2018

Techno-economic analysis of biochemicals and biofuels production via thermal and electrochemical processes

Denis Bbosa
Iowa State University

Follow this and additional works at: https://lib.dr.iastate.edu/etd

Part of the Mechanical Engineering Commons, and the Oil, Gas, and Energy Commons

Recommended Citation
https://lib.dr.iastate.edu/etd/16316

This Dissertation is brought to you for free and open access by the Iowa State University Capstones, Theses and Dissertations at Iowa State University Digital Repository. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Techno-economic analysis of biochemicals and biofuels production via thermal and electrochemical processes

by

Denis Bbosa

A dissertation submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY

Major: Mechanical Engineering

Program of Study Committee:
Mark Mba-Wright, Major Professor
Xianglan Bai
Marjorie Rover
Thomas J. Brumm
Robert C. Brown

The student author, whose presentation of the scholarship herein was approved by the program of study committee, is solely responsible for the content of this dissertation. The Graduate College will ensure this dissertation is globally accessible and will not permit alterations after a degree is conferred.

Iowa State University

Ames, Iowa

2018

Copyright © Denis Bbosa, 2018. All rights reserved.
DEDICATION

This dissertation is dedicated to my mom Miss Jane Nantongo, Miriam Nakabiito, Cindy Stroup, Loyd Stroup, and Ronald Sserunkuma.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>ix</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>xi</td>
</tr>
<tr>
<td>CHAPTER 1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1.1 Significance of the Problem</td>
<td>3</td>
</tr>
<tr>
<td>1.2 Overall Objectives</td>
<td>5</td>
</tr>
<tr>
<td>1.3 References</td>
<td>6</td>
</tr>
<tr>
<td>CHAPTER 2. LITERATURE REVIEW</td>
<td>8</td>
</tr>
<tr>
<td>2.1 Lignin and Its Properties</td>
<td>8</td>
</tr>
<tr>
<td>2.2 Paper and Pulp Industry</td>
<td>9</td>
</tr>
<tr>
<td>2.3 Lignin Extraction</td>
<td>14</td>
</tr>
<tr>
<td>2.4 Other Pulping Processes</td>
<td>17</td>
</tr>
<tr>
<td>2.5 Thermal Conversion of Biomass</td>
<td>18</td>
</tr>
<tr>
<td>2.5.1 Hydrothermal Conversion</td>
<td>19</td>
</tr>
<tr>
<td>2.5.2 Gasification</td>
<td>24</td>
</tr>
<tr>
<td>2.5.3 Fast Pyrolysis</td>
<td>25</td>
</tr>
<tr>
<td>2.6 Hydroxymethylfurfural (HMF), 2,5-dimethylfuran (DMF), Furfural, and 2-Methylfuran (MF)</td>
<td>31</td>
</tr>
<tr>
<td>2.7 Carbon Dioxide</td>
<td>33</td>
</tr>
<tr>
<td>2.8 Renewable Electricity</td>
<td>34</td>
</tr>
<tr>
<td>2.9 Techno-Economic Analysis</td>
<td>35</td>
</tr>
<tr>
<td>2.10 References</td>
<td>44</td>
</tr>
<tr>
<td>CHAPTER 3. MORE THAN ETHANOL: A TECHNO-ECONOMIC ANALYSIS OF CORN STOVER-ETHANOL BIOREFINERY INTEGRATED WITH HYDROTHERMAL LIQUEFACTION PROCESS TO CONVERT LIGNIN INTO BIOCHEMICALS</td>
<td>52</td>
</tr>
<tr>
<td>3.1 Abstract</td>
<td>52</td>
</tr>
<tr>
<td>3.2 Introduction</td>
<td>53</td>
</tr>
<tr>
<td>3.3 Material and Methods</td>
<td>55</td>
</tr>
<tr>
<td>3.3.1 Biomass Feedstock and Lignin-Derived Chemicals</td>
<td>57</td>
</tr>
<tr>
<td>3.3.2 Process Model Description</td>
<td>57</td>
</tr>
</tbody>
</table>
3.3.3 Handling and Pretreatment ................................................................. 58
3.3.4 Enzymatic Hydrolysis/Saccharification and Fermentation ..................... 58
3.3.5 Enzyme Production ............................................................................. 59
3.3.6 Recovery and Wastewater Treatment .................................................. 59
3.3.7 Boiler/Combustor and Storage ............................................................. 59
3.3.8 Hydrothermal Liquefaction ................................................................ 60
3.3.9 Techno-Economic Analysis ................................................................. 64
3.4 Results and Discussion .......................................................................... 69
3.4.1 Mass and Energy Balance .................................................................... 69
3.4.2 Capital and Operating Cost Analysis .................................................... 71
3.4.3 Minimum Ethanol Selling Price Sensitivity Analysis ............................... 74
3.4.4 Minimum Ethanol Selling Price Uncertainty Analysis ............................ 74
3.5 Conclusions ............................................................................................ 76
3.6 References .............................................................................................. 76

CHAPTER 4. TECHNO-ECONOMIC ANALYSIS OF 2,5-DIMETHYLFURAN (DMF) PRODUCTION USING AN ELECTROLYZER/ELECTROCHEMICAL REACTOR ......................................................... 82
4.1 Abstract .................................................................................................. 82
4.2 Introduction ............................................................................................ 83
4.3 Materials and Method ............................................................................ 85
4.3.1 Feedstock ............................................................................................ 86
4.3.2 Process Model Description ................................................................. 87
4.3.3 Techno-Economic Analysis (TEA) ....................................................... 88
4.3.4 Sensitivity Analysis ............................................................................ 92
4.4 Results and Discussion .......................................................................... 92
4.4.1 Aspen Model Results ......................................................................... 92
4.4.2 Economic Results ............................................................................... 93
4.4.3 Sensitivity Analysis Results ............................................................... 96
4.5 Conclusions ............................................................................................ 98
4.6 References .............................................................................................. 98
CHAPTER 5. ELECTROCHEMICAL PRODUCTION OF 2-METHYLFURAN (MF) FROM FURFURAL: A TECHNO-ECONOMIC ANALYSIS

5.1 Abstract
5.2 Introduction
5.3 Materials and Method
  5.3.1 Feedstock
  5.3.2 Process Model Description
  5.3.3 Techno-Economic Analysis (TEA)
  5.3.4 Sensitivity Analysis
5.4 Results and Discussion
  5.4.1 Process Model Results
  5.4.2 Sensitivity Analysis Results
5.5 Conclusions
5.6 References

CHAPTER 6. ELECTROCHEMICAL PROCESSING OF CARBON DIOXIDE (CO₂) TO FISCHER TROPSCH (FT) BIOFUELS USING RENEWABLE ELECTRICITY: A TECHNO-ECONOMIC ANALYSIS

6.1 Abstract
6.2 Introduction
6.3 Materials and Method
  6.3.1 Process Model Description
  6.3.2 Economic Analysis Methodology
  6.3.3 Sensitivity Analysis
6.4 Results and Discussion
  6.4.1 Process Results
  6.4.2 Techno-Economic Results
  6.4.3 Sensitivity Analysis Results
6.5 Conclusions
6.6 References

CHAPTER 7. GENERAL CONCLUSIONS

CHAPTER 8. RECOMMENDATIONS FOR FUTURE WORK

APPENDIX A. SUPPORTING INFORMATION OF CHAPTER 3

APPENDIX B. SUPPORTING INFORMATION OF CHAPTER 4
APPENDIX C. SUPPORTING INFORMATION OF CHAPTER 5 ........................................ 147
APPENDIX D. SUPPORTING INFORMATION OF CHAPTER 6 ........................................ 149
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Kraft processing method of wood [15].</td>
<td>11</td>
</tr>
<tr>
<td>2-2</td>
<td>Kraft recovery processing method of wood [15].</td>
<td>12</td>
</tr>
<tr>
<td>2-3</td>
<td>Simplified lignoboost process schematic.</td>
<td>15</td>
</tr>
<tr>
<td>2-4</td>
<td>Some of the thermochemical processes and operating conditions.</td>
<td>19</td>
</tr>
<tr>
<td>2-5</td>
<td>U.S. net electricity generation by renewable sources.</td>
<td>36</td>
</tr>
<tr>
<td>2-6</td>
<td>Process flow diagram of ethanol and lignin value-added chemical production.</td>
<td>41</td>
</tr>
<tr>
<td>3-1</td>
<td>Ethanol production and hydrothermal liquefaction hierarchy block diagram.</td>
<td>63</td>
</tr>
<tr>
<td>3-2</td>
<td>Hydro-oil production section.</td>
<td>64</td>
</tr>
<tr>
<td>3-3</td>
<td>Extraction of lignin-derived biochemicals section.</td>
<td>64</td>
</tr>
<tr>
<td>3-4</td>
<td>Separation of lignin-derived chemicals from bio-oil produced under hydrothermal liquefaction detailed flow diagram. A) Aqueous Phase (AP) recovery of acetaldehyde, formic acid, and acetic acid. B) Phenolic Phase (PHL) recovery of furfural, catechol, phenols, and cresols.</td>
<td>68</td>
</tr>
<tr>
<td>3-5</td>
<td>Total biorefinery installed equipment cost by area for corn stover conversion to ethanol and lignin-derived chemicals.</td>
<td>72</td>
</tr>
<tr>
<td>3-6</td>
<td>Sensitivity analysis of MESP on selected parameters.</td>
<td>74</td>
</tr>
<tr>
<td>3-7</td>
<td>Minimum ethanol-selling price probability and cumulative density functions.</td>
<td>75</td>
</tr>
<tr>
<td>4-1</td>
<td>Hierarchy blocks for HMF production from fructose (part 1).</td>
<td>90</td>
</tr>
<tr>
<td>4-2</td>
<td>Process flow diagram of the electrochemical conversion of HMF to DMF (part 2).</td>
<td>90</td>
</tr>
<tr>
<td>4-3</td>
<td>Aspen Plus process flow diagram of electrochemical conversion of HMF to DMF</td>
<td>95</td>
</tr>
<tr>
<td>4-4</td>
<td>Economic and technical parameters affecting the MPSP of DMF production.</td>
<td>97</td>
</tr>
<tr>
<td>5-1</td>
<td>Aspen Plus furfural to MF process model.</td>
<td>107</td>
</tr>
<tr>
<td>5-2</td>
<td>Sensitivity analysis results of MF production from furfural vial electrochemical processing.</td>
<td>113</td>
</tr>
<tr>
<td>6-1</td>
<td>Detailed process flow diagram of CO₂ electrochemical conversion into Fischer-Tropsch fuels.</td>
<td>123</td>
</tr>
<tr>
<td>6-2</td>
<td>Total purchased equipment cost of CO₂ electrochemical conversion to F-T fuels.</td>
<td>127</td>
</tr>
<tr>
<td>6-3</td>
<td>Sensitivity analysis results of CO₂ electrochemical conversion to F-T fuels.</td>
<td>131</td>
</tr>
<tr>
<td>A1-1</td>
<td>General economic assumptions and base case values for the ethanol and lignin-derived chemicals production manuscript.</td>
<td>139</td>
</tr>
<tr>
<td>A1-2</td>
<td>Material costs for the ethanol and lignin-derived chemicals production manuscript.</td>
<td>140</td>
</tr>
<tr>
<td>A1-3</td>
<td>Capital and labor costs for the ethanol and lignin-derived chemicals production manuscript.</td>
<td>141</td>
</tr>
</tbody>
</table>
Figure A1-4: Other functions and fuel out for the ethanol and lignin-derived chemicals production ........................................................................................................... 142

Figure A2-1: Aspen plus process flow diagram (PFD) of DMF production from HMF. 143

Figure A3-1: Aspen plus PFD of MF production from furfural ........................................ 147

Figure A4-1: Aspen plus PFD for A100 of CO2 electrochemical conversion ............... 149
Figure A4-2: Aspen plus PDF for A200 (Water-gas shift) CO2 electrochemical conversion ............................................................................................................................. 149
**LIST OF TABLES**

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>Costs of producing bio-oil from Kraft lignin [23]</td>
<td>37</td>
</tr>
<tr>
<td>2-2</td>
<td>Estimated cost of Kraft lignin recovery using ultrafiltration [86]</td>
<td>39</td>
</tr>
<tr>
<td>2-3</td>
<td>MAE product price under different scenarios and their effect on ethanol MSP</td>
<td>42</td>
</tr>
<tr>
<td>6</td>
<td>Operating costs and MPSP of CO</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>DCFROR of DMF production from HMF (26 to 30 years)</td>
<td>6</td>
</tr>
<tr>
<td>3</td>
<td>Fructose conversion to DMF process model results</td>
<td>7</td>
</tr>
<tr>
<td>3-5</td>
<td>Ethanol and lignin-derived chemicals production output, computed and market purity levels, recovery rates, and market prices for a 2000 MTPD biorefinery</td>
<td>70</td>
</tr>
<tr>
<td>3-6</td>
<td>Investment costs for corn Stover to ethanol and lignin-derived biochemicals</td>
<td>71</td>
</tr>
<tr>
<td>5</td>
<td>Annual operating costs of ethanol and hydrothermal liquefaction of lignin to chemicals</td>
<td>73</td>
</tr>
<tr>
<td>5-1</td>
<td>Parameters used to compute total capital investment (TPI)</td>
<td>91</td>
</tr>
<tr>
<td>5-2</td>
<td>DCFROR assumptions</td>
<td>91</td>
</tr>
<tr>
<td>5-3</td>
<td>Furfural to MF Aspen Plus results</td>
<td>91</td>
</tr>
<tr>
<td>5-4</td>
<td>Investment estimates of furfural to MF via electrochemical approach</td>
<td>93</td>
</tr>
<tr>
<td>5-5</td>
<td>Annualized cost of producing MF from furfural via electrochemical process</td>
<td>96</td>
</tr>
<tr>
<td>5-6</td>
<td>Percentage of different components in the hydroprocessing section [17]</td>
<td>97</td>
</tr>
<tr>
<td>6-1</td>
<td>CO2 electrochemical conversion economic assumptions</td>
<td>108</td>
</tr>
<tr>
<td>6-2</td>
<td>CO2 electrolysis conversion model results</td>
<td>109</td>
</tr>
<tr>
<td>6-3</td>
<td>Investment requirement of CO2 electrochemical conversion to F-T fuels</td>
<td>110</td>
</tr>
<tr>
<td>6-4</td>
<td>Operating costs and MPSP of CO2 electrochemical conversion to F-T fuels</td>
<td>111</td>
</tr>
<tr>
<td>6-5</td>
<td>Annual capital investment parameters [22]</td>
<td>112</td>
</tr>
<tr>
<td>4-1</td>
<td>DCFOR assumed parameters and their values</td>
<td>117</td>
</tr>
<tr>
<td>4-2</td>
<td>Fructose conversion to DMF process model results</td>
<td>118</td>
</tr>
<tr>
<td>4-3</td>
<td>Fructose to DMF economic analysis results (2011$)</td>
<td>119</td>
</tr>
<tr>
<td>4-4</td>
<td>Fructose to DMF annual operating costs and MPSP (2011$)</td>
<td>120</td>
</tr>
<tr>
<td>4-5</td>
<td>Mass flow rates of DMF production from HMF</td>
<td>121</td>
</tr>
<tr>
<td>5-5</td>
<td>DCFROR of DMF production from HMF (-3 to 10 years)</td>
<td>122</td>
</tr>
<tr>
<td>5-6</td>
<td>DCFROR of DMF production from HMF (11 to 26 years)</td>
<td>123</td>
</tr>
<tr>
<td>5-7</td>
<td>DCFROR of DMF production from HMF (26 to 30 years)</td>
<td>124</td>
</tr>
<tr>
<td>5-8</td>
<td>Electrolyzer cost computation for DMF production</td>
<td>125</td>
</tr>
<tr>
<td>A2-1</td>
<td>Mass flow rates of DMF production from HMF</td>
<td>126</td>
</tr>
<tr>
<td>A2-2</td>
<td>DCFROR of DMF production from HMF-assumptions</td>
<td>127</td>
</tr>
<tr>
<td>A2-3</td>
<td>DCFROR of DMF production from HMF (-3 to 10 years)</td>
<td>128</td>
</tr>
<tr>
<td>A2-4</td>
<td>DCFROR of DMF production from HMF (11 to 26 years)</td>
<td>129</td>
</tr>
<tr>
<td>A2-5</td>
<td>DCFROR of DMF production from HMF (26 to 30 years)</td>
<td>130</td>
</tr>
<tr>
<td>A2-6</td>
<td>Electrolyzer cost computation for DMF production</td>
<td>131</td>
</tr>
</tbody>
</table>

---

**TABLES**

- Table 2-1: Costs of producing bio-oil from Kraft lignin [23]
- Table 2-2: Estimated cost of Kraft lignin recovery using ultrafiltration [86]
- Table 2-3: MAE product price under different scenarios and their effect on ethanol MSP
- Table 6: Operating costs and MPSP of CO
- Table 4: Investment requirements of CO
- Table 3: CO
- Table 5: Investment costs for corn Stover to ethanol and lignin-derived biochemicals
- Table 3-7: Annual operating costs of ethanol and hydrothermal liquefaction of lignin to chemicals
- Table 4-1: Assumed total capital investment parameters [22]
- Table 4-2: DCFOR assumed parameters and their values
- Table 4-3: Fructose conversion to DMF process model results
- Table 4-4: Fructose to DMF economic analysis results (2011$)
- Table 4-5: Fructose to DMF annual operating costs and MPSP (2011$)
- Table 5-1: Parameters used to compute total capital investment (TPI)
- Table 5-2: DCFROR assumptions
- Table 5-3: Furfural to MF Aspen Plus results
- Table 5-4: Investment estimates of furfural to MF via electrochemical approach
- Table 5-5: Annualized cost of producing MF from furfural via electrochemical process
- Table 5-6: Percentage of different components in the hydroprocessing section [17]
- Table 6-1: CO2 electrochemical conversion economic assumptions
- Table 6-3: CO2 electrolysis conversion model results
- Table 6-4: Investment requirement of CO2 electrochemical conversion to F-T fuels
- Table 6-5: Operating costs and MPSP of CO2 electrochemical conversion to F-T fuels
- Table A2-1: Mass flow rates of DMF production from HMF
- Table A2-2: DCFROR of DMF production from HMF assumptions
- Table A2-3: DCFROR of DMF production from HMF (-3 to 10 years)
- Table A2-4: DCFROR of DMF production from HMF (11 to 26 years)
- Table A2-5: DCFROR of DMF production from HMF (26 to 30 years)
- Table A2-6: Electrolyzer cost computation for DMF production
Table A3-1: Mass flow rates of MF production from furfural ............................................. 147
Table A3-2: Equipment list for MF production from furfural ........................................... 148
Table A3-3: Electrolyzer cost computation for MF production from furfural ...................... 148

Table A4-1: DCFROR of CO₂ electrochemical conversion-assumptions.......................... 150
Table A4-2: DCFROR of CO₂ electrochemical conversion (upto 10 years) ....................... 150
Table A4-3: DCFROR of CO₂ electrochemical conversion (11 to 26 years) .................... 151
Table A4-4: DCFROR of CO₂ electrochemical conversion (27 to 30 years) .................... 151
Table A4-5: Different costs of CO₂ electrochemical conversion catalyst .......................... 152
Table A4-6: F-T reactor and PSA costing ............................................................................ 152
Table A4-7: Electrolyzer costing for CO₂ electrochemical conversion ......................... 152
Table A4-8: Equipment list for CO₂ electrochemical conversion ................................. 153
ABSTRACT

Climate change is leading to concerning fluctuations in weather patterns mainly due to anthropogenic activities such as deforestation and burning of fossil fuels which are and will affect different sectors such as food chains, wildlife and most importantly the human life. The upcoming generations must be left with an environment worth to live in thus humans must intervene to reduce the emissions of greenhouse gases and that is why sustainable means must be used to provide clean energy and renewable-based chemicals. For the U.S., the USDOE and USDA proposed a 25% and 20% vision for biomass-based chemicals and fuels respectively by the year 2030.

The different chapters of this dissertation are: 1) introduction, 2) literature review, 3) “more than ethanol: a techno-economic analysis of corn stover-ethanol biorefinery integrated with hydrothermal liquefaction (HTL) process to convert lignin into biochemicals”, 4) “techno-economic analysis of 2,5-dimethylfuran (DMF) production using an electrolyzer/electrochemical reactor”, 5) “electrochemical production of 2-methylfuran (MF) from furfural: a techno-economic analysis”, and 6) “electrochemical processing of CO₂ into Fischer Tropsch (FT) fuels using renewable electricity: a techno-economic analysis”, 7) general conclusions, and 8) recommendations for future work.

