1170</td>
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<tr>
<td>Upgrading methods</td>
<td>Treatment condition /requirement</td>
<td>Reaction mechanism /process</td>
<td>Technique feasibility</td>
<td>Cons.</td>
<td></td>
</tr>
<tr>
<td>-----------------------------------------</td>
<td>--------------------------------------------------------------------------------------------------</td>
<td>---------------------------------------------------------------------------------------------</td>
<td>------------------------------------------</td>
<td>----------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>Hydrocracking/hydrogenolysis /catalytic cracking</td>
<td>Severe condition (&gt;350°C, 100~1000Psi), a chemical needed: H₂/CO or H₂ donor solvents, catalyst(e.g., Ni/Al₂O₃-TiO₂)</td>
<td>Hydrogenation with simultaneous cracking (eliminating N, O and S as NH₃, H₂O, and H₂S)</td>
<td>The cheaper route commercialized already</td>
<td>High coking (8~25%) and poor quality of fuels obtained</td>
<td></td>
</tr>
<tr>
<td>Sub-/super-critical fluid</td>
<td>Mild conditions, organic solvents needed such as alcohol, acetone, ethyl acetate, glycerol</td>
<td>Promotes the reaction by its unique transport properties: gas-like diffusivity and liquid-like density, thus dissolved materials not soluble in either the liquid or gaseous phase of the solvent</td>
<td>Higher oil yield, better fuel quality (lower oxygen content, lower viscosity)</td>
<td>Need complicated equipment, excess cost, catalyst deactivation, reactor clogging</td>
<td></td>
</tr>
<tr>
<td>Solvent addition (direct add solvent or esterification of the oil with alcohol and acid catalysts)</td>
<td>The mild condition, polar solvents needed such as water, methanol, ethanol, and furfural</td>
<td>Reduces oil viscosity by three mechanisms: (1) physical dilution, (2) molecular dilution or by changing the oil microstructure, (3) chemical reactions like esterification and acetalization</td>
<td>The most practical approach (simplicity, the low cost of some solvents and their beneficial effects on the oil properties)</td>
<td>Mechanisms involved in adding solvent are not quite understood yet</td>
<td></td>
</tr>
<tr>
<td>Emulsification/emulsions</td>
<td>Mild conditions need surfactant(e.g., CANMET)</td>
<td>Combines with diesel directly. Bio-oil is miscible with the aid of surfactants</td>
<td>Simple, less corrosive</td>
<td>Requires high energy of production</td>
<td></td>
</tr>
<tr>
<td>Steam reforming</td>
<td>High temperature (800-900°C) need catalyst(e.g., Ni)</td>
<td>Catalytic steam reforming + water-gas shift</td>
<td>Produces H₂ as a clean energy resource</td>
<td>Complicated, requires steady dependable, fully developed reactors</td>
<td></td>
</tr>
<tr>
<td>Chemical extraction from the bio-oil</td>
<td>Mild condition</td>
<td>Solvent extraction, distillation, or chemical modification</td>
<td>Extract valuable chemicals</td>
<td>Low-cost separation and refining techniques still needed</td>
<td></td>
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Table 8. Brief of the current techniques used for upgrading bio-oil
Table 9. Operating parameters of UHS chemical activation experiments

<table>
<thead>
<tr>
<th>Exp. No</th>
<th>Temp. (°C)</th>
<th>Heating ratio (°C/Min)</th>
<th>Reaction Time (min)</th>
<th>Impregnation Ratio</th>
<th>Activation Chemical</th>
<th>Preparation method</th>
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<tr>
<td>1</td>
<td>500</td>
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<tr>
<td>3</td>
<td>500</td>
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<td>75</td>
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<tr>
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<tr>
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<td>125</td>
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<tr>
<td>8</td>
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<td>600</td>
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<td>2</td>
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H₂ flow rate was 0.25 ml/min; acetone flow rate was 6 ml/hour.
Table 11. Operating parameters of the furfural ECH experiments

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For experiment 15, 14, 13 and 12, H₂ flow rate was 0.25 ml/min, others were 0.15 ml/min; acetone solution flow rate was 0.2 ml/min.
VITA

Chen Li exxli001@odu.edu

PROFESSIONAL PROFILE

A compassionate, results-driven, and performance-oriented Ph. D graduate in Environmental Engineering with a sound academic background and teaching experience in the field of biomass, water/wastewater treatment, treatment plant design and electrochemistry. Perfect understanding of working with mainstream and diverse student populations and developing and implementing various curricula based on state and federal educational standards and requirements. An effective and resourceful motivator, team-builder, and facilitator with exceptional communication and presentation skills possessing an innate ability to perform accurate student assessments and conceptualize and employ individualized education plans. Proven experience in utilizing electrochemical method to investigate bio-oil upgrading problems, with focus on biomass composition analysis, biomass hydrolysis, electrolysis and organic compound hydrogenation.

EDUCATION

OLD DOMINION UNIVERSITY
Ph.D. Candidate in Environmental Engineering
GPA:3.92/4.00. Advisor: Sandeep Kumar
Thesis: Value-added Products from Lignin and Biomass Derivative.
Sept. 2012 – Present

UNIVERSITY OF SCIENCE TECHNOLOGY & BEIJING
Master Degree in Environmental Engineering
GPA:3.22/4.00. Advisor: Chunbao Sun
Thesis: Experiment Research of Supercritical Water Oxidation of the Tobias Acid Production Wastewater.
Sept. 2007 – Jan. 2010

ZHENGZHOU UNIVERSITY, Zhengzhou, China
Bachelor Degree in Environmental Science
GPA:3.05/4.00.
Project: Biomass Gasification Products Identified by Infrared Spectroscopy Method.

PUBLICATION