The project of integrating corn stover biorefinery with HTL evaluates a 2000 metric tonne per day (MTPD) corn stover biorefinery producing 61 MMgal/yr. of ethanol and different yields of lignin-based biochemicals. A minimum ethanol selling price (MESP) of $1.03±0.19 per gal was estimated considering the production of lignin-derived catechol, phenol, cresols, acetic acid, formic acid, furfural, and acetaldehyde. The most influential factors on MESP are fixed capital investment, internal rate of return, feedstock price, cresols,
catechol, and acetic acid prices. In terms of costs, the total purchased equipment cost is $114.5 million (MM), total installed cost (TIC) is $345.7 MM, and total capital investment is $624.5 MM. Producing lignin-derived biochemicals using hydrothermal liquefaction (HTL) is in the early stages of development thus more research is needed to establish its commercialization potential.

The 2,5-dimethylfuran (DMF) project evaluates the techno-economic feasibility of producing DMF using an electrolyzer/electrochemical reactor. A 300-metric ton per day (MTPD) fructose biorefinery was considered producing 34 MTPD levulinic acid as a byproduct and 174 MTPD of hydroxymethylfurfural/5-hydroxymethylfurfural (HMF). The HMF is further converted to DMF through an electrochemical process producing 95 MTPD of 2,5-dimethylfuran (DMF) and the byproducts being 59 MTPD 2,5-bis(hydroxymethyl)furan and 21 MTPD 5-methylfurfuryl alcohol. A minimum product-selling price (MPSP) of $12.51/gal of DMF was estimated. The sensitivity analysis results showed that DMF yield, fixed capital investment, internal rate of return (IRR), 2,5-bis(hydroxymethyl)furan price, and fructose feedstock price are the most influential parameters on the MPSP. The biorefinery considered in this analysis requires a total purchased equipment cost (TPEC) of $146 MM, $442 MM of total installed cost (TIC), and $799 MM as the total capital investment. Using an electrolyzer/electrochemical reactor process to produce bioproducts is promising though in the early stages of development thus more research should be done to enable commercialization of the electrochemical process.

The 2-methylfuran project investigated the techno-economic feasibility of producing 2-methylfuran (MF) from furfural using an electrolyzer that utilizes renewable electricity. Furfural flowrate assumed was 300 MTPD producing over 239 MTPD with byproducts of
furoic acid (30 MTPD) and furfuryl alcohol (30 MTPD). MPSP is $9.07/gal and its mostly influenced by MF yield, fixed capital investment, furfural price, and acetonitrile price. The different cost are $79 MM, $240 MM, and $433 MM for total purchased equipment cost, total installed cost, and total capital invest cost respectively.

The CO₂ project, analyzed a 2000 MTPD biorefinery producing Fischer Tropsch biofuel gasoline gallon equivalent (GGE). The electrochemical conversion of CO₂ into biofuels is an alternative to carbon sequestration and/or its release into the atmosphere that causes global warming. The biorefinery considered produces 70.7 MM gal/yr GGE (1236 MTPD, C₈ and C₁₆ hydrocarbons) and 253 MTPD of propane (CH₄ – C₃ hydrocarbon mixture). The estimated investments are $388 MM as total purchased equipment cost (TPEC), $1.2 BB for total installed costs (TIC), $1.8 BB as fixed capital investment (FCI) and $2.1 BB as the total investment cost. The estimated MPSP is $4.69/gal GGE and is mostly influenced by F-T GGE yield ($3.91 – 5.86/GGE), fixed capital investment ($3.86 – 5.53/GGE), IRR ($4.11 – 5.28/GGE), and income tax rate ($$4.51-4.91/GGE). Electrochemical conversion of CO₂ is a promising technology to combat global warming though more research is needed to ascertain the electrolyzer functionality in converting CO₂.

The overall conclusion is that techno-economic analysis (TEA) is a good method to evaluate the feasibility of a project before being scaled-up from a laboratory to a pilot scale and then to a commercial facility. The evaluation provides insights of the minimum product selling price(s) and the factors that affect it most. This helps in comparison of biomass-based verses fossil-based products. Also, TEA provides estimates of total purchased equipment costs, total installation cost, and total capital investment. Overall, to have a bioeconomy, biofuels
must be produced with biochemicals and CO\textsubscript{2} capture and conversion into useful products will minimize and/or eliminate global warming.
CHAPTER 1. INTRODUCTION

Climate change is leading to concerning fluctuations in weather patterns mainly due to anthropogenic activities which will affect different sectors such as food chains, wildlife and most importantly the human life [1]. The upcoming generations must be left with an environment that is not hot thus humans must intervene to reduce the emissions of greenhouse gases and that is why sustainable means must be used to provide clean energy and renewable-based chemicals. For the U.S. in particular, the USDOE and USDA proposed a 25% and 20% vision for biomass-based chemicals and fuels respectively by the year 2030 [2].

To have a sustainable bioeconomy, the three components of lignocellulose that is sustainable must be fully exploited thus the motivation to analyze the techno-economics of lignin that is less economically utilized compared to cellulose and hemicellulose. On the hand, other biomass-based products such as fructose and furfural can be processed to produce transportation fuels, and the carbon dioxide should be efficiently utilized to produce also biofuels. The different chapters of this dissertation are entitled as 1) introduction, 2) literature review, 3) “more than ethanol: a techno-economic analysis of corn stover-ethanol biorefinery integrated with hydrothermal liquefaction process to convert lignin into biochemicals”, 4) “techno-economic analysis of 2,5-dimethylfuran (DMF) production using an electrolyzer/electrochemical reactor”, 5) “electrochemical production of 2-methylfuran (MF) from furfural: a techno-economic analysis”, 6) “electrochemical processing of carbon dioxide (CO₂) to Fischer Tropsch (FT) biofuels using renewable electricity: a techno-economic analysis”, 7) general conclusions, and 8) recommendations for future work.

Lignin underutilization presents research opportunities in terms of techno-economic analysis and life cycle assessment to produce value-added chemicals. The research direction is
to be able to integrate ethanol bio-refineries with lignin thermochemical processing section to provide an added source of revenue from renewable-based chemicals while protecting the environment. On the other hand, some renewable energies such as solar and wind energies that experience a storage challenges thus presenting excess electricity that can be used in an electrolyzer for electrochemical reactions such as hydroxymethylfurfural (HMF) conversion to 2,5-dimethylfuran (DMF) and CO2 conversion to F-T fuels though also other renewable electricity resources like ocean, hydropower, biomass, and geothermal are considered.

The world is blessed with an abundance of biomass in terms of forests, energy dedicated crops, prairies, fisheries, and marshes. Biomass and/or biorenewable resource is defined as an organic material of recent biological origin [3]. The biomass definition is broad, and its intention is to distinguish it from fossil fuels resources. The biotic environment provides organic material in terms of wastes such as municipal solid wastes, agricultural residues, manure, food processing waste, yard waste, and dedicated energy crops like short rotation woody crops and herbaceous energy crops. Part of this dissertation focuses on lignocellulosic lignin component of biomass. Lignocellulose is comprised of cellulose, hemicellulose, and lignin. Lignocellulose is available in abundance and easily accessible [4–6]. The composition of lignocellulose varies according to the type of feedstock and Limayem et al., [7] provided a full table of this data. Cellulose is a polysaccharide of glucose monomers interlinked with β (1--->4) glycosidic bond with a crystalline and matrix structure and it is a long chain [7]. Hemicellulose on the other hand has a variable structure that is composed of 6-C and 5-C sugars (glucose, mannose, galactose, xylose, and arabinose) which transform into an amorphous branched solid structure that depolymerizes easily [4,7]. Hemicellulose binds the cellulose polymer together to make strong fibers. Lignin is composed of coumaryl, coniferly,
and sinapyl phenolic monomers that provide the strength and rigidity to the plant [4,7]. Since lignin is made-up of aromatic molecules, they are crosslinked and interwoven with cellulose and hemicellulose. These aromatic compounds are also produced from fossil-based fuel.

Petroleum companies produce fuels and other products such as chemicals and similarly, it is feasible that a biorefinery can produce bio-power, biofuels, and biochemicals thus having a sustainable bio-based bioeconomy that will provide energy independence accompanied by proper management of greenhouse gas emissions [8–11]. Under a bioeconomy, bio-refining must take place and according to the International Energy Agency [12], it is defined as the processing of biomass in a sustainable way such that it produces energy and marketable products. Therefore, for the bioeconomy to be successful and sustainable in the future, all components of the lignocellulose must be fully utilized. Cellulose and hemicellulose are converted into different products via biochemical and thermochemical pathways whereas lignin though having a potential of being a good resource hasn’t been techno-economically and environmentally assessed to be utilized. Overall the focus of this dissertation will be on conversion of biomass into biofuels and biochemicals and in particular lignin to biochemicals, conversion of fructose to HMF and then HMF to DMF, conversion of furfural to MF, and processing of CO₂ into biofuels.

1.1 Significance of the Problem

In the past, established biorefinery focus was only to produce biofuels from biomass and with time it has been realized that producing only biofuels might not outcompete existing fossil-based fuels. For the USA and in particular the Bioenergy Technologies Office (BETO) to achieve a target of $3/ gasoline gallon equivalent production by 2022, byproducts such as
biochemicals from biomass in addition to biofuels have to be produced based on market demand [13].

To make ethanol more competitive with fossil-based fuel products, biorefineries are researching for ways of producing other products other than only biofuels. One way to make ethanol more competitive is to produce biochemicals from lignin that is a solid waste diverted to boilers for combustion to produce process steam and electricity. Research is underway on how to convert lignin into biochemicals thus a need for techno-economic analysis to identify if it is worth an investment opportunity.

On the other hand, alternatives that can be used as biorenewable transportation fuels are being researched on, for example, Román-Leshkov et al. [14] researched about producing 2,5-dimethylfuran (DMF) from carbohydrates such as fructose which is a biomass product or by isomerization of glucose. Román-Leshkov et al. [14] claim that DMF has 40% more energy density than ethanol, its boiling temperature is 20K higher, and non-soluble in water. DMF is reported to have an energy content of 31.5 MJ/L which is approximately the same as that of gasoline compared to 23 MJ/L of ethanol [15,16]. Other advantages of DMF highlighted are; being stable during storage thus not absorbing atmospheric water compared to ethanol, having a high octane number of 119 thus improving fuel economy by providing high compression engine ratios, and it utilizes one-third of evaporation energy requirement during production compared to fermentation of ethanol and thus assumed to have lower greenhouse gas emissions [17].

Greenhouse gas emissions are causing global warming of the earth and CO₂ has been pointed out as the most contributor to climate change thus presenting a challenge to find ways to utilizing it. Among the promising methods is to use an electrochemical process to convert
CO₂ into syngas (CO and H₂) using renewable electricity over possibly metal-free carbon-based catalysts. This will not only positively impact the carbon balance, but also useful fuels will be produced to meet the energy demand of the world’s increasing population.

They are gaps in the techno-economic analysis of producing lignin value-based chemicals, MF and DMF production from the biomass-based feedstock, and the conversion of CO₂ into biofuels using electrochemical processes thus the focus of this research.

1.2 Overall Objectives

➢ To evaluate the techno-economic analysis (TEA) of integrating corn stover based ethanol plants with hydrothermal liquefaction process to produce biochemicals from lignin.
➢ To evaluate the techno-economic analysis of 2,5-dimethylfuran (DMF) production from fructose using an electrochemical reactor/electrolyzer.
➢ To evaluate the techno-economic analysis of electrochemical processing of furfural to 2-methylfuran (MF).
➢ To evaluate the techno-economic analysis of electrochemical processing of CO₂ to F-T biofuels using renewable electricity.

The purpose of this dissertation is to provide a review of the literature on lignin conversion, HMF, DMF, MF, CO₂, and TEA. To accomplish this goal, we reviewed almost 100 articles from literature.
1.3 References


CHAPTER 2. LITERATURE REVIEW

2.1 Lignin

Lignin is regarded as a polyphenolic material having an amorphous and 3D biopolymer structure due to sinapyl, ciniferyl, and p-coumaryl alcohols (i.e. the three cinnamyl alcohols). It is being enzyme-initiated and dehydrogenatively polymerized. Lignin is amorphous because of its racemic, branched and partly random structure. Biologically, this property helps to fill up cavities in the polysaccharide network and technically it is very difficult to obtain low molecular weight fractions from lignin which are homogeneous compared to cellulose [1].

Basically, lignin structure has two components; the C₃ chain and the aromatic part and the OH group is the only usable reaction site[2]. Lignin consists of 4-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) structures which are connected with carbon atoms in phenylpropanoid units. The H:G:S ratio differs between softwood (made up of mostly G units) and hardwood (made up of mostly G and S units). The lignin content, molecular weight, and composition differ from plant to plant with lignin content decreasing in the order of softwoods>hardwoods>grasses [3]. Different feedstocks have different cellulose, hemicellulose, and lignin composition with a varying range, for example; hardwood stems are composed of 40-55% cellulose, 24-40% hemicellulose, and 18-25% lignin; softwood stems are composed of 45-50% cellulose, 25-35% hemicellulose, and 25-35% lignin; corn cobs are composed of 45% cellulose, 35% hemicellulose, and 15% lignin; and switchgrass is composed of 45% cellulose, 31.4% hemicellulose, and 12% lignin [4].

Model lignin compounds are categorized as carbon-carbon (C-C) bonded lignin and ether (C-O) linked lignin that contains 4-O-5, β-5, β-1, β-β, dibenzodioxocin, and β-O-4
linkages. The predominant one is β-O-4 linkage [5]. The β-O-4 linkage is approximately 1.5 times more in hardwood lignin than in softwood. Ether linkages in lignin account for more than two-thirds. Lignin and the polysaccharides of lignocellulose mostly hemicellulose is bonded with several covalent bonds though also cellulose and pectin. Also, ethers to α-carbon and phenyl glycoside bonds occur, though C-C and ester to α-carbon bonds have been proposed [6–8].

Lignin is more hydrophobic than polysaccharides because of its aromatic structure and affords possibilities for charge-transfer interactions (π-binding, aromatic interaction) as a complement to covalent bonds. Lignin being made up of aromatics, it can technically be used to produce chemicals and adhesives. At neutral pH, lignin possesses poor solubility in water due to a high degree of polymerization, though, it dissolves in organic solvents like acetone and aqueous alkali solution.

Lignin having more reduced carbons than carbohydrates makes it have an average redox number of approximately -0.4 while it is 0 for carbohydrates [5] thus being energy-rich than polysaccharides. This energy can be harnessed during combustion though it cannot be used for biological purposes such as carbon/energy source in fermentation like cellulose to produce ethanol due to its complex structure [1]. A lower energy content might be experienced because of the technical processing that lignin undergoes through like pulping which might alter the lignin structure.

### 2.2 Paper and Pulp Industry

Lignin is known to be mostly and largely produced by the paper and pulp industry as a waste product [9,10] and because of its challenges to volatilize, it has been and continues to be
burnt to provide process heat. Bugg et al., [11] hypothesize that more lignin-based streams will be produced from the lignocellulosic bioethanol plants as a low-value by-product with approximately 60 M tonne/year of lignin by the year 2022 [12] in the US. Furthermore, Bugg et al., [11] mentions that Brazil (Alagoas site) and Italy (Crescentino site) have large-scale bioethanol refineries producing 82 M liter/yr. and 20 M liter/yr. of ethanol respectively presenting rich streams of lignin with the fraction of lignin obtainable varying depending most likely on feedstock type.

In the paper industry, the Kraft process (Figure 2-1), which utilizes sodium hydroxide and sodium sulfide, is the most used method in pulping because the paper output quality is the best as measured in terms of thickness, strength, and brightness [13,14]. Globally, two-thirds of the pulp production is by Kraft process. The Kraft process has been much used because of its potential to process both hard and soft kinds of wood, and there is approximately 97% favorable economic recovery of chemicals used in the process [15]. Half of the wood feedstock input is dissolved and together with the pulping chemicals, they form the black liquor (a mixture of salt ions, water, lignin and polysaccharide clusters) (Figure 2-1). The black liquor is then separated from the pulp by washing and then forwarded to the recovery process that recovers the pulping inorganic chemicals whereas the dissolved organics are utilized to generate power and steam (Figure 2-2).
The Kraft recovery processing method of wood (Figure 2-2) aims a) to recover and recycle sodium hydroxide and sodium sulfide; b) to reduce and/or minimize the black liquor waste material impact to the environment, and c) to co-generate steam and power. The black liquor is recovered through a series of evaporators and concentrators. The heavy black liquor is distributed into the boiler where it is burnt in an oxygen-free environment. As mentioned earlier, the pulping chemicals are recovered as molten smelt that is mostly composed of sodium carbonate and sodium sulfide. The smelt is forwarded to be dissolved in a water dissolving tank resulting in green liquor. In the causticizing plant, sodium carbonate reacts with calcium oxide to form sodium hydroxide plus calcium carbonate and the sodium sulfide is unaffected by the process thus recovering the pulping chemicals. The calcium carbonate aka lime mud is washed and then heated to high temperatures in the lime kiln to regenerate calcium oxide. Production of steam leads to the generation of electricity by using the organic portion of the black liquor.
The Kraft process seems to be a straightforward process however, it experiences numerous challenges. Among the problems experienced include fouling, corrosion due to non-processing elements (NPE), and foaming in evaporators that result in bailouts and too much consumption of steam with low solid output [15]. For the boiler, they also experience the same problems as evaporators in addition to destitute water circulation, smelt explosions, emissions, and blackouts. In the kiln process, there are challenges of dusting, low thermal efficiencies, emissions, too much fuel consumption, and quality of lime. Due to the operational challenges, paper and pulp industry faces challenges of high energy consumption, environmental pollution, capacity production and quality.

Cardoso et al., [16] studied the effect of black liquor recovery from eucalyptus Kraft and bamboo soda from six Brazilian mills. They studied the chemical properties (elementary analysis, lignin molar mass and concentration, and organic: inorganic ratio) and physical properties (density, boiling point rise, rheological behavior, and heating value). Some of the
equipment and techniques used included elemental analyzer, atomic absorption, combustion, and HPLC with gel permeation. They concluded that both feedstocks have higher lignin concentrations with different molar masses and higher non-processing elements (like iron, calcium, aluminum, potassium, and silicon ions) compared to black liquor from pine thus presenting eucalyptus Kraft and bamboo soda black liquor with distinctive rheological properties. Among the eucalyptus Kraft and bamboo soda black liquor, bamboo had a higher lignin and silicon concentration though with lower sulfur and subsequently a higher apparent viscosity because the lignin and polysaccharide concentrations form an amorphous cluster.

Saif et al., [14] studied the energy efficient ways to reduce wastewater in the pulp and paper industry by reverse osmosis (RO) membrane approach. The objective of the study was to reduce the concentration of salts in wastewater streams for easy recycling to minimize fresh water demands since the pulp and paper industry consume a lot of water. Non-processing elements (NPE) were mentioned to present an operational challenge to the direct water recycling tactic. They concluded that RO network should be implemented to minimize water consumption before the evaporators equipment and the investment is justifiable considering the reduced labor and maintenance costs of the multiple evaporators and the reduced waste and wastewater.

Bajpai [17] wrote a book about the biological odor treatment emissions from the pulp and paper industry. The problem of public and environment concerns about the odor from the pulp and paper industry has been a challenge for years and thought to originate from the sulfide in the white liquor. Bajpai [17] highlights the concerns having been mentioned way back in 1992 by Smook [18] and in 1993 by Springer and Courtney [19]. The odor is thought to be due to reduced Sulfur compounds and/or total reduced sulfur that includes methyl, dimethyl,
methyl mercaptan, and hydrogen sulfides, and dimethyl disulphide. Hydrogen sulphide has been thought of as the most toxic compound and the lungs easily absorb it and it stops cellular uptake of oxygen as reported by Hessel [20]. Bajpai [17] published his book in 2014 and by that time he still recommended the paper industry to try and reduce odorous gas emissions effective competitiveness in terms of the environment and improving the public relations.

2.3 Lignin Extraction

Lignin can be extracted from the black liquor by different approaches and Öhman et al., [21] patented one of the methods. Öhman et al., [21] process involves: a) acidification of the black liquor taken from the evaporation section to precipitate lignin followed by dewatering b) suspending the lignin filter cake from a) to get a second lignin suspension and to adjust its pH appropriately c) second lignin suspension is then dewatered d) washing water is added to the outcome from c) to accomplish a displacement washing with the aim of maintaining the pH stable e) the lignin cake from d) is dewatered into a high dryness to produce lignin.

One of the industrial applications to separate lignin from black liquor is the lignoboost approach [22]. Lignoboost involves (Figure 2-3): a) acidification of the black liquor taken from the evaporation section especially using carbon dioxide followed by filtration (in the traditional method, it would be followed by washing after filtration) b) re-dispersion and acidification follows forming a slurry c) the slurry undergoes filtration and washing by displacement washing. The full details and general layout about lignoboost are well described by Tomani [22]. Some of the lignoboost process advantages are: a) lower ash and carbohydrate contents in the lignin; b) dry solids in the lignin are of higher content; c) lower costs are encountered since the sulphuric acid need is lower, and d) the general capital investment is
lower since the volume of acidic washing water and filter area can be minimized without affecting the outcome.

Figure 2-3: Simplified lignoboost process schematic

Farag and Chaouki [23] highlight in their paper of a process that can be used to precipitate lignin out of the black liquor. This process is thought to increase paper production without expanding the recovery boiler capacity. The processes involved in sequence are acidification, filtration, and washing though at times oxidation could be done prior to acidification for better lignin quality.

Zhu et al., [24] investigated and characterized lignin in the lignoboost process. The objective of the study was to investigate the effect of operating parameters/process conditions on the yield of lignin from mixed softwood and hardwoods’ liquor using UV and Klason methods. The results indicated that the precipitation yield of lignin rose with a decline in pH and temperature or with a rise in ion strength of black liquor. Mixing hardwood and softwood
liquors decreased the precipitated yield of lignin and at a higher yield, the lignin had higher concentrations of phenolic hydroxyl and methoxyl though lower mean molecular weight.

Wallmo et al., [25] investigated the influence of hemicellulose in Kraft black liquor during precipitation. The objective of this research was to examine whether hemicellulose level content had effects on the filtration properties of black liquor. The research involved using lignoboost knowledge and membrane filtration. Prior to precipitation, the back-liquor hemicellulose levels were lowered using pretreatment methods of heat treatment, ultrafiltration, and nanofiltration combined with ultrafiltration. Evaporated hardwood and softwood black liquor’s filtration properties were used as a reference point to be compared to the pretreated samples. The results showed that by lowering the hemicellulose content prior to precipitation, reduces the filtration resistance and a more purified lignin with lower sodium was produced.

Brebu and Spiridon [26] investigated the co-pyrolysis of synthetic polymers with lignoboost lignin. To increase liquid production from biomass, co-pyrolyzing biomass with polyolefins was considered since this approach lowers the oxygen content given the fact that polymers like polypropylene, polyethylene have approximately 14 wt% hydrogen [27–30]. The objective of the study was to obtain mass yields and composition of degraded products of biomass co-pyrolyzed with polyethylene, polycarbonate, polystyrene, and polypropylene to categorize the interaction between components. The experiments were carried out in a semi-batch reactor of self-regulating pressure and 500°C. They concluded that the stronger interaction between lignoboost and polymers (1:1) led to the higher yields of pyrolysis oil (39 – 52%) and co-pyrolysis of lignoboost lignin with polycarbonate being observed to behave in
a special way that was different from the rest of the synthetic polymers. In general, the degradation of synthetic polymers was improved while that of lignin was slightly reduced.

Brodin et al., [31] studied the effects of membrane filtration on Kraft lignin as a chemical source feedstock. A purification procedure is necessary since lignin from paper and pulp industry is heterogeneous and impure. For this study, four industrial Kraft black liquor from different sources were used. Each obtained liquor was fractionated using either a 15- or 5- kDa ceramic membrane trailed by ion exchange of the precipitated lignin to assess the effect of heterogeneity and purity concerns of separated lignin with little ash and carbohydrate content and then after which a comprehensive thermal and chemical characterization was done on the resulting lignin to categorize wood species and discover separation conditions that could produce homogeneous and pure Kraft lignin of highest yield. They concluded that from a macromolecular structure and behavior perspective, there occurs a big difference, however, after membrane fractionation, there was an improvement in macromolecular homogeneity followed by isolation and purification by ion exchange. Hardwood lignin showed close similarities while those from softwood showed a range of variation in terms of mass molecular distribution. All types of lignin contained substantial amounts of volatile material in spite of the purification process done and this was probably due to the low molecular mass lignin fragments. The fractionation technique was thought of a promising approach to upgrading lignin into a homogeneous poly-aromatic macromolecule appropriate for advanced conversion.

2.4 Other Pulping Processes.

Apart from the Kraft pulp processing, other pulping processes are sulfite, soda, and neutral sulfite semi-chemical (NSSC). Sulfite pulping follows similar steps as Kraft process
through the difference comes in with the chemicals used. Sulfite pulping uses sulfurous acid and bisulfite ion in the form of sodium, calcium, ammonium, or magnesium bisulfate. In this process, chemical separation from the pulp might or might not be recovered depending on the economics. This can either be done in batch or continuous digesters at high pressures and temperatures. NSSC pulping processes wood in a neutral solution of sodium carbonate and sodium sulfite. Lignin in the wood reacts with sulfite ions while sodium carbonate (Na$_2$CO$_3$) buffers and maintains a neutral solution. The other difference between semi-chemical approach with Kraft and sulfite process is that the former only removes a portion of lignin during the “cooking” and then this is followed by mechanical disintegration. Soda pulping (sulfur free alkali processing of pulp) mostly processes fiber plants, straws, and bagasse from agricultural wastes [32]. Only 10 to 15% sodium hydroxide is necessary for delignification of the feedstocks due to their low lignin content and the rate at which lignin is extracted from soda pulping is low compared to Kraft pulping [32]. On the other hand, organosolv pulping depends on low organic solvents such as alcohols (methanol and ethanol), organic acids (acetic and formic acids), and mixed organic solvents-inorganic alkali chemicals for delignification. Organosolv pulping employs sulfur-free chemicals.

2.5 Thermal Conversion of Biomass

Efforts have been, and they continue to be made to convert lignin into useful products other than being burnt in boilers to produce process steam that is used in processes such as pretreatment, distillation, and in the production of electricity. The paragraphs below describe some of the thermochemical research about feedstock conversion (Figure 2-4).
2.5.1 Hydrothermal Conversion

The word hydrothermal comes from the field of geology since 1850 [33] and is defined as any heterogeneous reaction that occurs at elevated pressures and temperatures in the presence of aqueous solvents to dissolve and recover materials that are somewhat insoluble under ordinary conditions [34]. Byrappa and Yoshimura [34] have more descriptive definitions of hydrothermal.

Hasegawa et al., [35] studied hydrothermal oxidation to depolymerize lignin using dilute hydrogen peroxide to produce organic acids. The authors of this paper reported that limited lignin was being used in dispersants and/or pellet binder materials other than mostly being burnt for energy recovery. The objective of the study was to utilize hydrothermal conditions to obtain organic acids with 0.1% hydrogen peroxide solution at 150-200°C reactor temperature. They oxidized alkali lignin at 200°C for two minutes yielding organic acids
(acetic, succinic, and formic acids) as high as 0.45 g/g of lignin whereas for organosolv lignin oxidized at 160°C yielded 0.2 g/g lignin and oligomers of $M_w = \text{ca} 300$. They concluded that the structural differences between the lignin samples contributed to the product spread-out and that the test method was valid to produce lignin value-added chemicals from any source of lignin.

Tang and Zhou [36] studied about Kraft lignin degradation by the hydrothermal process to produce phenolics. The objective was to study the effect of residence time (15 and 60 mins) and temperatures of 130°C, 180°C, and 230°C on phenolics and oil yields. Lignin used was obtained from eucalyptus by Kraft process and a 250 mL SLM micro-reactor was used to carry out the experiments. Acid soluble and insoluble lignin of Kraft lignin was determined by the Klason hydrolysis. GC-MS equipped with a mass selective detector was used to identify the main compounds present and guaiacol was identified to be the dominant and its yield was in the range of 12% to 15% and the oil yields were in the range of 7 to 10%. They concluded that the optimal reaction conditions were 130°C and 15 minutes to obtain a yield of 10% yield of oil from Kraft lignin and 55% guaiacol.

Lee et al., [37] studied on ways how to maximise monomeric aromatic chemical production using hydro- and solvo-thermolysis on Kraft lignin as a starting material. The objective was to investigate the effect of purified water: ethanol (99.5%) ratio as a solvent on monomeric aromatic compounds’ yield. A 30 cm³ custom-built batch reactor made from nickel-molybdenum chromium wrought alloy was used to prevent corrosion and to withstand the temperature and pressure. To agitate and heat the reactor, a shaker driven by a motor and a salt molten bath were used. The temperature for the reactor was influenced by the molten salt temperature, whereas the pressure was determined by the lignin and solvent amount processed. The results showed that as ethanol fraction was increased, there was an increase in the yield of
monomeric aromatics except for catechol and the highest yield of 35% was obtained with 100% ethanol at 300°C. The monomers that were enhanced in ethanol included guaiacol, alkylguaiacol, and phenol whereas catechol was prevailing in water. They concluded that the formation of compounds such as vanillin, homovanillic, and acetoguaiacone wasn’t affected by the solvent.

Nguyen et al., [38] studied the conversion of lignobooeast Kraft lignin by catalytic depolymerization into liquid products by means of near-critical water. Softwood Kraft lignin was utilized and the catalyst was heterogeneously composed of zirconia pellets. Potassium carbonate (99.5%) was used as the homogeneous co-catalyst and crystalline phenol (99.5%) as a co-solvent. A 500 cm³ continuous reactor was utilized under 350°C and 25 MPa. The lignin was first dispersed in an aqueous solution of potassium carbonate (0.4 – 2.2%) and phenol (~4.1%). The flow rate was 1 kg/h and the residence time was 11 minutes which involved internal recirculation inside the reactor at a rate of 10 kg/h. The products from the experiment consisted of phenolic chemicals in an aqueous phase and the bio-oil had a heating value of 32 MJ/kg that was 15% higher than the original value. The dry lignin bio-oil yield was 70% with respect to the dry lignin feedstock. As the potassium carbonate increased, there was an increase in yield of 1-ring aromatic compounds from 17 to 27% based on dry lignin basis. They concluded that aromatic products dominantly present were: alkylphenols, catechols, anisoles, and guaiacols with ethyl and methyl side chains.

Singh et al., [39] used hydrothermal process to convert lignin from agricultural fibrous feedstocks into aromatic ethers and phenols. The objective was to evaluate different temperatures (200°C, 250°C, and 280°C) and residence time conditions (15, 30, and 45 min) on product yield. A 35-ml stainless steel tubular reactor was used for this experiment and the
loading of lignin to ethanol/methanol was 1:10 by weight. The air inside the reactor was removed by purging it five times using nitrogen. After heating the reactor in the furnace for a specific time, temperature and residence time, the reactor was then submerged into a water bath up to room temperature. The contents of the reactor were filtered and washed with either ethanol or methanol. Liquid products were analyzed after removal of the solvent via evaporation under reduced pressure. The liquid product yield showed a decrease with an increase in temperature whereas an increase in residence time showed an increase and then a decrease. Phenols and aromatic ethers were detected. In conclusion, the maximum liquid yield of 85% was obtained at 200°C and 15 minutes and the authors compared their results with existing literature and found out that their study converted more lignin to liquid products and carbon by 72%.

Yong and Matsumura [40] researched about the kinetics of lignin hydrothermal in both subcritical and supercritical water conditions. The aim was to test the effect of temperature under subcritical conditions of 300 to 370°C and supercritical conditions of 390 to 450°C (research under supercritical was done by the same authors and it was used for comparison with subcritical conditions) at a residence time of 0.5 to 10 seconds and 25 MPa on lignin disintegration. For both conditions, there was rapid depolymerization of lignin though supercritical conditions were faster. Char formation was much experienced under supercritical temperature conditions and a conclusion of radical reaction having played an incredible role in char formation was made. Arrhenius behavior was obeyed for the rate constant of the overall lignin degradation.

Roberts et al., [41] studied the quantitative catalytic depolymerization of lignin by liquid phase hydrolysis. Base-catalyzed depolymerization (BCD) of organosolv lignin was
carried out in a continuous stainless-steel reactor. The objective was to investigate the effect of temperature (240 to 340°C), pressure (250 to 315 bar), residence time, and catalyst concentration on the BCD mechanism using kinetics and to experimentally increase oligomers and monomers yields using boric acid to stabilize the phenolic compounds. The lignin: sodium hydroxide (NaOH) ratios were varied in the range 2.5-5 to study the depolymerization of lignin. The primary products of BCD were phenolic monomers while oligomers were secondary. The product oil obtainable with low molecular weight (MW) phenolics was limited by the polymerization and oligomerization on the highly reactive products. They concluded that utilizing boric acid as a capping agent inhibited condensation and addition reactions on the initially formed products thus increasing the yield to more than 85%.

Wang et al., [42] reviewed the different chemical lignin depolymerization methods that are being used that included; acid catalyzed, base catalyzed, supercritical fluid assisted, ionic liquid assisted, and metallic catalyzed depolymerization. They concluded that the selectivity of base and acid catalyzed approach was low though they were straightforward, however, the high pressure, temperature, and extreme pH necessities special reactors that are costly to buy and maintain; the supercritical and ionic liquid assisted depolymerization of lignin had high selectivity although they were not commercially applied because of the costly expenses that can be incurred in recycling. Metallic catalyzed lignin depolymerization was sighted out to have several advantages including its high selectivity to certain monomers. Wang et al. [42] hypotheses that if appropriate metallic catalysts can be synthesized it will make lignin conversion much easier.
2.5.2 Gasification

Gasification is the thermochemical conversion of organic carbonaceous materials in the presence of controlled oxygen/steam at a temperature more than 700°C to produce syngas/producer gas (CO, H2, and CO2) [43]. Gasification process has also been researched on as a thermochemical mean to utilize the abundant lignin as described in the paragraphs below.

Kang et al., [44] worked on an experiment and modeling study to gasify lignin in supercritical water by the non-catalytic approach in a batch reactor to produce hydrogen. The objective was to optimise and/or identify main effects and interactions of hydrogen production under different temperatures (399 to 651°C), pressures (23 to 29 MPa), and water: biomass ratio (3 to 8). Dry amorphous powdered alkali lignin with 4 wt% sulfur and a tubular supercritical water reactor made from stainless steel were used in this study. Distilled water and HPLC grade acetone were used as solvents. The central composite design (CCD) methodology was utilized for model building, experimental, and data analysis. CCD is an optimisation classical experimental design procedure which can be used in engineering problems. The 651°C was very desirable to obtain the highest hydrogen production through a change in pressure from 23 to 29 MPa didn’t show significant hydrogen yield. Water: biomass and temperature strong interaction was observed at temperatures greater than 525°C though a decrease in hydrogen production was observed at temperatures greater than 600°C with an increase in water: biomass ratio. In conclusion, the optimum model conditions were 651°C, 25 MPa and a water: biomass ratio of 3.9 to have a hydrogen yield of 1.6 mmol/g.

Sato et al., [45] researched about the gasification of residuals from an ethanol plant of Japanese cedar using graphite-supported ruthenium catalyst with 5 wt% ruthenium metal in a batch reactor. Solid residues from an ethanol plant were obtained and pulverized using a
tandem mill and then treated with 5 wt% cellulase in a sodium acetate medium of 0.02 M for 48 h at 50°C and a pH of 5. The solid fraction was filtered after saccharification followed by distillation water washing and then oven dried for 12h at 105°C and after which sieved to obtain 0.15 to 0.5 mm particle sizes. Lignin fraction of the residue sample was the insoluble portion in 72% sulphuric acid and it was expressed as a weight percentage. The quantities for a reactor were a 0.05g catalyst, 0.1 g residue, 0.5 g/cm³ water at 400°C. Organosolv and cellulose were gasified as controls. The resultant gaseous product was composed of 55% CH₄, 40% CO₂, 4% H₂ and less than 1% C₂-C₄ compounds. They concluded that the gasification of organosolv lignin (0.07 g) and cellulose (0.03 g) compared to the residue (0.1 g) had similar behavior. Also, the catalyst (0.15 g) was observed to be stable under supercritical water conditions.

2.5.3 Fast Pyrolysis.

Fast pyrolysis is a thermochemical process which converts biomass/organic compounds rapidly into liquids, gases, and solids/char in the absence of oxygen/steam at moderate temperatures (400 to 600°C) [32,43]. Fast pyrolysis of lignocellulose has been recently much been focused on though also the fast pyrolysis of lignin component is gaining momentum because of the abundant lignin produced from paper industry and more is excepted from ethanol bio-refineries. The paragraphs below describe research work about the fast pyrolysis of lignin.

Azadi et al., [32] hypothesizes that the pyrolysis of isolated lignin is totally different from the pyrolysis of lignocellulosic and wood biomass in terms of the composition and product distribution of char, gases, and bio-oil. Therefore, for each biomass type and isolation processes, temperature and residence times should be optimised. Lignin pyrolysis can occur in
the temperature range of 160 to 900°C in comparison to 220 to 400°C for polysaccharides [46].

Char produced from pyrolysis of lignin is much more compared to non-fractionated and carbohydrates biomass and the char is reported to have lower specific surface area though the C/O and C/H ratios increase with increasing temperature.

To some extent, lignin decomposition and conversion research has been done mostly on model compounds rather than lignin itself which simplifies the process. Such kind of research helps to better understand the transformation pathways, kinetics, and investigates the stability of intermediate products.

Patwardhan et al., [47] investigated the pyrolysis of lignin extracted from corn Stover. The objective of the study was to minimize secondary reactions that occur during pyrolysis of lignin and to offer understandings of lignin pyrolysis fundamental mechanism that can be used to develop descriptive models. Also, the effect of temperature and presence of minerals (CaCl₂, NaCl, MgCl₂, and KCl) was investigated. Corn Stover lignin used was bought from Archer Daniels Midland and was extracted using the organosolv method. The lignin was purified by washing it with HCl for 15 minutes followed by double deionized water washing. A micro-
pyrolyzer coupled with GC-MS/FID was used and the bio-oil composition was investigated using gel permeation chromatography and GC-MS techniques. The results indicated that monomers were the primary products of lignin pyrolysis (dominant compounds were; phenol, 2, 6-dimethoxy phenol, 2 methoxy 4-vinyl phenol, and 4 vinyl phenol) whereas oligomers were secondary products after the monomers recombined during condensation and in total twenty-four lignin products were quantified and identified. They concluded that char yield decreased linearly with increasing temperature whereas low molecular and gaseous products increased. Methoxylated phenol maximum yield was attained at 600°C while alkylated phenols’ yield
was increasing with increasing temperature. Lignin pyrolysis products were not significantly affected by the addition of minerals.

Nowakowski et al., [48] investigated the fast pyrolysis of lignin. This study was regarded as being international because it involved making tests with fourteen laboratories in eight countries. The objective of the study was an attempt to establish the potential of lignin pyrolysis and to relate results and procedures. Two lignin samples were used for the research, one was the lignin produced from soda pulp process streams obtained from sarkanda grass and wheat straw and the second sample was an ethanol production residue from softwood two stage weak hydrolysis with 50% cellulose. Analysis done encompassed analytical analysis, thermogravimetric analysis, ultimate and proximate analysis. Entrained flow and fluidized bed reactor systems were utilized. The researchers concluded that the lignin sample that contained 50% cellulose behaved distinctively like biomass though with lower bio-oil yield compared to lignocellulose whereas pure lignin wouldn’t undergo fast pyrolysis easily and it produced very low bio-oil. Specialised reactor designs were recommended other than the typical fluidized bed reactors to handle very concentrated lignin samples.

Yu et al., [49] investigated the zeolite selectivity catalytic fast pyrolysis of lignin and the shape role of these catalysts in the process. The zeolite catalysts included Y, ZSM-5, beta, and mordenite zeolites that had different crystallographically static pore sizes in the range of 5.6 to 7.6 Å. Zeolites are important in catalytic fast pyrolysis because they dictate the yield and chemical composition of the final product and their pore structure and surface chemistry influence the conversion process. Quantum chemical calculation was applied to determine the molecular dimensions of lignin products. At 650°C, the effectiveness of pore sizes of the zeolites was determined by examining the transformation behavior and molecular size of the
products. The results indicated that zeolite pore structure, when distorted thermally at elevated temperatures increases the crystallographically determined by zeolite pores in the range of 2.5 to 3.4 Å implying that oxygenates derived from lignin of molecular size greater than the static pore size entered the zeolite pores to get converted under catalytic fast pyrolysis. The aromatic yield was in the order ZSM-5>beta>mordenite>Y zeolite. Lignin deoxygenation was effectively achieved with Y and beta zeolites. In conclusion, the ZSM-5 catalyst was appropriate to deoxygenate and produce aromatics from an optimum point for softwood while beta zeolite was appropriate for hardwood derived lignin to convert oxygenates.

Mukkamala et al., [50] studied the fast pyrolysis of lignin by pretreating it with calcium formate. Lignin has been known to recalcitrance for chemical conversions though research has been made to convert it to useful products like nanostructured carbon-based products, liquid chemicals, and fuels. The authors reported some of the barriers of lignin fast pyrolysis being agglomeration and/or continuous feeding and processing challenges and very low product yields probably due to char being formed most and the low melting point due to lignin chemical structure composed mostly of methoxylated phenyl propane subunits. Some strategies identified to overcome such challenges include catalytic pyrolysis, pyrolysis reactor adjustments, and high-pressure solvolysis performed with ethanol and formic acid solvents. The objectives of this study were to prove if there could be improvements on fast pyrolysis of lignin (1 g) mixed with formate salt (1 g) compared to conventional fast pyrolysis and to prove if the pyrolysis of the mixture provides in-situ source of reactive hydrogen to decrease oxygen: carbon ratio and/or increase the carbon content in the liquid product. The feedstock used was prepared as follow, 120 g of lignin was mixed with 30 g of Ca(OH)₂ (purity >98%) in the presence of 600 ML of water with stirring having been done for 1 h at 60°C. Formic acid
(purity >90%) was added to the mixture in the quantities of 60 g to lower the pH and after an hour, it had stabilized at 4.2. Neutralisation proceeded with 30 g of Ca(OH)$_2$. At 100°C, the solution was oven dried and after which grounded and sieved to particles of less than 425 µm. Entrained flow reactor was utilized and sand as a heat carrier was avoided to prevent agglomeration of lignin with sand. The bio-oil yield was at 33% and had a HHV of 41.7 MJ/kg and an oxygen: carbon ratio of 0.067 with aromatics being the most compounds present. They concluded that fast pyrolysis of lignin pretreated with formic acid reduced oxygen content by deoxyhydrogenation in lignin liquid products, agglomeration challenges were mitigated, and higher bio-oil yields are possible upon optimising formate-assisted concentration and residence time.

Ma et al., [51] studied lignin selective deoxygenation through catalytic fast pyrolysis. The objective was to determine how specific and/or different catalysts such as supported transition metal catalysts and transition metal oxides influence the desirable valuable products and to provide a synopsis of catalytic fast pyrolysis. The mentioned catalysts were compared with alumina silicate catalysts yields from literature. Alkaline lignin mixed with catalysts (1:4) was subjected to fast pyrolysis in a pyro-probe microreactor for 60 seconds at 650°C. Catalysts were calcined prior to pyrolysis at 550°C in the air for approximately 5 h and corresponding nitrates were calcined the same way to obtain transition metal oxides. Wet impregnation approach was utilized to synthesize zeolite supported transition metal catalysts. The results indicated that a complex mixture of chemicals such as phenol, aromatic hydrocarbons, guaiacol, and vanillin were produced under non-catalytic fast pyrolysis and deoxygenation yielded slightly different products predominantly aromatic hydrocarbons. Vanillin highest yield was experienced with copper oxide catalyst. They concluded that to some degree the
selectivity of the product can be achieved, and a strong distinction was observed with different catalysts. They hypothesized that catalytic lignin fast pyrolysis would be economic and feasible by developing highly selective and active catalysts.

Zhou et al., [52] investigated the effect of pretreating technical lignin with calcium hydroxide to overcome agglomeration. Fast pyrolysis bio-oil was mentioned to be like the liquid produced by solvent liquefaction. Batch studies on minute quantities were reported to have been done by other researchers to provide insights of lignin fast pyrolysis and/or depolymerization however, continuous lignin applicable commercially was the motivation for this study. Lignin used for this experiment were corn Stover lignin extracted by acetosolv method from Archer Daniels Midland, mixed hardwood supercritically hydrolyzed lignin from Renmatix, alkaline softwood lignin from Sigma-Aldrich, and enzymatically hydrolyzed corn Stover lignin. Most of the experiments were done on lignin from Archer Daniels Midland. Model compounds that represented lignin-derived fast pyrolysis were vanillin and phenol. Each lignin type (950 g) was mixed with 50 g of calcium hydroxide at room temperature in water. Water from the mixture was removed by oven drying until a moisture content of ≤5% was attained. Fluidised bed reactor was used at a temperature range of 450 – 600°C. From the results, approximately 38% bio-oil was produced. Zhou et al. [52] concluded that depolymerization of lignin into dimers and phenolic monomers was effectively achieved since the mean molecular weight was <288 Da for bio-oil. The char from un-pretreated lignin would form clusters (agglomerate) probably due to the existence of aldehydes, carboxylic acid, and phenolic hydroxyls whereas the one from pretreated lignin was fine powdered probably because Ca(OH)₂ helped in forming compounds that prevent agglomeration such as phenolic
carboxylate salts, phenolic alcohols, and hydroxylcaicium phenoxides. Finally, the pretreated lignin char surface area was way lower than that of un-pretreated lignin.

2.6 Hydroxymethylfurfural (HMF), 2,5-dimethylfuran (DMF), Furfural, and 2-Methylfuran (MF)

HMF is a 30 to 34°C melting yellow organic compound that is produced from carbohydrates like fructose, cellulose, and others by dehydration [53]. In the biorefinery industry, HMF is a critical building block that can be used to produce compounds such as 2,5-diformylfuran, 2,5-furandicarboxylic acid (FDCA), 2,5-furandicarbaldehyde, 2,5-dihydroxymethylfuran, and 2,5-dimethylfuran which is considered as an alternative liquid biofuel. FDCA is produced by selective oxidation and can be used as an alternative/substitute of terephthalic acid to produce polyesters such as polybutyleneterephthalate and polyethyleneterephthalate [54,55]. Alcohol-HMF derived chemicals can be used as substitutes in polyester production like 2,5-bis(hydroxymethyl)tetrahydrofuran thus having a whole biomass-derived polymer if combined with FDCA. Huber et al., [56] suggest that HMF can be used as a precursor to produce liquid alkanes (C$_7$ – C$_{15}$) to be used as transportation fuels.

Fructose conversion to HMF has been studied using heterogeneous and homogeneous catalysts and without the use of catalyst(s) nevertheless reasonably good yields are achieved with the use of catalysts such as zeolites and ion exchange resins [57–60]. Some of the used catalysts are regarded as being expensive, toxic and non-recoverable. In some heterogeneous systems, organic high boiling solvents are used to give HMF a high selectivity though making HMF separation at high temperatures almost impossible by distillation. An alternative is the use of water due to its abundance, non-toxicity and being an environmentally friendly reaction
media. Fructose dehydration to HMF using water as a solvent is the best option because among all the sugars fructose is the most soluble in water though low HMF selectivity is achieved with pure water as a solvent [53]. In addition, due to the high HMF solubility in water, its extraction is not easily achieved.

Dumesic et al., [61–63] have studied fructose dehydration with HCl dissolved in water and supplementing the aqueous phase with modifiers for HMF selectivity improvement using butanol and/or methyl isobutyl ketone (MIBK) or combined to increase extraction efficiency. Okano et al., [53] thinks that Dumesic et al.’s approach (HCl-aqueous catalyzed organic biphase) solves all the mass production concerns like HMF easy separation, low-cost catalyst, use of water as the solvent, and high HMF yields.

Román-Leshkov et al., [62] developed a process to selectively produce HMF by dehydrating fructose at 10-50 wgt% high concentration. HCl and/or acidic ion-exchange resin catalyst was used with dimethylsulfoxide in a 2-phase reactor to dehydrate fructose in the aqueous phase and to suppress unintended reactions. The organic phase was modified with 2-butanol to enhance HMF continuous extraction thus separating it from the aqueous reactive solution. In conclusion, a 90% conversion of fructose and 80% selectivity of HMF were achieved.

Chheda et al., [63] researched about the dehydration of xylose, glucose, and fructose to furfural and HMF using biphasic reactor composed of aqueous reactive phase improved with dimethylsulfoxide (DMSO) and methyl-isobutyl-ketone-butanol (7:3 w/w)/dichloromethane mixture. Temperatures of 170°C and 140°C were used when acid mineral catalysts and dichloromethane were considered as extraction agent respectively. The selectivity to dehydrate the sugars to HMF were 53%, 89%, and 91% for glucose, fructose, and xylose respectively.
They concluded that dehydrating the inexpensive and highly abundant functionalized polysaccharides eliminates the need of obtaining carbohydrates using acid hydrolysis as a processing separate step.

On the other hand, furfural is a triple product dehydration of xylose and a very important chemical that has been industrially produced from many agricultural wastes such as sawdust, corn stover and cobs, rice husks, bagasse, and much more [64–66]. Furfural is used industrially to produce products in the agrochemical, plastic, and pharmaceutical sectors with more than 250,000 tons/year that are organic and unsaturated produced from carbohydrates [67,68]. More furfural literature can be found in [64–68]. The vapor phase of furfural is used to produce other products such as tetrahydrofuran, 2-methylfuran (MF), and furfuryl alcohol via hydrogenation. MF can be used to produce perfume intermediates, pesticides, and chloroquine lateral medical chain intermediates.

2.7 Carbon Dioxide

Carbon dioxide (CO$_2$) is among the greenhouse gases emitted into the atmosphere that causes global warming. A concentration of 400 ppm threshold was reached increasing the global temperature by 1.5°C compared to prior industrial revolution [69]. By 2040, the CO$_2$ emission is expected to increase to 45 gigatonnes (Gt) as compared to 32 Gt of CO$_2$ that was emitted in 2013 [70]. On average, 45% of the anthropogenic emissions are released into the atmosphere, 33% absorbed by plants on earth through photosynthesis while the rest, 22% is absorbed by oceans [71]. Of all the emissions absorbed by oceans, 40% is through the southern ocean which brings about unequal absorption [72] and there are concerns that by 2030 the
emissions will have noticeable effects of ocean native organisms which might in the end affect the food web [73].

Due to increased anthropogenic CO$_2$ emission into the atmosphere and its threat to the environment efforts are being made to reduce its emission such as carbon capture and storage (CCS), commonly referred to as sequestration. Some technological approaches are being investigated to utilize CO$_2$ to produce products such as plastics [74], propylene [75], polymers [76], dimethyl ether [77], oxalates [78], and formates [79]. On the other hand, research is in progress to convert CO$_2$ via electrochemical process into biofuels and bioproducts such as formic acid, methanol, methane [80], organic molecules fuels [81].

CCS is reported to be the mostly used method to reduce CO$_2$ [69] and the CCS Institute identified 38 potential large projects of which 20 of them by the end of 2017 will be operating [82]. CCS capacity of operating plants and those under construction is estimated to be 40 million tonnes per year, however to achieve a target of Paris ‘well below’ 2°C climate target, the International Energy Agency (IEA), predicts that there is a need to CCS 4000 million tonnes per year by 2040 [82].

2.8 Renewable Electricity

The U.S. renewable electricity generation has increased in recent years due to the abundant and diverse renewable resources of solar, ocean, biomass, hydropower, geothermal, and wind [83]. Due to the diversity and abundance of renewable resources in the U.S., multiple renewable technologies can be combined to reduce greenhouse gas emission and water usage. The renewable resources are widely spread in almost every state and commercial generation technologies are used such as hydropower, onshore wind, stand-alone biopower, CSP, fixed-
bottom offshore wind, distributed PV, hydrothermal geothermal, and utility-scale PV and in total, they contribute about 15% of electricity supply in the U.S. [84]. According to EIA [84] by 2016, hydropower, wind, biomass, solar, and geothermal power provided 7%, 6%, 2%, 1%, <1% of the total U.S. electricity generation respectively. By 2016, the total electricity generated in the U.S. was 4.1 trillion KWh with renewable, petroleum, nuclear, coal, and natural gas accounting for 15%, 1%, 20%, 30%, and 34% respectively [84]. Figure 2-5 shows how the U.S. net generation of electricity has been since 2001 with other renewables wind and leading the trend.

From the Renewable Electricity Future Study (RE Futures) [83], it is possible to have a U.S. electricity system dominated by renewable resources with a supply of more than 80% (50% from solar PV and wind) based on commercially available technologies today in conjunction with a more flexible electric system by 2050. RE futures will depend on the supply-and-demand balancing in terms of new transmissions, generation, storage, power systems operation and responsiveness to load. For more information about RE futures, the reader is referred to [83].

2.9 Techno-Economic Analysis

There are a few articles on the techno-economic analysis of lignin-based products, hydroxymethylfurfural (HMF), 2,5-dimethylfuran (DMF) production, and CO₂ to F-T biofuels. Corn Stover feedstock process flow diagram (Figure 2-6) shows the different steps to produce ethanol and value-added chemicals from lignin.
Figure 2-5: U.S. net electricity generation by renewable sources.

Farag and Chaouki [23] economically evaluated an on-site value-addition of Kraft lignin via fast pyrolysis. The objective was to determine the selling value of bio-oil produced from lignin of an already existing paper industry. Kraft softwood lignin was utilized with the proximate analysis results (dry basis, d.b) of 37 wt% fixed carbon, 62 wt% volatiles, and 1 wt% ash and ultimate analysis results of 63.27 wt% carbon, 5.79 wt% hydrogen, 0.07 wt% nitrogen, and 1.56 wt% Sulphur. The plant capacity considered was of 50 t/d db. From the results, $3100/t was determined as the minimum bio-oil selling price. A sensitivity analysis was done with feedstock price and bio-oil yield being the most influential parameters affecting the minimum selling price. The overall costs are shown in Table 2-1.
Table 2-1: Costs of producing bio-oil from Kraft lignin [23].

<table>
<thead>
<tr>
<th>Breakdown of capital investment</th>
<th>Cost ($MM)</th>
<th>Overall costs</th>
<th>Cost ($MM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purchased equipment</td>
<td>2.2</td>
<td>Total capital investment</td>
<td>11.3</td>
</tr>
<tr>
<td>Purchased equipment installation</td>
<td>0.9</td>
<td>Raw materials</td>
<td>7.3</td>
</tr>
<tr>
<td>Instrumentation and controls</td>
<td>0.6</td>
<td>Maintenance</td>
<td>0.3</td>
</tr>
<tr>
<td>Piping</td>
<td>0.7</td>
<td>Labor</td>
<td>0.15</td>
</tr>
<tr>
<td>Electrical</td>
<td>0.2</td>
<td>Insurance</td>
<td>0.2</td>
</tr>
<tr>
<td>Buildings</td>
<td>0.6</td>
<td>Overheads</td>
<td>0.2</td>
</tr>
<tr>
<td>Yard improvements</td>
<td>0.3</td>
<td>Electric energy</td>
<td>0.4</td>
</tr>
<tr>
<td>Service facilities</td>
<td>1.2</td>
<td>Water</td>
<td>0.003</td>
</tr>
<tr>
<td>Land</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Engineering and supervision</td>
<td>0.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Construction</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Legal expenses</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contractors fees</td>
<td>0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Contingency</td>
<td>0.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Working capital</td>
<td>1.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total capital investment</td>
<td>11.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Jones and Zhu [85] carried out the preliminary techno-economic analysis of producing lignin bio-oil in a cellulosic ethanol biorefinery. Two scenarios were considered, one being a base cellulosic ethanol plant that utilizes the whole lignin as an input to produce process steam and power whereas the second scenario (alternative) utilized lignin to produce bio-oil. A 2000 metric tonne per day (MTPD) corn Stover biorefinery was considered and for the alternative scenario, part of corn Stover is considered burnt to provide process steam and power reducing the ethanol output per year from 60 to 54 million gallons per year. The minimum ethanol selling price (MESP) for the alternative was found to be in the range of $1.40 and $1.48 (2007 $) with an assumption of pyrolysis bio-oil value being similar to Btu-adjusted residual oil. The alternative scenario MESP was considered higher in comparison to $1.33 2007 state of
technology model price. They concluded that producing lignin bio-oil wasn’t an economical approach, however, they recommended future studies if lignin bio-oil was to be upgraded. They also recommended other processes like wet gasification or high-pressure liquefaction.

Jönsson and Wallberg [86] estimated the cost of Kraft lignin recovery using ultrafiltration. The objective of the research was to compare the cost of Kraft hardwood lignin extraction from evaporated black liquor and cooking liquor by ultrafiltration. The lignin used was supplied by a company that had a 75,000 tonnes/yr. capacity. The cooking liquor used was the one obtained after digestion whereas the black liquor used was obtained from the third evaporator under the section of evaporation and both had a pH range of 13 to 14. A Kerasep ceramic membrane having a nominal cut-off of 15000 Da was used with ultrafiltration at 90°C. For cooking liquor, it contained 45% and 55% lignin before and after ultrafiltration whereas for black liquor the content was 40% and 38% before and after ultrafiltration. The cost breakdown is as shown in Table 2-2. The exchange rate of 1€ = $1.13 was assumed. They concluded that lignin recovery from cooking liquor would cost ~$68/tonne whereas from black liquor could be ~$37/tonne.

Pourhashem et al., [87] studied the alternative uses of lignin in terms of cost and GHG emission tradeoffs from the secondary ethanol production process. The lignin component of lignocellulose during bioconversion together with little fractions of cellulose and hemicellulose entrained during the process forming a lignin stream that is also referred to as “high lignin fermentation byproduct (HLFB)” by the authors. The objective of the study was to compare the cost and life-cycle assessment of lignin to be used in energy recovery or as a
soil amendment. Agricultural waste feedstock considered comprised of wheat straw, corn Stover, and barley. Three lignin utilization scenarios were investigated; a) use lignin as a soil amendment (scenario 1); b) co-firing lignin with coal after drying (scenario 2); and c) combusting lignin to produce process steam and electricity and selling surplus electricity as a co-product (scenario 3). Biogas produced from wastewater treatment (WWT) for scenarios 1 and 2 was assumed to provide the process stream whereas electricity was purchased. A 2000 dry MT/day was assumed with three site locations, Boone Co., Iowa, Lenoir Co., North Carolina, and Queen Anne’s Co., Maryland. The three agricultural wastes were considered for the sites in MD and NC whereas only corn Stover was considered for IA. The project lifetime assumed was 20 years and 1 MJ functional unit of ethanol production. Process modeling was done using Aspen Plus, SimaPro7.3.2 software for life cycle analysis, and terrestrial ecosystem model DayCent for residue removal, and nutrient replacement. Their result indicated that the GHG intensity was in ascending order of scenario 1 (-25 to -2 g CO$_2$e M/J), scenario 2 (4 to

<table>
<thead>
<tr>
<th>Table 2-2: Estimated cost of Kraft lignin recovery using ultrafiltration [86].</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Area of the membrane (m$^2$)</strong></td>
</tr>
<tr>
<td>---------------------------------</td>
</tr>
<tr>
<td>Investment cost (M$)</td>
</tr>
<tr>
<td>Capital cost (k$/yr.)</td>
</tr>
<tr>
<td>Required electricity (kWh/m$^3$)</td>
</tr>
<tr>
<td>Cost of electricity (k$/yr.)</td>
</tr>
<tr>
<td>Replacement cost of the membrane (k$/yr.)</td>
</tr>
<tr>
<td>Cost for cleaning (k$/yr.)</td>
</tr>
<tr>
<td>Labour and maintenance cost (k$/yr.)</td>
</tr>
<tr>
<td>Operating costs (k$/yr.)</td>
</tr>
<tr>
<td>Total cost (k$/yr.)</td>
</tr>
<tr>
<td>Produced lignin (tonne/yr.)</td>
</tr>
<tr>
<td>Cost of production ($/tonne of lignin)</td>
</tr>
</tbody>
</table>
32 g CO₂e M/J), and scenario 3 (36 to 41 g CO₂e M/J). Lower required equipment and onsite biogas generation contributed to the lowest capital cost required by scenario 1 (land amendment).

Fornell et al., [88] investigated the techno-economic analysis of producing both dimethyl ether (DME) and ethanol in a Kraft based mill biorefinery. The aim of the study was to convert Kraft pulp mill (softwood) into a biorefinery that utilizes both biochemical and thermochemical processes. The process consisted of digesting the feedstock at 160°C to produce two streams. One stream was made up of pulp (mainly cellulose) that was thoroughly hydrolyzed, fermented, and the product purified to produce ethanol. The second stream (residue liquor) containing mainly lignin underwent evaporation to produce dry content that was then gasified to produce syngas that was further upgraded to DME. A 2065 MT/day dry wood capacity plant was assumed producing 410 m³/day of ethanol. Mass and energy balances of the different steps were obtained from Aspen plus. From their results, a 65% conversion efficiency of biomass to liquid was achieved. Assuming the annuity of 10%, $28.25 M/yr. (25 M€/yr.) revenue was obtained whereas a 20% annuity yielded $-28.25 M/yr. (2-5 M€/yr.). It was concluded that the ethanol and DME prices affected the biorefinery feasibility than the cost of investment and the pulp mill purchase price derived a lot of uncertainty as the single largest capital cost. A positive 30% increase in ethanol and DME prices, yielded an increase in revenue by $34 M/yr. (30 M€/yr.).
Bergeron and Hinman [89] studied the techno-economic analysis of converting lignin to methyl aryl ethers (MAE). MAE have vapor pressures and blending octane numbers that make them good choices to enhance gasoline octane. MAE can be produced by reacting the aromatic compounds of lignin with methanol with appropriate catalysts [89]. The assumptions made included: aspen wood containing 24% lignin, 51.5 MM gal/yr. of ethanol, 20 to 30 MM gal/yr. of MAE, ethanol and lignin processing were treated independently and they would need inputs and energy at a cost of 2.56 cents/lb. of lignin, 55% initial moisture content of lignin but it reduced to 41% prior burning, $2.44/MMBTU was credited on the lignin facility as the
fuel value of wood, $5.50/MMBTU onsite steam generation cost, 2.92 cents/KWh purchase cost of electricity, natural gas was imported by the lignin facility to produce methanol and hydrogen to convert to ether and the phenols produced in the hydrocracker. The economic assumptions in this study were based on [90]. Six scenarios were considered with 1 to 5 having the same flow rate and lignin initial moisture content whereas scenario 6, the incoming lignin was presumed to be dry. A sensitivity analysis of MAE product cost was done on four parameters: lignin, moisture content, hydrogen recovery, phenol conversion, and hydrocracker yield. The results obtained are as shown in Table 2-3 and the authors concluded that having oil price at ~ $25/bbl, converting lignin from a wood to ethanol biorefinery into MAE would be better economical than being used as a boiler fuel.

Table 2-3: MAE product price under different scenarios and their effect on ethanol MSP [89].

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Oil price ($/bb 1)</th>
<th>Hydrogen recycle</th>
<th>Hydrocracker yield (%)</th>
<th>Phenol conversion (%)</th>
<th>Lignin moisture content (%)</th>
<th>Reactant cost (cents/gal of MAE)</th>
<th>MAE price (cents/gal)</th>
<th>Ethanol price change (cents/gal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15 35</td>
<td>No</td>
<td>48</td>
<td>23</td>
<td>55</td>
<td>97</td>
<td>152</td>
<td>+34</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>148</td>
<td>203</td>
<td>+23</td>
</tr>
<tr>
<td>2</td>
<td>15 35</td>
<td>No</td>
<td>48</td>
<td>100</td>
<td>55</td>
<td>94</td>
<td>134</td>
<td>+30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>144</td>
<td>184</td>
<td>+14</td>
</tr>
<tr>
<td>3</td>
<td>15 35</td>
<td>Yes</td>
<td>48</td>
<td>23</td>
<td>55</td>
<td>79</td>
<td>131</td>
<td>+29</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>104</td>
<td>157</td>
<td>+3</td>
</tr>
<tr>
<td>4</td>
<td>15 35</td>
<td>Yes</td>
<td>48</td>
<td>100</td>
<td>55</td>
<td>81</td>
<td>119</td>
<td>+21</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>103</td>
<td>141</td>
<td>-4</td>
</tr>
<tr>
<td>5</td>
<td>15 35</td>
<td>Yes</td>
<td>72</td>
<td>100</td>
<td>55</td>
<td>57</td>
<td>93</td>
<td>+17</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>74</td>
<td>111</td>
<td>-24</td>
</tr>
<tr>
<td>6</td>
<td>15 35</td>
<td>Yes</td>
<td>72</td>
<td>100</td>
<td>0</td>
<td>40</td>
<td>76</td>
<td>+7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>59</td>
<td>95</td>
<td>-32</td>
</tr>
</tbody>
</table>
Table 2-4: MAE capital and operating estimates [89].

<table>
<thead>
<tr>
<th>Breakdown of capital investment</th>
<th>Cost ($MM)</th>
<th>Overall costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Purchased equipment</td>
<td>2.2</td>
<td>Total capital investment</td>
</tr>
<tr>
<td>Purchased equipment installation</td>
<td>0.9</td>
<td>Raw materials</td>
</tr>
<tr>
<td>Instrumentation and controls</td>
<td>0.6</td>
<td>Maintenance</td>
</tr>
<tr>
<td>Piping</td>
<td>0.7</td>
<td>Labor</td>
</tr>
<tr>
<td>Electrical</td>
<td>0.2</td>
<td>Insurance</td>
</tr>
<tr>
<td>Buildings</td>
<td>0.6</td>
<td>Overheads</td>
</tr>
<tr>
<td>Yard improvements</td>
<td>0.3</td>
<td>Electric energy</td>
</tr>
<tr>
<td>Service facilities</td>
<td>1.2</td>
<td>Water</td>
</tr>
<tr>
<td>Land</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Engineering and supervision</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>Construction</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Legal expenses</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Contractors fees</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Contingency</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>Working capital</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>Total capital investment</td>
<td>11.3</td>
<td></td>
</tr>
</tbody>
</table>

Kazi et al., [91] performed a techno-economic analysis of producing hydroxymethylfurfural (HMF) and 2,5-dimethylfuran (DMF) from fructose biomass-based feedstock. The areas which fructose undergoes to produce the required products are categorized as synthesis and purification areas. The production of HMF and DMF were considered separately with a biphasic continuously stirred tank reactor (CSTR) used which creates an organic and aqueous phase. For the DMF production, 3-train additional fixed bed catalytic plug flow tubular reactor (PFTR) were added to convert HMF into DMF. They assumed a 300 metric tonne per day (MTPD) flow rate of fructose and a 20-year plant life. They estimated a $102 M and $122 M installed equipment cost for HMF and DMF respectively (all prices are in the US $2007). Minimum product selling price computed were $1.33/l (HMF)
and 2.02/l (DMF) and they are sensitive to product yield, feedstock cost, total purchased equipment cost (TPEC), and byproduct price. The authors recommended more experimental and pilot performance and cost data to reduce on the economic uncertainty of the process model.

Oloman and Li [80] reported that some research was done to produce formate by reducing CO$_2$ using 100A trickle-bed continuous electrochemical reactor under industrial practical conditions with the assumption that cathode stability and formate crossover problems can be overcome. In their techno-economic analysis, they assumed a 100 metric tonne per day (MTPD) CO$_2$ plant, negative carbon credit, 80% current efficiency, 100% selectivity from CO$_2$ to formate/formic acid, and 100% conversion. They estimated that $MM 70 (2005-dollars) would be required as the installed cost of the electrochemical reactors whereas $MM 170 was the installed cost of the whole biorefinery.

2.10 References


CHAPTER 3. MORE THAN ETHANOL: A TECHNO-ECONOMIC ANALYSIS OF CORN STOVER-ETHANOL BIOREFINERY INTEGRATED WITH HYDROTHERMAL LIQUEFACTION PROCESS TO CONVERT LIGNIN INTO BIOCHEMICALS

This manuscript has been published by Biofuels, Bioproducts, and Biorefining journal

Denis Bbosa\textsuperscript{a}, Mark Mba-Wright\textsuperscript{a**}, Robert C. Brown\textsuperscript{ab}

\textsuperscript{a}Department of Mechanical Engineering Iowa State University, Ames, Iowa 50011, United States

\textsuperscript{b}Bioeconomy Institute Iowa State University, Ames, Iowa 50011, United States

**Corresponding author

3.1 Abstract

High-value chemicals from lignin could increase the profitability of lignocellulosic biorefineries. Besides lignin from the paper and pulp industry, ethanol plants produce lignin as a waste stream, thus, the objective of this work is to evaluate the techno-economics of integrating hydrothermal liquefaction of lignin to produce biochemicals within ethanol biorefineries. This paper evaluates a 2000 metric tonne per day (MTPD) corn stover biorefinery producing 61 MMgal/yr. of ethanol and different yields of lignin-derived biochemicals. A minimum ethanol selling price (MESP) of $1.03 \pm 0.19$ per gallon was computed considering the production of lignin-derived catechol, phenol, cresols, acetic acid, formic acid, furfural, and acetaldehyde. The most influential factors on MESP identified are fixed capital investment, internal rate of return (IRR), feedstock price, cresols, catechol, and
acetic acid prices. In terms of costs, the total purchased equipment cost is $114.5 MM, total installed cost (TIC) is $345.7 MM, and total capital investment is $624.5 MM. However, ethanol biorefineries adopting this lignin-to-chemicals strategy could still face higher levels of price uncertainty. Hydrothermal liquefaction process to produce lignin-derived chemicals is in the early stages of development, thus more research (laboratory and pilot scale) is needed to establish its commercialization potential.

Keywords: lignin chemicals; hydrothermal liquefaction; techno-economic analysis; fermentation

3.2 Introduction

A growing global population is increasing energy demand while fossil fuels are causing environmental concerns. Thus, scientists are developing sustainable alternatives for producing fuels and chemicals. Biomass can provide clean and renewable biofuels and biochemicals, but the biomass-based products are currently more expensive than fossil-based products. Advanced biorefineries have focused on the production of liquid fuels such as ethanol from cellulose and hemicellulose biomass sugars. Biomass lignin, despite representing over 15% of biomass content [1], is often combusted for heat and power generation. Producing high-valued biochemicals from lignin could enhance the profitability of biorefineries. Recent research has focused on the use of thermochemical technologies for converting lignin to biochemicals, however, recovering lignin biochemicals at high yields and purities remains a challenge.

Lignin is an amorphous, complex 3-D polymer composed of various units of methoxylated phenylpropanoid [2]. Biomass type and plant part influence the composition and structure of lignin [3]. In a plant, lignin provides mostly biological and chemical protection
of cellulose and hemicellulose [4]. Lignin is a readily available renewable resource with aromatic units, and its chemical structure makes it a suitable material to produce aromatic chemicals. Worldwide, the paper and pulp industry produces more than 170 million metric tonnes dry solids in black liquor that is mostly composed of lignin [5]. Lignin is mostly used in the production of power and heat and is regarded as a waste stream [6], and only 5% of produced lignin is reported to be utilized in process steam and power [3] and/or as an additive in concrete [7]. Research is underway to improve biorefinery revenues by producing biochemicals and biofuels from lignin which accounts for 40% of biomass energy, and 10 to 35% by weight [8]. Other lignin applications have been summarised in reviews [9,10] such as emulsifier, epoxy resins, dispersant, automotive brakes, polyurethane, thermoplastics, polymers, panel wood products, and foams. Besides the paper and pulp industry, ethanol plants also produce lignin as a waste stream with a high moisture content. The thermochemical processes under trial to process lignin include fast pyrolysis and hydrothermal liquefaction (HTL).

Hydrothermal liquefaction (HTL) can be used to thermochemically convert high moisture containing feedstock into liquid (hydro-oil/bio-oil/bio-crude), gas, and solid (biochar/hydro-char) products. HTL is a direct liquefaction method [11] that occurs in the presence of water within the temperature range of 250 – 380°C, 50 – 300 atm of pressure, and residence time of 5 – 60 min [12–15]. The primary HTL product is bio-crude, which is dependent on HTL reaction step [15]. Different authors have researched about improving HTL bio-oil yield by investigating the effect of different parameters such as pressure, residence time, temperature, and biomass particle size [16–20]. HTL bio-oil has attractive properties such as low bio-oil oxygen content of 10 to 20 wt% [21], and higher oil heating value of 35 MJ/kg
The bio-crude oxygen content is reduced during HTL by forming carbon dioxide and water [12,22] in the effluent gas. HTL can process high moisture content biomass and avoid the energy required to dry biomass for other thermochemical processes. Furthermore, under HTL, compressed water remains in the liquid phase, avoiding the energy lost from evaporation [13].

HTL research is in its early stages and this presents an opportunity to evaluate the economic feasibility of the technology to help guide policymakers and commercial efforts. Published literature on HTL economics is available for converting woody biomass [13] and microalgae as a whole [23] into transportation fuels, however, there are no articles that evaluate the economics of converting lignin via HTL within an integrated biofuel and biochemicals facility. Thus, the objective of this work is to evaluate the techno-economics of integrating ethanol biorefineries with hydrothermal liquefaction (HTL) of lignin to produce high-value biochemicals.

### 3.3 Material and Methods

The process design is based on previous work by the National Renewable Energy Laboratory (NREL) for an ethanol biorefinery [1], Pacific Northwest National Laboratory (PNNL) work on HTL [24], and public work by Ou et al., [25] and Dang et al., [26]. Process modeling cost estimates and profitability were determined by employing techno-economic analysis (TEA). Processing modeling was conducted in Aspen Plus™ 9.0. Capital cost for common equipment purchase such as pump price is estimated using Aspen Process Economic Analyzer, whereas complex customised equipment costs are estimated by scaling quotes from the public literature using the economies of scale power law [1]. A 30-year discounted cash
flow rate-of-return (DCFROR) was used to evaluate the investment returns. Below are the major assumptions made for this analysis.

➢ The feedstock considered is corn stover with 20% moisture content on average costing $64.50/metric ton (2007-dollar value).
➢ The biorefinery processes 2000 dry metric tonne per day (MTPD) of corn stover and operates 8400 hours/year (96% process uptime).
➢ The pretreatment reactor operates at 158°C and 5.5 atm with a sulphuric acid loading rate of 18 mg/dry g of feedstock and a five minutes residence time.
➢ Enzymatic hydrolysis section operates at 48°C, 84 h residence time and a cellulase loading rate of 20 mg protein/g cellulose.
➢ Fermentation operates at 32°C temperature and a residence time of 36 h.
➢ By-product lignin from corn stover fermentation and recovery undergoes hydrothermal liquefaction (HTL) process.
➢ Eighty percent of the solids/lignin is diverted for HTL to produce lignin-derived biochemicals and the remaining is combusted for power and heat.
➢ HTL reactor operating conditions assumed were 350°C and 204 atm (3000 psig).
➢ Assumed HTL lignin-derived biochemicals were catechol, phenol, cresols, acetic acid, formic acid, furfural, and acetaldehyde [27–29].
➢ Multi-stage distillation separates and recovers biochemicals at commercial purity levels.
➢ Cost analysis represents an nth plant design, which implies that all engineering breakthroughs have been accomplished and technical challenges resolved. This contrasts with a pioneer biorefinery which has higher capital and operating costs due
to challenges such as construction delays, cost underestimation, low capacity factors, and high frequency of unscheduled downtime.

3.3.1 Biomass Feedstock and Lignin-Derived Chemicals

The biorefinery modeled in this study processes corn stover. Corn stover is an agricultural by-product of corn production, and it is abundant in the U.S. with a projection of 56 to 127 million dry ton under normal practices and 200 to 245 million dry ton under intensive aggressive agricultural practices by the year 2030 [30]. Shah and Darr [31] report that 87% of this corn stover will be from 12 states from the Midwest assuming constant removal rate of corn stover throughout the USA. Corn stover refers to any part of the corn plant above the ground excluding the kernel [1]. Corn stover contains over 15% lignin, and the corn stover composition employed in this study is shown in Table 3-1. The lignin-derived chemicals considered in this study are catechol, phenol, cresols (m-, o-, and p-cresol), formic acid, acetic acid, furfural, and acetaldehyde. Their yields from HTL can be found in the public literature [27–29].

3.3.2 Process Model Description

The model comprises of the following areas: feed handling (A100), pretreatment (A200), fermentation (A300), enzyme production (A400), recovery (A500), waste water treatment (WWT) (A600), storage (A700), boiler (A800), utilities (A900), and hydrothermal liquefaction (A1000) as shown in Figure 3-1. The A1000 comprises of sub-areas of producing hydro-oil, extraction of chemicals, and separation. The process model description is summarized below and details are available in other sources [1,24,25].
Table 3-1. Corn Stover composition [1].

<table>
<thead>
<tr>
<th>Component</th>
<th>Dry wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucan</td>
<td>35.05</td>
</tr>
<tr>
<td>Xylan</td>
<td>19.53</td>
</tr>
<tr>
<td>Lignin</td>
<td>15.76</td>
</tr>
<tr>
<td>Ash</td>
<td>4.93</td>
</tr>
<tr>
<td>Acetate</td>
<td>1.81</td>
</tr>
<tr>
<td>Protein</td>
<td>3.10</td>
</tr>
<tr>
<td>Extractives</td>
<td>14.65</td>
</tr>
<tr>
<td>Arabinan</td>
<td>2.38</td>
</tr>
<tr>
<td>Galactan</td>
<td>1.43</td>
</tr>
<tr>
<td>Mannan</td>
<td>0.60</td>
</tr>
<tr>
<td>Sucrose</td>
<td>0.77</td>
</tr>
<tr>
<td>Total structural carbohydrate</td>
<td>58.99</td>
</tr>
<tr>
<td>Total structural carbohydrate + sucrose</td>
<td>59.76</td>
</tr>
<tr>
<td>Moisture (bulk wt. %)</td>
<td>20.00</td>
</tr>
</tbody>
</table>

3.3.3 Handling and Pretreatment

During handling, corn stover is homogenized and preprocessed to uniform-format moisture content, size (less than 0.25 inches), and density. Pretreatment converts hemicellulose into soluble sugars via hydrolysis reactions with the inputs of ammonia, sulphuric acid, and steam. Pretreatment also eases enzymatic hydrolysis by reducing cellulose chain length and cell wall structure disruption.

3.3.4 Enzymatic Hydrolysis/Saccharification and Fermentation

In this area, cellulase enzymes are brought in to convert cellulose to glucose by first going through the high-solids continuous reactor followed by parallel reactors and batch reactors. The formed glucose and other sugars from pretreatment are then co-fermented to ethanol using Zymomonas mobilis.
3.3.5 Enzyme Production

Cellulase enzyme is produced in this area to facilitate the formation of glucose from cellulose by hydrolysis using inputs of nutrients and glucose. Cellulase is composed of different enzymes that perform different roles i.e. a) exoglucanases outbreak the ends of crystalline cellulose fibers; b) endoglucanases reduces the chain length by randomly attacking the cellulose fiber and c) β-glucosidase converts small cellulose fragments to glucose by hydrolysis.

3.3.6 Recovery and Wastewater Treatment

The recovery area recovers ethanol, solids, and water by separating the fermentation broth. Recovery of ethanol from the fermentation beer is achieved using molecular sieve adsorption and distillation. To protect the environment, wastewater (WW) from different streams must be treated and recycled, and it is assumed to be safe for reuse. This method minimizes the fresh makeup water that might be required. Aerobic and anaerobic processes are used to digest organic matter in the streams, and biogas is produced by anaerobic digestion that is transferred to the boiler/combustor area. Solids/lignin is separated from the rest using a vacuum filter press.

3.3.7 Boiler/Combustor and Storage

Production of electricity and steam is achieved by burning non-condensable gases, wastewater treatment sludge, biogas and other organic materials. In this study, 20% of the solids are forwarded to the boiler. Process chemicals, ethanol, and produced chemicals are stored in the storage area. Stored items include; gasoline denaturant used as an ethanol product denaturant, purchased enzyme, corn steep liquor, diammonium phosphate, sulfuric acid, ammonia, and water used in fire suppression.
3.3.8 Hydrothermal Liquefaction

The HTL section is an addition to the NREL ethanol model [1]. NREL’s ethanol model is publically available, and it was adapted for this study. The HTL section consists of the following subsections: bio-oil production, extraction of chemicals, and separation. The bio-oil production via HTL is adopted from Knorr et al., [24] and it has the same working principles as that of Ou et al. [25]. Figure 3-2 shows the flow diagram of hydro-oil/bio-oil production whereas Figure 3-3 shows the extraction of lignin-derived biochemicals.

The HTL section of this analysis utilizes 80% of the solids/lignin from the recovery section to produce lignin-derived biochemicals. The remaining 20% is employed to generate heat and power for the facility. This approach is hypothesized to increase biorefinery revenues from high-valued biochemicals while supporting facility energy demands. An alternative approach would be to eliminate the power generation and purchase heat and power. However, this approach may increase the environmental footprint of the process, but this analysis is beyond the scope of this study.

Separated lignin from the ethanol biorefinery is diverted to the HTL section (Figure 3-2) and pumped at 217.75 atm (3200 psig) into a crusher to form uniform and un-clustered particles. The uniform particles are mixed with recycled water and preheated with streams of hot water and oil using a heat exchanger with the hot stream outlet temperature being 350 °C. The reactor feed then proceeds to the HTL reactor operating at 350 °C and 204.14 atm (3000 psig) to produce bio-crude, gases, and biochar. Hydro-oil/bio-crude composition was modeled based on published yields of various lignin-derived biochemical products and the yields (wt%) of catechol, phenol, cresols, formic acid, acetic acid, furfural, and acetaldehyde were 28%, 7%, 11%, 0.12%, 39%, 0.02%, and 0.04% respectively (Table 3-2) [27–29]. The biochar
precipitates from the bio-crude and gases in the separator, and the flash unit operating at 347°C and 201.42 atm (2960 psig) separates the bio-crude and gases. For further processing, the bio-crude is cooled to 240°C at a pressure of 200 atm (2939 psig). Separated water is recycled. The bio-crude is forwarded to the extractor subsection.

Extraction (Figure 3-3) recovers target chemicals [using extractors (EXTRACT), pumps (PMP), mixers (MIX), distillation column (DSTWU), and separation units i.e. flash (FLASH) and decanter (DEC)] which is accomplished by simultaneously adding a hydrophobic-polar ethyl acetate solvent (ETHYL), alkali and sodium hydroxide (NAOHIN1) pumped through mixers to the first extractor (EXTRACT1). The performance of adding hydrophobic-polar solvent to bio-crude is reported by Fele et al., [32]. The addition of water (anti-solvent) and/or sodium hydroxide is necessary to improve phase separation. Solvent and anti-solvent addition to bio-crude separates and partitions the major phenolics in the organic/extract phase and partitions the water-soluble components into the aqueous phase [32]. Partitioning of aldehydes and acids in the organic phase is also possible depending on the solvent and anti-solvent being used. For example, Felle et al., [32] mentioned that using methyl isobutyl ketone (MIBK) or ethyl acetate with aqueous NaHSO₃ rinses aldehydes by reactive extraction of NaHSO₃ in the aqueous phase, and using an alkali solution with MIBK or ethyl acetate makes the acidic components precipitate from the aqueous phase in salt form. The aqueous phase is further extracted (EXTRACT3) to separate ethyl acetate (stream 3) from the rest of the chemicals in this phase. Recovered ethyl acetate is mixed with makeup solvent (MAKEUP) to be reused. The organic phase also undergoes further extraction (EXTRACT 2) with the addition of more sodium hydroxide (NAOHIN2). A flash unit (FLASH) is used to
separate sodium hydroxide (NaOH) from the organic phase. The stream numbers 27 and 26 are wastewater streams.

Table 3-2. Yield of lignin-derived chemicals [27–29].

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Yield (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catechol</td>
<td>28.37</td>
</tr>
<tr>
<td>Phenol</td>
<td>7.53</td>
</tr>
<tr>
<td>Cresols</td>
<td>11.67</td>
</tr>
<tr>
<td>Formic acid</td>
<td>0.12</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>39.00</td>
</tr>
<tr>
<td>Furfural</td>
<td>0.02</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Under the separation subsection (Figure 3-4), the extracted phases are separated into the target chemicals. Flow diagram A) shows the aqueous phase being pumped to a distillation column (DSTWU5) to separate acetaldehyde, formic acid, and acetic acid through different distillations columns. The chemicals are separated as shown on the flow diagram with acetaldehyde being separated using the distillation column (DISTALDE) from stream 3, formic acid is recovered from both streams 10 and 11, and acetic acid is separated using the distillation column (DISACT) from stream 12. The remaining streams are processed as wastewater in the biorefinery anaerobic digester. Flow diagram B) shows the organic phase being processed to separate furfural (stream 24), catechol (stream 26), phenol (stream 31), and cresols (stream 35) using a decanter, mixers, and distillation columns. More information about the streams is provided in the supporting documents.
Figure 3-1. Ethanol production and hydrothermal liquefaction hierarchy block diagram.
Figure 3-2. Hydro-oil production section.

Figure 3-3. Extraction of lignin-derived biochemicals section.

3.3.9 Techno-Economic Analysis

Aspen Plus™ 9.0 was used to build the process model to acquire the energy and material balance of ethanol production and lignin hydrothermal liquefaction. Operating conditions and energy and material balances are used to size the process equipment. Purchase costs of common equipment such as mixers and pumps are estimated using Aspen Process
Economic Analyzer (APEA) whereas custom engineered equipment purchase costs are obtained using data available to the public by scaling up quotes from public sources such as NREL reports [24]. Total Purchased Equipment Cost (TPEC) is estimated first, and direct and indirect installation costs such as instrumentation and controls, electrical systems, yard improvements, etc. are estimated as a percentage of TPEC. The total direct and indirect cost (TDIC) is the sum of total direct and indirect costs. A 20% contingency cost is included to account for unforeseen circumstances such as underestimated costs. The fixed capital investment (FCI) is a sum of TDIC and contingency cost. Land and working capital (WC) costs are then estimated. The total capital investment is the sum of FCI, WC, and land.

The annual operating costs for this 2000 dry MTPD corn Stover biorefinery are shown in Table 3-3 and include required inputs, waste disposal, byproducts credits, and fixed operating costs. The lignin-derived biochemical byproduct prices were obtained from Alibaba [33] whereas the rest of the prices were obtained from NREL report [1]. On the other hand, fixed operating costs including salaries, maintenance, and insurance and taxes were estimated using cost factors. The total salaries (TS) are based on employment numbers and salary estimates used by NREL[1]. The labor burden was estimated as 90% of TS, maintenance as 3% of inside battery limits (ISBL) equipment costs, and property insurance and tax as 0.7% of FCI. Finally, a 30-year DCFROR spreadsheet was used to calculate minimum ethanol selling prices (MESP). The Mathematica script used to compute the MPSP is provided in APPENDIX A.
Table 3-3. Variable operating prices, waste disposal, byproduct credits, and fixed operating costs.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Price ($/ MT)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Variable operating costs</strong></td>
<td></td>
</tr>
<tr>
<td>Corn Stover</td>
<td>64.5</td>
</tr>
<tr>
<td>Sulfuric acid, 93%</td>
<td>81.4</td>
</tr>
<tr>
<td>Ammonia</td>
<td>407.0</td>
</tr>
<tr>
<td>Corn steep liquor</td>
<td>51.6</td>
</tr>
<tr>
<td>Diammonium phosphate</td>
<td>895.0</td>
</tr>
<tr>
<td>Sorbitol</td>
<td>1,020.0</td>
</tr>
<tr>
<td>Purchased enzyme</td>
<td>-</td>
</tr>
<tr>
<td>Glucose</td>
<td>527.0</td>
</tr>
<tr>
<td>Ammonia</td>
<td>407.0</td>
</tr>
<tr>
<td>Host nutrients</td>
<td>745.0</td>
</tr>
<tr>
<td>Sulfur dioxide</td>
<td>276.0</td>
</tr>
<tr>
<td>Caustic</td>
<td>136.0</td>
</tr>
<tr>
<td>Boiler chemicals</td>
<td>4,530.0</td>
</tr>
<tr>
<td>FGD lime</td>
<td>181.0</td>
</tr>
<tr>
<td>Cooling tower chemicals</td>
<td>2,720.0</td>
</tr>
<tr>
<td>Makeup Water</td>
<td>0.23</td>
</tr>
<tr>
<td>Ethyl acetate</td>
<td>347.0</td>
</tr>
<tr>
<td>Sodium hydroxide</td>
<td>149.0</td>
</tr>
<tr>
<td><strong>Waste disposal</strong></td>
<td></td>
</tr>
<tr>
<td>Ash disposal</td>
<td>28.9</td>
</tr>
<tr>
<td><strong>Byproduct credit</strong></td>
<td></td>
</tr>
<tr>
<td>Electricity ($/kWh)</td>
<td>0.0572</td>
</tr>
<tr>
<td>Catechol</td>
<td>985.0</td>
</tr>
<tr>
<td>Phenol</td>
<td>1,080.0</td>
</tr>
<tr>
<td>Cresols (m-, p-, o-)</td>
<td>2,820.0</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>493.0</td>
</tr>
<tr>
<td>Formic acid</td>
<td>690.0</td>
</tr>
<tr>
<td>Furfural</td>
<td>1,030.0</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>98.5</td>
</tr>
<tr>
<td><strong>Fixed operating costs</strong></td>
<td></td>
</tr>
<tr>
<td>Total Salaries</td>
<td>-</td>
</tr>
<tr>
<td>Labor burden</td>
<td>90% of TS</td>
</tr>
<tr>
<td>Maintenance</td>
<td>3% of ISBL</td>
</tr>
<tr>
<td>Property insurance and tax</td>
<td>0.7% of FCI</td>
</tr>
</tbody>
</table>
3.3.9.1 Sensitivity analysis

During the operation of chemical plants, process parameters change and thus raising a need to evaluate parameters that might impact the MESP. Sensitivity analysis is done by varying one parameter while holding others constant to assess their impact on MESP changes. The critical parameters considered in this analysis include feedstock cost, process yields, internal rate of return (IRR), FCI, income tax rate, and others. Sensitivity analysis parameters are varied within a ±20% range. Base, low, and high cases are considered when calculating the MESP.

3.3.9.2 Uncertainty analysis

The impact of techno-economic uncertainty due to variability in key assumptions was assessed using uncertainty analysis. Uncertainty analysis employs Monte Carlo simulation to investigate the impact of simultaneous changes in multiple parameter values. In this study, key parameters identified by the sensitivity analysis were chosen for the uncertainty analysis. Table 3-4 shows the uncertainty analysis parameters with their distributions and 10%/90% quantiles. Most parameter distributions are triangular distributions using the same ranges as the sensitivity analysis. The feedstock price distribution employed historical data gathered by the Texas A&M Forestry Service [34] to identify a best-fit distribution based on Anderson-Darling test scores. The industrial electricity price distribution is based on finding a best-fit distribution of historical prices gathered by the Energy Information Administration [35]. The Monte Carlo simulation employed 10,000 random data samples to evaluate the MESP probability function.
Figure 3-4. Separation of lignin-derived chemicals from bio-oil produced under hydrothermal liquefaction detailed flow diagram. A) Aqueous Phase (AP) recovery of acetaldehyde, formic acid, and acetic acid. B) Phenolic Phase (PHL) recovery of furfural, catechol, phenols, and cresols.
Table 3-4. Uncertainty analysis parameter distributions and 10%/90% quantiles.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Distribution</th>
<th>10% Quantile</th>
<th>90% Quantile</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boiler chemicals price ($/MT)</td>
<td></td>
<td>4030.</td>
<td>5030.</td>
</tr>
<tr>
<td>Glucose to ethanol yield</td>
<td></td>
<td>0.795</td>
<td>0.905</td>
</tr>
<tr>
<td>Xylose to ethanol yield</td>
<td></td>
<td>0.784</td>
<td>0.866</td>
</tr>
<tr>
<td>H2SO4 price ($/MT)</td>
<td></td>
<td>72.4</td>
<td>90.4</td>
</tr>
<tr>
<td>IRR</td>
<td></td>
<td>0.0889</td>
<td>0.111</td>
</tr>
<tr>
<td>FCI ($MM)</td>
<td></td>
<td>518.</td>
<td>647.</td>
</tr>
<tr>
<td>Catechol price ($/MT)</td>
<td></td>
<td>876.</td>
<td>1090.</td>
</tr>
<tr>
<td>Phenol price ($/MT)</td>
<td></td>
<td>964.</td>
<td>1200.</td>
</tr>
<tr>
<td>Cresols price ($/MT)</td>
<td></td>
<td>2510.</td>
<td>3140.</td>
</tr>
<tr>
<td>Acetic Acid price ($/MT)</td>
<td></td>
<td>438.</td>
<td>548.</td>
</tr>
<tr>
<td>Formic acid price ($/MT)</td>
<td></td>
<td>614.</td>
<td>766.</td>
</tr>
<tr>
<td>Furfural price ($/MT)</td>
<td></td>
<td>920.</td>
<td>1150.</td>
</tr>
<tr>
<td>Acetaldehyde price ($/MT)</td>
<td></td>
<td>88.1</td>
<td>110.</td>
</tr>
<tr>
<td>Feedstock cost ($/MT)</td>
<td></td>
<td>54.8</td>
<td>74.8</td>
</tr>
<tr>
<td>Industrial electricity price ($/kwh)</td>
<td></td>
<td>5.08</td>
<td>7.26</td>
</tr>
</tbody>
</table>

3.4 Results and Discussion

3.4.1 Mass and Energy Balance

The Aspen Plus™ process model assumed a 2000 dry MTPD of corn stover that gets converted into 352.5 MTPD of ethanol (Table 3-5) and other lignin-derived biochemicals. Among the lignin-derived chemicals, acetic acid yielded 166.6 MTPD accounting for 39% of the total chemical yield followed by 122.9 MTPD (29%) catechol, and 46.2 MTPD (11%) cresols (m-, p-, and o-cresol). The lowest yield observed was 2.9 MTPD of furfural accounting for less than 1% of the biochemical yields. The process model lignin-derived chemical purities were designed to meet or exceed market purities for a given price point at the expense of
recovery rates (Table 3-5). Recovery rates are defined as the ratio of the amount recovered to
the output of the HTL reactor. Acetaldehyde has the highest recovery rate of 99.8% followed
by catechol (98.9%), and acetic acid (98.7%). The lowest recovery rates were obtained for
phenol and furfural at 63.7% and 32.7%, respectively. The recovery rate was based on the mass
flow rate of a particular chemical in the outlet stream in relation to the HTL reactor outlet
stream, and purity was based on the mass fraction of the chemical at the outlet stream.

Table 3-5. Ethanol and lignin-derived chemicals production output, computed and market
purity levels, recovery rates, and market prices for a 2000 MTPD biorefinery.

<table>
<thead>
<tr>
<th>Product</th>
<th>Output (MTPD)</th>
<th>Computed purity (%)</th>
<th>Market purity (%)</th>
<th>Recovery rate (%)</th>
<th>Market price</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
<td>352.5</td>
<td>99.3</td>
<td>99.5</td>
<td>97.1</td>
<td>1.94[^a]</td>
</tr>
<tr>
<td>Catechol</td>
<td>122.9</td>
<td>98.7</td>
<td>99.0</td>
<td>98.9</td>
<td>990[^b]</td>
</tr>
<tr>
<td>Phenol</td>
<td>20.8</td>
<td>99.7</td>
<td>99.0</td>
<td>63.6</td>
<td>1090[^b]</td>
</tr>
<tr>
<td>Cresols</td>
<td>46.2</td>
<td>99.9</td>
<td>99.3</td>
<td>91.6</td>
<td>2850[^b]</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>166.6</td>
<td>99.9</td>
<td>99.6</td>
<td>98.7</td>
<td>500[^b]</td>
</tr>
<tr>
<td>Formic acid</td>
<td>52.1</td>
<td>97.7</td>
<td>85.0</td>
<td>98.1</td>
<td>690[^b]</td>
</tr>
<tr>
<td>Furfural</td>
<td>2.9</td>
<td>96.4</td>
<td>98.5</td>
<td>32.7</td>
<td>1040[^b]</td>
</tr>
<tr>
<td>Acetaldehyde</td>
<td>17.3</td>
<td>99.9</td>
<td>99.0</td>
<td>99.8</td>
<td>100[^b]</td>
</tr>
</tbody>
</table>

[^a][36] ($/gal)  \[ ^b][33] ($/MT)

The process simulation model also provided results of wastewater contribution per area/section
with 9158 MTPD from the recovery section (Area 500), 936 MTPD from pretreatment section
(Area 200), 216 MTPD from utilities (Area 900), and 72 MTPD from the boiler (Area 800).
The treated wastewater is recycled into different areas of the chemical plant with 144 MTPD
being delivered to the boiler section. Biogas also produced from the WWT (Area 600) is
delivered to the boiler section at 561 MTPD with 65% being CO₂ and 25% CH₄ as the gas
composition. Recovered gases and solid waste are delivered at a rate of 329 MTPD to the boiler
and 309 MTPD respectively from the recovery section with a mass fraction of 35% lignin.
Approximately 80% of the solids recovered are diverted to HTL section. The hydrophobic-polar solvent of ethyl acetate and alkali solvent of sodium hydroxide are assumed to be recovered for recycling.

### 3.4.2 Capital and Operating Cost Analysis

The different costs of the biorefinery plant are shown in Table 3-6. The assumed 2000 MTPD biorefinery has a total purchased equipment cost of $114.5 MM and a total installed cost (TIC) of $345.7 MM, that is higher than computed by [1] because of the added HTL section. The HTL section accounts for 40% of the total TIC (Figure 3-5) and is higher probably because of the HTL reactors, extractors, and distillation columns that have not been used and sized before. The Total capital investment is $624.5MM.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Assumption</th>
<th>Cost ($ MM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total purchased equipment cost (TPEC)</td>
<td>1</td>
<td>114.5</td>
</tr>
<tr>
<td>Purchased equipment installation</td>
<td>0.39</td>
<td>44.6</td>
</tr>
<tr>
<td>Instrumentation and controls</td>
<td>0.26</td>
<td>29.8</td>
</tr>
<tr>
<td>Piping</td>
<td>0.1</td>
<td>11.4</td>
</tr>
<tr>
<td>Electrical systems</td>
<td>0.31</td>
<td>35.5</td>
</tr>
<tr>
<td>Buildings (including services)</td>
<td>0.29</td>
<td>33.2</td>
</tr>
<tr>
<td>Yard improvements</td>
<td>0.12</td>
<td>13.7</td>
</tr>
<tr>
<td>Service facilities</td>
<td>0.55</td>
<td>63.0</td>
</tr>
<tr>
<td>Total installed cost (TIC)</td>
<td>3.02*TPEC</td>
<td>345.7</td>
</tr>
<tr>
<td>Engineering</td>
<td>0.32</td>
<td>36.6</td>
</tr>
<tr>
<td>Construction</td>
<td>0.34</td>
<td>38.9</td>
</tr>
<tr>
<td>Legal and contractor’s fees</td>
<td>0.23</td>
<td>26.3</td>
</tr>
<tr>
<td>Indirect cost (IC)</td>
<td>0.89*TPEC</td>
<td>101.9</td>
</tr>
<tr>
<td>Total direct and indirect costs (TDIC)</td>
<td>TIC + IC</td>
<td>447.6</td>
</tr>
<tr>
<td>Contingency</td>
<td>20% of TDIC</td>
<td>89.5</td>
</tr>
<tr>
<td>Fixed capital investment (FCI)</td>
<td>TDIC + Contingency</td>
<td>537.1</td>
</tr>
<tr>
<td>Working capital (WC)</td>
<td>15% of FCI</td>
<td>80.6</td>
</tr>
<tr>
<td>Land use</td>
<td>6% of TPEC</td>
<td>6.9</td>
</tr>
<tr>
<td>Total capital investment (with land)</td>
<td>FCI+ WC + Land</td>
<td>624.5</td>
</tr>
</tbody>
</table>
Results for annual operating costs are presented in Table 3-7. The major costs are feedstock and handling with an annual cost of $45.2 MM, $19.4 MM for capital depreciation, $12.3 for fixed costs, $11.8 MM for enzyme production, and $10.2 MM for average income tax.

![Table 3-7: Total Biorefinery Equipment Cost by Area for Corn Stover Conversion to Ethanol and Lignin-Derived Chemicals](image)

Figure 3-5. Total biorefinery installed equipment cost by area for corn stover conversion to ethanol and lignin-derived chemicals.
Table 3-7. Annual operating costs of ethanol and hydrothermal liquefaction of lignin to chemicals.

<table>
<thead>
<tr>
<th>Item</th>
<th>Price (SMM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock &amp; handling</td>
<td>45.2</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>1.5</td>
</tr>
<tr>
<td>Ammonia</td>
<td>5</td>
</tr>
<tr>
<td>Enzyme production</td>
<td>11.8</td>
</tr>
<tr>
<td>Raw materials - others</td>
<td>7.1</td>
</tr>
<tr>
<td>Waste disposal</td>
<td>0.7</td>
</tr>
<tr>
<td>Lignin-derived biochemicals</td>
<td>-139.1</td>
</tr>
<tr>
<td>Fixed costs</td>
<td>12.3</td>
</tr>
<tr>
<td>Capital depreciation</td>
<td>19.4</td>
</tr>
<tr>
<td>Average income tax</td>
<td>10.2</td>
</tr>
<tr>
<td>Average return on investment</td>
<td>79.1</td>
</tr>
</tbody>
</table>

The minimum ethanol selling price (MESP) computed while considering the lignin-derived biochemicals’ market prices (Table 3-5) is $1.03/gal. The computed MESP is affected by the biochemical yields and market chemical price. The MESP of $1.03/gal with lignin-derived biochemical production is lower than the $1.94/gal average selling price of ethanol for the year 2007 [36] and much lower than the $2.15/gal obtained while considering only ethanol production [1].

Production of lignin-derived chemicals using the HTL process and separation of the produced chemicals is in the early stages of development; thus, more investment in terms of fixed and operating cost might be required for future commercial biorefinery plants than those obtained in this analysis. Additional laboratory and pilot scale experiments could lower the costs and commercialization risks of pioneer facilities.
3.4.3 Minimum Ethanol Selling Price Sensitivity Analysis

Due to several sources of uncertainty such as lack of enough data, assumptions made, and the novelty of the proposed process, sensitivity analysis is done on the MESP. The most influential factors on MESP are determined through sensitivity analysis (Figure 3-6). Sensitivity analysis was done by employing a ±20% to the base case values of key parameters used in TEA. The most influential factors on MESP identified were fixed capital investment, and internal rate of return (IRR), feedstock price. Among the chemical prices, cresols, catechol, and acetic acid are the most influential chemicals on the MESP probably due to their higher market price and chemical yield. Sensitivity analysis was also performed on the prices of water, sodium hydroxide, cooling tower chemicals and boiler chemicals but these did not substantially affect MESP.

![Sensitivity analysis of MESP on selected parameters](image)

Figure 3-6. Sensitivity analysis of MESP on selected parameters.

3.4.4 Minimum Ethanol Selling Price Uncertainty Analysis

The results of the uncertainty analysis are shown in Figure 3-7. The MESP ranges between $0.4 and $1.8 per gallon with 90% probability of being between $0.82 and $1.30 per
gallon. The base case estimate of $1.03/gal falls close to the expected mean of $1.06 per gallon. A limitation of this uncertainty analysis is that it does not include major risk factors such as a significant drop in product yields or increase in costs which are both more common in a pioneer plant. Thus, the uncertainty for ethanol biorefineries adopting this lignin-to-chemicals strategy could still face higher levels of price uncertainty.

Figure 3-7. Minimum ethanol-selling price probability and cumulative density functions
3.5 Conclusions

This analysis evaluated the minimum ethanol selling price for a 2000 MTPD corn stover biorefinery integrated with hydrothermal liquefaction to produce biochemicals from the lignin co-product of lignocellulosic ethanol production.

A MESP of $1.03 ± 0.19/gal was computed considering the production of lignin-derived biochemicals. The most influential factors on MESP identified were fixed capital investment, IRR, and feedstock price as well as cresols, catechol, and acetic acid prices. Total purchased equipment cost, total installed cost (TIC), and total capital investment are $114.5 MM, $345.7 MM, and $624.5 MM respectively.

Lignin-derived chemicals using HTL and separation of the produced chemicals are in the early stages of development, thus more investment in terms of fixed and operating cost might be required for future commercial biorefinery plants than those obtained in this analysis. The uncertainty for ethanol biorefineries adopting this lignin-to-chemicals strategy could still face higher levels of price uncertainty. Fuel/ethanol production accompanied by HTL chemical production from lignin is a promising technological development that will increase the profitability and competitiveness of bio-products to fossil fuel-based products.

3.6 References


[34] Texas A&M Forest Service. Texas Timber Price Trends Reports. 2014.


CHAPTER 4. TECHNO-ECONOMIC ANALYSIS OF 2,5-DIMETHYLFURAN (DMF) PRODUCTION USING AN ELECTROLYZER/ELECTROCHEMICAL REACTOR

4.1 Abstract

Electrochemical production of bioproducts is a novel and promising technological process. The objective of this research is to evaluate the techno-economic feasibility of producing 2,5-dimethylfuran (DMF) using an electrolyzer/electrochemical reactor. A 300-metric ton per day (MTPD) fructose biorefinery was considered producing 34 MTPD levulinic acid as the first byproduct and 174 MTPD of hydroxymethylfurfural/5-hydroxymethylfurfural (HMF). The HMF is further converted to DMF through electrochemical approach producing 95 MTPD of 2,5-dimethylfuran (DMF) and the other byproducts being 59 MTPD 2,5-bis(hydroxymethyl)furan and 21 MTPD 5-methylfurfuryl alcohol. A minimum product-selling price (MPSP) of $12.51/gal of DMF was estimated. Sensitivity analysis results showed that DMF yield, fixed capital investment, internal rate of return (IRR), 2,5-bis(hydroxymethyl)furan price, and fructose feedstock price are the most influential parameters on the MPSP. The biorefinery considered in this analysis requires a total purchased equipment cost (TPEC) of $146 MM, $442 MM of total installed cost (TIC), and $799 MM as the total capital investment. Using an electrolyzer to produce bioproducts is in the early stages of development thus more research should be done to enable commercialization of the process.

Keywords: 2,5-dimethylfuran, hydroxymethylfurfural, fructose, electrolyzer
4.2 Introduction

The current world population (as of 2017) is more than 7 billion people with an 80% probability to increase to a range of 9.6 billion and 12.3 billion people by 2100 [1]. The population increase presents a challenge of supplying sustainable energy and chemicals. To supply such demand, biofuels and biochemicals must be the number one priority compared to petroleum/oil-based fuels and chemicals reason being that there is a declining supply of petroleum resources and the combustion of petroleum products has negative effects on the environment [2,3]. The fossil-based sector supplies more than one-third of the world primary energy supply [4] thus the remaining demand has to come from biomass-based resources.

Biomass is organic material of recent biological origin [5] that can be upgraded through biochemical and thermochemical processes into valuable chemicals. Biomass is renewable and abundant, thus being a sustainable alternative to produce biofuels and intermediate valuable biochemicals such as ketones, alcohols, carboxylic acids, and aldehydes. These chemicals are used to produce polymeric products and drugs [6]. There is growing interest in producing biochemicals to supplement lower valued biofuels. Biofuels are currently not competitive [7] with fossil fuels due to low crude oil prices and the high capital investment required to construct biorefineries. Among the many biochemicals that could be produced, hydroxymethylfurfural/5-hydroxymethylfurfural (HMF) from fructose is attractive because of its high value as a chemical intermediate.

HMF production proceeds through a series of complex chemical reactions from lignocellulose that include hydrolysis to produce glucose from cellulose, isomerization to produce fructose from glucose, and dehydration to produce HMF from fructose [8,9].
Production of HMF from fructose is regarded as an efficient utilization of biomass [6,10]. HMF is an intermediate that can be converted to different products such as 2,5-dimethylfuran (DMF) that can be used as a liquid fuel in the transport sector, 2,5-dihydroxy methylfuran, 2,5-bis(hydroxymethyl)tetrahydrofuran, and 2,5-furandicarboxyl acid that can be used for polyester production [11].

Kazi et al., [12] performed a techno-economic analysis of producing hydroxymethylfurfural (HMF) and 2,5-dimethylfuran (DMF) from fructose. The HMF biorefinery utilized a biphasic continuously stirred tank reactor (CSTR) yielding both organic and aqueous phases that were further processed whereas the DMF biorefinery utilized a CSTR reactor with 3-train fixed bed catalytic plug flow tubular reactor (PFTR). A 300 metric tonne per day (MTPD) flow rate of fructose and a 20-year plant life were assumed. DMF production required $188.58 MM as the total capital investment cost resulting in a $7.63/gal DMF minimum product selling price (MPSP) that was highly sensitive to feedstock cost, product yield, total purchased equipment cost (TPEC), and byproduct price. The MPSP for HMF estimated was $5.03/gal with a total capital investment of $158.4 MM. All prices are in 2007 dollars.

Electrochemical processes provide an alternative approach to produce DMF using an electrolyzer. This approach is attractive because of its potential for replacing thermal heat with renewable electrons. Nilges and Schroder [13] reported that 5-hydroxymethylfurfural could be electrochemically converted to DMF, and they claimed to be the first for having done so at the highest selectivity of 35.6%. The process utilized an electrolyzer with material inputs of HMF, 0.5 M sulphuric acid in a mixture of 1:1 ethanol and water operating at room temperature and ambient pressure. Currently, the costs of DMF production using an electrolyzer reactor are
not available in the public literature. Thus, the purpose of this paper is to assess the techno-
economics of a biorefinery producing DMF using an electrochemical process.

4.3 Materials and Method

The design process flow modeled by Kazi et al., [12] is modified to have an electrolyzer
instead through the production of DMF though the production of HMF from fructose remains
the same and no modeling was done for this part due to lack of electrochemical conversion
data from literature of HMF from fructose. Profitability, process modeling, and cost
evaluations were determined using techno-economic analysis (TEA). Aspen Plus™ 9.0 was
used for process modeling. Common equipment capital cost was obtained using Aspen Process
Economic Analyzer, while multifaceted customised equipment costs were estimated by
scaling-up quotes from the public literature using the economies of scale power law [14]. The
electrolyzer cost was estimated using an approach from Goodridge and Scott [15]. Return on
investment was estimated using a 30-year discounted cash flow rate-of-return (DCFROR). The
major assumptions in the analysis are outlined below.

- The feedstock is fructose flowing at 300 MTPD as modeled by Kazi et al., [12]
  producing 174 metric tonnes/day (MTPD) of HMF that is modeled through an
electrolyzer to produce DMF.
- Biorefinery lifetime is assumed to be 30 years.
- A 10% internal rate of return (IRR) and 40% equity are assumed.
- Input raw material costs are $300/ MT for fructose, $1350/ MT for butanol, $93.7/ MT
  for hydrochloric acid (HCl), $1.1/ MT for water, and $100/ MT for sulphuric acid [12].
Assumed byproducts are 2,5-bis(hydroxymethyl)furan, 5-methylfurfuryl alcohol, and levulinic acid with the market price of $2500/MT, $3000/MT, and $300/MT respectively.

An electrolyzer powered with renewable electricity will facilitate the conversion of HMF to the desired products thus being the source to drive electrochemical reactions.

Sulphuric acid is bought in year one with a makeup of 1% of the original quantity in the following years.

Electrolyzer operates at room temperature and ambient pressure.

Uninstalled capital cost of $10,000 per square meter of the geometric area was assumed [16].

No use of hydrogen gas instead water is used as the proton source.

A selectivity of (>80%) and current efficiency (>90%) at a superficial current density of 1 kA/m$^2$ are assumed.

Average renewable electricity price is $0.055/kWh [16] and is assumed to be from a non-fossil based resource.

All processes operate under steady-state conditions.

4.3.1 Feedstock

In this study, the biorefinery processes fructose to HMF (part 1) and then HMF is electrochemically processed to DMF (part 2). HMF is an organic compound that is produced from carbohydrates like fructose, cellulose, and others by dehydration that melts at 30 to 34°C and has a yellow tint [17]. In the biorefinery industry, HMF is a critical building block that can be used to produce compounds such as 2, 5-diformylfuran; 2,5-furandicarboxylic acid (FDCA); 2,5-furandicarbaldehyde, 2,5-dihydroxymethylfuran, and 2,5-dimethylfuran (DMF).
which is considered as an alternative liquid biofuel. HMF has been referred to as a “sleeping giant” and an intermediate bio-based chemical by Kazi et al., [12] and HMF is ranked among the top promising biomass chemical by the US DOE’s study [18] due to its ability to substitute fossil fuel-based products as a building block.

### 4.3.2 Process Model Description

The process diagram consists of two parts (part 1 and 2): Figure 4-1 (Part 1) is the process diagram illustrating the steps to produce HMF from fructose and consists of the following areas: biphasic reactor (A100), partial separation (A200), HMF purification (A300), and levulinic and fructose separation (A400). In A100, HMF is produced from fructose using a biphasic reactor in a 2-phase system of butanol and water at 180°C for three minutes and HCl acts as the catalysts. In A200, there is a partial separation of wastewater, HMF from fructose and levulinic acid by washing with water. Purification of HMF (99% purity) occurs in A300 while the separation of the byproduct levulinic acid (98% purity) from fructose occurs in A400. For more detailed description the reader is referred to Kazi et al., [12].

Figure 4-2 (Part 2) shows the HMF to DMF process flows and consists of the following areas: pre-handling (A500), electrolyzer (A600), sulfuric acid recovery (A700) byproduct recovery (A800), and DMF separation (A900). During pre-handling, the HMF is well-mixed with other inputs that include ethanol, water and sulfuric acid (HMF: water: ethanol: ratio was 1:1:1). The outlet stream from the mixer is then pumped to the electrolyzer [13,19]. There were no other ratios of water: ethanol that we came across, and these were selected because a full conversion of HMF to DMF was achieved according to Nilges and Schroder [13]. The products from the electrolyzer are forwarded to a distillation column in which sulfuric acid is recovered as the heavy end at 99.98% purity for recycling. Ethanol and water are also recyclable streams.
The electrolyzer is assumed to be supplied with excess renewable electricity from sources such as wind and solar that require a storage medium. By using such resources, we anticipate solving a storage challenge of electrical energy into chemical energy. From the Renewable Electricity Future Study (RE Futures) [20], it is possible to have the U.S. electricity system dominated by renewable resources with a supply of more than 80% of which 50% can be produced from solar PV and wind based on commercially available technologies today in conjunction with a more flexible electric system by 2050. The electrochemical conversion was modeled in Aspen Plus™ 9.0 as a Ryield reactor operating at steady state conditions. The byproducts 2,5-bis(hydroxymethyl)furan and 5-methylfurfuryl alcohol are recovered using distillation columns \{(D1- reflux ratio =2, condenser and reboiler pressure = 25 atm, light key component = 5-methylfurfuryl alcohol and heavy key component = sulphuric acid), (D2 – number of stages =3, condenser and reboiler pressure = 1 atm, light key component = DMF and heavy key component = 5-methylfurfuryl alcohol)\} and finally DMF is recovered in A900 using one decanter and two distillation columns (Figure 4-2) \{(D3 - number of stages =3, condenser and reboiler pressure = 1 atms, light key component = ethanol, and heavy key component = DMF), (D4 -reflux ratio =0.5, condenser and reboiler pressure = 1 atms, light key component = DMF, and heavy key component = 2,5-bis(hydroxymethyl)furan)\}

4.3.3 Techno-Economic Analysis (TEA)

TEA was employed using Aspen Plus™ 9.0 to acquire material and energy balances of the process model for DMF production from HMF (part 2). Operating conditions, material, and energy balances are used to size the process equipment. Common equipment such as pump procurement cost is appraised using Aspen Process Economic Analyzer while custom
engineered equipment purchase costs are obtained using data available to the public by scaling up quotes from public sources such as NREL reports [21]. Total purchased equipment cost (TPEC) is computed first, then fixed capital investment (FCI), and lastly the total project investment (TPI) as suggested by Peters and Timmerhaus [22]. Part 1 process diagram TPEC were obtained from Kazi et al., [12]. TPEC from part 1 and part 2 process diagrams were combined to obtain the total TPEC cost. Estimation of FCI and TPI is achieved by computing different parameters as a percentage of TPEC (Table 4-1). The contingency cost was included to account for unforeseen circumstances such as delays, underestimated equipment cost, etc. Investment returns were computed using a 30-year discounted cash flow rate of return (DCFROR) to compute the minimum product selling price (MPSP). Some of the assumptions used in DCFROR are presented in Table 4-2.

The following steps were followed to estimate the electrolyzer cost: actual molar flow rate of the main product was obtained from Aspen Plus and then multiplied with the operating hours. The total number of Coulombs were then obtained (number of electrons for the dehydration of HMF to DMF are known) followed by total amperes and then total area. The uninstalled cost was finally obtained by multiplying the cost per square meter of the area with the total area. On the other hand, electricity cost was obtained by linear scaling-up of the required electricity by that obtained by Oloman and Li [16].
Figure 4-1: Hierarchy blocks for HMF production from fructose (part 1)
Source [12]

Figure 4-2: Process flow diagram of the electrochemical conversion of HMF to DMF (part 2).
Table 4-1: Assumed total capital investment parameters [22].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Assumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total purchased equipment cost (TPEC)</td>
<td>100%</td>
</tr>
<tr>
<td>Purchased equipment installation</td>
<td>39%</td>
</tr>
<tr>
<td>Instrumentation and controls</td>
<td>26%</td>
</tr>
<tr>
<td>Piping</td>
<td>10%</td>
</tr>
<tr>
<td>Electrical systems</td>
<td>31%</td>
</tr>
<tr>
<td>Buildings (including services)</td>
<td>29%</td>
</tr>
<tr>
<td>Yard improvements</td>
<td>12%</td>
</tr>
<tr>
<td>Service facilities</td>
<td>55%</td>
</tr>
<tr>
<td>Total installed cost (TIC)</td>
<td>3.02*TPEC</td>
</tr>
<tr>
<td>Engineering</td>
<td>32%</td>
</tr>
<tr>
<td>Construction</td>
<td>34%</td>
</tr>
<tr>
<td>Legal and contractor’s fees</td>
<td>23%</td>
</tr>
<tr>
<td>Indirect cost (IC)</td>
<td>0.89*TPEC</td>
</tr>
<tr>
<td>Total direct and indirect costs (TDIC)</td>
<td>TIC + IC</td>
</tr>
<tr>
<td>Contingency</td>
<td>20% of TDIC</td>
</tr>
<tr>
<td>Fixed capital investment (FCI)</td>
<td>TDIC + Contingency</td>
</tr>
<tr>
<td>Working capital (WC)</td>
<td>15% of FCI</td>
</tr>
<tr>
<td>Land use</td>
<td>6% of TPEC</td>
</tr>
<tr>
<td>Total capital investment (with land)</td>
<td>FCI+ WC + Land</td>
</tr>
</tbody>
</table>

Table 4-2: DCFOR assumed parameters and their values.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equity</td>
<td>40%</td>
</tr>
<tr>
<td>Loan Interest</td>
<td>7.5%</td>
</tr>
<tr>
<td>Loan Term, years</td>
<td>10</td>
</tr>
<tr>
<td>Internal rate of return</td>
<td>10%</td>
</tr>
<tr>
<td>Income Tax Rate</td>
<td>35%</td>
</tr>
<tr>
<td>Salvage value</td>
<td>0</td>
</tr>
<tr>
<td>Years of construction</td>
<td>3</td>
</tr>
</tbody>
</table>
4.3.4 Sensitivity Analysis

The minimum product selling price (MPSP) in most cases is affected by the variation of different process parameters during the operation of a biorefinery. Sensitivity analysis computes the MPSP by varying one parameter at a time while holding other parameters constant. The following parameters were considered to impact the MPSP: feedstock price, product yield, TPEC, IRR, byproduct(s) price, income tax rate, and others. The base case scenario of the process parameters is manipulated by considering a ±20% case when computing the MPSP. In practice, several parameters could vary simultaneously though sensitivity analysis considers one parameter at a time.

4.4 Results and Discussion

4.4.1 Aspen Model Results

The analysis assumed a 300 MTPD flow of fructose to produce HMF (part 1) with butanol, water, and hydrochloric acid as other required inputs. Part 2 process flow diagram analyzed a 174 MTPD of HMF with 1:1:1 ratio of the ethanol-water mixture with sulphuric acid. The biorefinery produces 24 MTPD of levulinic acid, 174 MTPD of HMF, 59 MTPD of 2,5-bis(hydroxymethyl)furan, 21 MTPD of 5-methylfurfuryl alcohol, and 95 MTPD of DMF (Table 4-3 and Figure 4-3). The DMF yield rate of 94.95 MTPD as the main product for our analysis is slightly lower than that obtained by Kazi et al., (96.60 MTPD) [12] probably due to some DMF having been lost in wastewater.
Table 4-3: Fructose conversion to DMF process model results.

<table>
<thead>
<tr>
<th>Description</th>
<th>Quantity</th>
<th>Unit</th>
<th>Purity (%)</th>
<th>Recovery rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Major inputs</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fructose</td>
<td>300</td>
<td>MTPD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Butanol</td>
<td>1.37</td>
<td>MTPD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HCl</td>
<td>3.83</td>
<td>MTPD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ethanol</td>
<td>174</td>
<td>MTPD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>986.27</td>
<td>MTPD</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Process yields</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HMF</td>
<td>174</td>
<td>MTPD</td>
<td>99.34(^{a})</td>
<td></td>
</tr>
<tr>
<td>2,5-bis(hydroxymethyl)furan</td>
<td>59</td>
<td>MTPD</td>
<td>99.83</td>
<td>99.88</td>
</tr>
<tr>
<td>5-methylfurfuryl alcohol</td>
<td>21</td>
<td>MTPD</td>
<td>92.95</td>
<td>99.96</td>
</tr>
<tr>
<td>Levulinic acid</td>
<td>34</td>
<td>MTPD</td>
<td>97.66(^{a})</td>
<td></td>
</tr>
<tr>
<td>DMF</td>
<td>95</td>
<td>MTPD</td>
<td>99.76</td>
<td>99.70</td>
</tr>
<tr>
<td>Required electricity</td>
<td>120</td>
<td>MW</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^{a}[12]\)

Also, from the model simulation (Figure 4-2), we computed the purity and recovery rates of the byproducts and the main product as shown in Table 4-3. The purity of recovered 2,5-bis(hydroxymethyl)furan and DMF are above 99% whereas that of 5-methylfurfuryl alcohol is slightly lower compared to that of the two at 93% probably due to the presence of other products in its outlet stream that are not worth to remove compared to the cost needed. On the other hand, the recovery rates of all the two byproducts and the main product, DMF are higher than 99%. From part 1, the HMF purity obtained was 99% whereas that of levulinic acid was 98%.

4.4.2 Economic Results

The major economic results are presented in Table 4-4 and Table 4-5. The minimum product selling price (MPSP) was estimated to be $12.51/gal of DMF which is approximately 15% higher than $10.94/gal ($2011) as obtained by Kazi et al et., [12]. The difference in MPSP
could be attributed to the expensive electrolyzer that is considered in this analysis and to the best of our knowledge this is the first of its kind TEA work for DMF production via electrochemical processing. The higher DMF MPSP could also be attributed to a lower yield difference of 1.65 MTPD for this analysis obtained or due to the higher DMF purity of 99.76% compared to 97.74% c. The $10.94/gal ($2011) obtained by Kazi et al. et., [12] was obtained assuming 100% equity and when we consider the same condition, the MPSP increases from $12.51/gal of DMF to $13.41/gal of DMF. The full DCFROR is provided in APPENDIX B.

The biorefinery considered in this analysis requires a total purchased equipment cost (TPEC) of $146 MM and a total installed cost (TIC) of $442 MM compared to $174.8 MM (2011$) estimated by Kazi et al., [12]. The total capital investment including land is $799 MM ($790 MM excluding land) of this analysis and that estimated by Kazi et al., [106] is $270 MM excluding land. Annual operating costs are presented in Table 4 5 with $45 MM for fructose cost, $44 MM for ethanol, and $29 MM for total fixed operating costs representing 36%, 35%, and 23% respectively of the total annual costs.
Figure 4-3: Aspen Plus process flow diagram of electrochemical conversion of HMF to DMF.
Table 4-4: Fructose to DMF economic analysis results (2011$).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Assumption</th>
<th>Cost ($MM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total purchased equipment cost (TPEC)</td>
<td>1</td>
<td>146</td>
</tr>
<tr>
<td>Purchased equipment installation</td>
<td>0.39</td>
<td>57</td>
</tr>
<tr>
<td>Instrumentation and controls</td>
<td>0.26</td>
<td>38</td>
</tr>
<tr>
<td>Piping</td>
<td>0.1</td>
<td>15</td>
</tr>
<tr>
<td>Electrical systems</td>
<td>0.31</td>
<td>45</td>
</tr>
<tr>
<td>Buildings (including services)</td>
<td>0.29</td>
<td>42</td>
</tr>
<tr>
<td>Yard improvements</td>
<td>0.12</td>
<td>18</td>
</tr>
<tr>
<td>Service facilities</td>
<td>0.55</td>
<td>81</td>
</tr>
<tr>
<td>Total installed cost (TIC)</td>
<td>3.02*TPEC</td>
<td>442</td>
</tr>
<tr>
<td>Engineering</td>
<td>0.32</td>
<td>47</td>
</tr>
<tr>
<td>Construction</td>
<td>0.34</td>
<td>50</td>
</tr>
<tr>
<td>Legal and contractor’s fees</td>
<td>0.23</td>
<td>34</td>
</tr>
<tr>
<td>Indirect cost (IC)</td>
<td>0.89*TPEC</td>
<td>130</td>
</tr>
<tr>
<td>Total direct and indirect costs (TDIC)</td>
<td>TIC + IC</td>
<td>572</td>
</tr>
<tr>
<td>Contingency</td>
<td>20% of TDIC</td>
<td>114</td>
</tr>
<tr>
<td>Fixed capital investment (FCI)</td>
<td>TDIC +</td>
<td>687</td>
</tr>
<tr>
<td>Working capital (WC)</td>
<td>15% of FCI</td>
<td>103</td>
</tr>
<tr>
<td>Land use</td>
<td>6% of TPEC</td>
<td>9</td>
</tr>
<tr>
<td>Total capital investment (with land)</td>
<td>FCI+ WC + Land</td>
<td>799</td>
</tr>
</tbody>
</table>

4.4.3 Sensitivity Analysis Results

The sensitivity analysis results were computed with ±20% range for all parameters that were thought to have the most influential on the MPSP and are presented in Figure 4-4. The DMF yield has the most influential effect on the MPSP with ±20% resulting in $10.43/gal to $15.64/gal price range. Other influential parameters in descending order are fixed capital investment, internal rate of return (IRR), 2,5-bis(hydroxymethyl)furan price, and fructose feedstock price. The least influential parameters are butanol, sulphuric acid, hydrochloric acid, and ethanol prices.
Table 4-5: Fructose to DMF annual operating costs and MPSP (2011$).

<table>
<thead>
<tr>
<th>Annual costs</th>
<th>$ MM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fructose</td>
<td>45.18</td>
</tr>
<tr>
<td>Butanol</td>
<td>0.93</td>
</tr>
<tr>
<td>HCl</td>
<td>0.18</td>
</tr>
<tr>
<td>Ethanol</td>
<td>43.67</td>
</tr>
<tr>
<td>H2SO4-first year</td>
<td>4.37</td>
</tr>
<tr>
<td>H2SO4-second year and beyond</td>
<td>0.04</td>
</tr>
<tr>
<td>Water</td>
<td>0.54</td>
</tr>
<tr>
<td>Renewable electricity</td>
<td>2.31</td>
</tr>
<tr>
<td>Other utilities</td>
<td>0.09</td>
</tr>
<tr>
<td>Total fixed operating costs</td>
<td>29.16</td>
</tr>
<tr>
<td>Total annual operating cost</td>
<td>126.47</td>
</tr>
<tr>
<td>Minimum Product Selling Price ($/gal)</td>
<td>12.51</td>
</tr>
</tbody>
</table>

Figure 4-4: Economic and technical parameters affecting the MPSP of DMF production.
4.5 Conclusions

Previous studies have evaluated the production of DMF from renewable sources. However, this study is the first of its kind to the best of our knowledge that evaluates the economic feasibility of an electrochemical conversion biorefinery to produce DMF as the main product using a renewable source of electricity and an electrolyzer operating at room temperature and ambient pressure.

The minimum product selling price was estimated at $12.51/gal of DMF and is mostly affected by DMF yield, fixed capital investment, internal rate of return (IRR), 2,5-bis(hydroxymethyl)furan price, and fructose feedstock price according to sensitivity analysis. The total capital investment required is $799 MM. The electrochemical conversion of HMF to DMF is still in the early stages of development thus to improve its commercialization potential, more research should be done.

4.6 References


CHAPTER 5. ELECTROCHEMICAL PRODUCTION OF 2-METHYLFURAN (MF) FROM FURFURAL: A TECHNO-ECONOMIC ANALYSIS

5.1 Abstract

In this study, we investigated the techno-economic feasibility of producing 2-methylfuran (MF) from furfural using an electrolyzer and renewable electricity from sources such as wind, solar, biomass, geothermal, ocean, and geothermal. Among the assumed challenges with solar and wind renewable resources is the storage challenge. Furfural flowrate assumed was 300 metric tonnes per day (MTPD) producing over 239 MTPD of 2-methylfuran (MF) with 30 MTPD of furoic acid and 30 MTPD of furfuryl alcohol as byproducts. The minimum product selling price (MPSP) is $9.07/gal and its mostly affected by MF yield, fixed capital investment, furfural price, and acetonitrile price. The different estimated costs are $79 MM, $240 MM, and $433 MM for total purchased equipment cost, total installed cost, and total capital investment cost respectively. No comparison would be performed for this study because no literature was found at the time of TEA evaluation.

Keywords: electrolyzer, renewable electricity, 2-methylfuran, furfural

5.2 Introduction

The increasing standards of living due to world population growth is exerting energy supply-demand [1–3] at 50% growth rate with 18 billion tonnes oil equivalents (toe) demand expected by 2030 globally [2,4]. Fossil-based products have been used for a long time to curb the human standards of living for decades and they are predicted to continue dominating the
supply of energy accounting for 75% global energy demand by 2035 according to IEA [4]. To reduce human dependence on fossil-based products and their effects such as global warming, due to mainly carbon dioxide emission that will increase by 27% in the year 2030 as predicted by BP [3], a lot of research is being done to produce sustainable, affordable, clean, and reliable renewable energy sources and among these is the utilization of carbohydrates to produce biochemicals and biofuels.

Carbohydrates have been reported by Nilges and Schroder [5] to be major contributors in the production of biofuels such as ethanol plus fine and platform biochemicals though still under intensive research development. Among them are the “furanics” biofuels produced from furan-based feedstock and the major precursors are furfural and 5-(hydroxymethyl)furfural (HMF) [6]. Both furfural and HMF are produced by carbohydrate dehydration and are significant building blocks [7].

Furfural is produced from carbohydrates such as hemicellulose/pentoses by dehydration and annually, more than 200,000 tons of furfural is produced from lignocellulosic biomass [5] and it has been reported in the literature as the most common renewable-based chemical produced industrially [8,9]. Furfural hydrogenation into 2-methylfuran (MF) is considered as a promising approach to produce a biofuel that can be used in the transportation sector and more particular in ignition engines [10,11].

Nilges and Schroder [5] performed laboratory experiments to investigate the electrochemical conversion of furfural to MF and they claimed having achieved a high selectivity ever. Electrochemistry approach criterion was fulfilled to produce MF from furfural
in which reactions were performed at room temperature and ambient pressure in aqueous solutions thus substituting the catalytic hydrogenation or reduction that require high temperatures. Electric current direct use in producing bioproducts instead of molecular hydrogen was reported as one way of storing renewable energy from sources such as solar and wind energy. Experiments were conducted using an H-type electrochemical cell with two chambers under potentiostatic control. The anode and cathode chambers were made of 50 mL glass cell being separated thru a cation exchange membrane. Different electrode materials and electrolyte were investigated and their effects on the selectivity. The copper (Cu) electrode material had the highest selectivity (over 80%) on MF production. Other products that were produced along with MF included furfuryl alcohol and furoic acid. They concluded that electrode material and composition of the electrolyte influence the selectivity. Thus, the objective of this research was to investigate the techno-economic analysis of producing 2-methylfuran (MF) from furfural via electrochemical process.

5.3 Materials and Method

The process design of the model was based on Nilges and Schroder [5]. Techno-economic analysis (TEA) was performed to evaluate costs and the profitability whereas process modeling was performed using Aspen Plus™ 9.0. Aspen Process Economic Analyzer was used to obtain the cost of most equipment whereas complex equipment such an electrolyzer by obtained using an approach from Goodridge and Scott [12]. A 30-year discounted cash flow rate-of-return (DCFROR) was used and the following assumptions were made for the analysis.
➢ Feedstock is furfural flowing at 300 metric tonnes per day (MTPD).

➢ Water: acetonitrile (1:1) mixed with sulphuric acid was assumed as the electrolytic with 1% makeup for sulphuric.

➢ Lifetime of the biorefinery is 30 years operating 4000 hours/year.

➢ Internal rate of return assumed was 10%.

➢ Electrolyzer operates at room temperature and ambient pressure.

➢ No use of hydrogen gas instead water is used as the proton source.

➢ Selectivity of 80% and current efficient of 90% at a superficial current density of 1 kA/m² are assumed.

➢ Continuous operation of the electrolyzer.

5.3.1 Feedstock

Furfural feedstock was considered in this analysis at a flow rate of 300 MTPD. Other inputs include 300 MTDP of water, 300 MTPD of acetonitrile, and 150 MTP of sulfuric acid for the first year and 2 MTPD for the following years. The produced products from electrochemical conversion include MF, furfuryl alcohol, and furoic acid at 80 %, 10%, and 10% selectivity respectively [5].

5.3.2 Process Model Description

The necessary material inputs are furfural, water, acetonitrile, and sulphuric acid which are well mixed in the mixer and then pumped into the electrolyzer that was modeled as a Ryield reactor that operated at room temperature and ambient pressure (Figure 5-1). The renewable electricity is from resources such as wind, solar, geothermal, ocean, biomass, and hydropower. The wind and solar renewable resources are assumed to encounter a
storage which presents an opportunity for effective utilization. From the Renewable Electricity Future Study (RE Futures) [13], it is possible to have the U.S. electricity system dominated by renewable resources with a supply of more than 80% of which 50% can be produced from solar PV and wind based on commercially available technologies today in conjunction with a more flexible electric system by 2050. The products from the electrolyzer are forwarded to a decanter that separates it into two streams. The first stream is forwarded to a centrifuge unit to separate furoic acid that was modeled as a solids separator with 0.999 fraction of liquid to liquid outlet and 0.001 liquid load of solid outlet. The second stream is forwarded to distillation unit 1 with 5 number of stages, 2 feed stages, 100 reflux ratio and 0.5 distillate to feed mole ratio. The distillation unit 2 has the same operating conditions as distillation unit one though separating different chemicals. Distillation unit 3 separates acetonitrile from the mixture of furfuryl alcohol and sulphuric acid and it was modeled with 0.5 reflux ratio, and 0.999 recovery rate of acetonitrile as the light key component. Distillation unit 4 separates furfuryl alcohol from sulphuric acid with 0.5 reflux ratio and furfuryl alcohol being the light key component at a recovery rate of 0.999. Distillation unit 5 is used to partly remove some of the wastewater from MF and was modeled with 10 number of stages and MF being the key light component with a recovery rate of 0.999 and finally decanter 2 is used to remove the remaining wastewater from MF (Figure 5-1).

5.3.3 Techno-Economic Analysis (TEA)

TEA was employed using Aspen Plus™ 9.0 to acquire material and energy balances of the process model for MF production from furfural. Operating conditions, material, and
energy balances are used to size the process equipment. Less compound equipment such as pump procurement cost is appraised using Aspen Process Economic Analyzer while custom engineered equipment purchase costs are obtained using data available to the public by scaling up like as for Swanson et al., [14]. Total purchased equipment cost (TPEC) is computed first, then fixed capital investment (FCI), and lastly the total project investment (TPI) as suggested by Peters and Timmerhaus [15].

Figure 5-1: Aspen Plus furfural to MF process model.
Estimation of FCI and TPI is achieved by computing different parameters as a percentage of TPEC (Table 5-1). The contingency cost was included to account for unforeseen circumstances such as delays, underestimated equipment cost, etc. The returns on investment were computed using a 30-year discounted cash flow rate of return (DCFROR) to compute the minimum product selling price (MPSP). Some of the assumptions used in DCFROR are presented in Table 5-2.

Table 5-1: Parameters used to compute total capital investment (TPI).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Assumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total purchased equipment cost (TPEC)</td>
<td>100%</td>
</tr>
<tr>
<td>Purchased equipment installation</td>
<td>39%</td>
</tr>
<tr>
<td>Instrumentation and controls</td>
<td>26%</td>
</tr>
<tr>
<td>Piping</td>
<td>10%</td>
</tr>
<tr>
<td>Electrical systems</td>
<td>31%</td>
</tr>
<tr>
<td>Buildings (including services)</td>
<td>29%</td>
</tr>
<tr>
<td>Yard improvements</td>
<td>12%</td>
</tr>
<tr>
<td>Service facilities</td>
<td>55%</td>
</tr>
<tr>
<td>Total installed cost (TIC)</td>
<td>3.02*TPEC</td>
</tr>
<tr>
<td>Engineering</td>
<td>32%</td>
</tr>
<tr>
<td>Construction</td>
<td>34%</td>
</tr>
<tr>
<td>Legal and contractor’s fees</td>
<td>23%</td>
</tr>
<tr>
<td>Indirect cost (IC)</td>
<td>0.89*TPEC</td>
</tr>
<tr>
<td>Total direct and indirect costs (TDIC)</td>
<td>TIC + IC</td>
</tr>
<tr>
<td>Contingency</td>
<td>20% of TDIC</td>
</tr>
<tr>
<td>Fixed capital investment (FCI)</td>
<td>TDIC + Contingency</td>
</tr>
<tr>
<td>Working capital (WC)</td>
<td>15% of FCI</td>
</tr>
<tr>
<td>Land use</td>
<td>6% of TPEC</td>
</tr>
<tr>
<td>Total capital investment (with land)</td>
<td>FCI + WC + Land</td>
</tr>
</tbody>
</table>
Table 5-2: DCFROR assumptions.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equity</td>
<td>40%</td>
</tr>
<tr>
<td>Loan Interest</td>
<td>7.5%</td>
</tr>
<tr>
<td>Loan Term, years</td>
<td>10</td>
</tr>
<tr>
<td>Internal rate of return</td>
<td>10%</td>
</tr>
<tr>
<td>Income Tax Rate</td>
<td>39%</td>
</tr>
<tr>
<td>Salvage value</td>
<td>0</td>
</tr>
<tr>
<td>Years of construction</td>
<td>3</td>
</tr>
</tbody>
</table>

5.3.4 Sensitivity Analysis

The minimum product selling price (MPSP) in most cases is affected by the variation of different process parameters during the operation of a biorefinery. Sensitivity analysis computes the MPSP by varying one parameter at a time while holding others constant. The parameters identified to impact the MPSP were feedstock price, product yield, TPEC, IRR, byproduct(s) price, income tax rate, and others. The base case scenario of the process parameters is manipulated by considering a ±20% case when computing the MPSP. In practice, several parameters could vary simultaneously though sensitivity analysis considers one parameter at a time.

5.4 Results and Discussion

5.4.1 Process Model Results

In this model, we assumed the flowrate of furfural to be 300 MTPD whereas the other material input flows were 300 MTDP for water, 300 MTPD for acetonitrile, and 150 MTP for sulfuric acid for the first year and 2 MTPD for the following years. The outputs were 30, 30,
and 239 MTPD of furoic acid, furfuryl alcohol and MF respectively (Table 5-3). The estimated renewable energy from sources such as wind and solar was estimated to be 120 MW. The recovery rates of furoic acid, furfuryl alcohol, and MF and purity are all above 99% as seen in Table 5-3.

Table 5-3: Furfural to MF Aspen Plus results.

<table>
<thead>
<tr>
<th>Description</th>
<th>Quantity</th>
<th>Unit</th>
<th>Purity (%)</th>
<th>Recovery rate (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major inputs</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Furfural</td>
<td>300</td>
<td>MTPD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Water</td>
<td>300</td>
<td>MTPD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>300</td>
<td>MTPD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>150</td>
<td>MTPD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Process yields</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Furoic acid</td>
<td>30</td>
<td>MTPD</td>
<td>99.14</td>
<td>100.00</td>
</tr>
<tr>
<td>Furfuryl alcohol</td>
<td>30</td>
<td>MTPD</td>
<td>99.27</td>
<td>99.56</td>
</tr>
<tr>
<td>MF</td>
<td>239</td>
<td>MTPD</td>
<td>99.98</td>
<td>99.52</td>
</tr>
<tr>
<td>Required electricity</td>
<td>120</td>
<td>MW</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The breakdown of the required investment estimates of electrochemical production of MF are shown in Table 5-4. The total purchased equipment cost is $79 MM. The highest TPEC goes to the electrolyzer and this is probably due that it hasn’t been used on a commercial scale yet or a quote from a potential manufacturer wasn’t obtained. This technology is under development and the processing of making an estimate is provided in APPENDIX C. The total installed cost is $240 MM whereas total direct and indirect costs and total capital investment cost are $310 MM and $433 MM respectively.
Table 5-4: Investment estimates of furfural to MF via electrochemical approach.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Assumption</th>
<th>Cost ($MM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total purchased equipment cost (TPEC)</td>
<td>1</td>
<td>79</td>
</tr>
<tr>
<td>Purchased equipment installation</td>
<td>0.39</td>
<td>31</td>
</tr>
<tr>
<td>Instrumentation and controls</td>
<td>0.26</td>
<td>21</td>
</tr>
<tr>
<td>Piping</td>
<td>0.1</td>
<td>8</td>
</tr>
<tr>
<td>Electrical systems</td>
<td>0.31</td>
<td>25</td>
</tr>
<tr>
<td>Buildings (including services)</td>
<td>0.29</td>
<td>23</td>
</tr>
<tr>
<td>Yard improvements</td>
<td>0.12</td>
<td>10</td>
</tr>
<tr>
<td>Service facilities</td>
<td>0.55</td>
<td>44</td>
</tr>
<tr>
<td>Total installed cost (TIC)</td>
<td>3.02*TPEC</td>
<td>240</td>
</tr>
<tr>
<td>Engineering</td>
<td>0.32</td>
<td>25</td>
</tr>
<tr>
<td>Construction</td>
<td>0.34</td>
<td>27</td>
</tr>
<tr>
<td>Legal and contractor’s fees</td>
<td>0.23</td>
<td>18</td>
</tr>
<tr>
<td>Indirect cost (IC)</td>
<td>0.89*TPEC</td>
<td>71</td>
</tr>
<tr>
<td>Total direct and indirect costs (TDIC)</td>
<td>TIC + IC</td>
<td>310</td>
</tr>
<tr>
<td>Contingency</td>
<td>20% of TDIC</td>
<td>62</td>
</tr>
<tr>
<td>Fixed capital investment (FCI)</td>
<td>Contingency</td>
<td>372</td>
</tr>
<tr>
<td>Working capital (WC)</td>
<td>15% of FCI</td>
<td>56</td>
</tr>
<tr>
<td>Land use</td>
<td>6% of TPEC</td>
<td>5</td>
</tr>
<tr>
<td>Total capital investment (with land)</td>
<td>FC I+ WC + Land</td>
<td>433</td>
</tr>
</tbody>
</table>

Table 5-5 shows the annualized operating costs of MF production with furfural feedstock requiring approximately $82 MM accounting for 48% of the annual cost to run the biorefinery. Other highly demanding operating costs that require considerable amount include acetonitrile at $68 MM, insurance and taxes at $8 MM, maintenance at $8 MM and these account for approximately 40%, 4%, and 4% respectively of the operating costs. The computed minimum product selling price (MPSP) is $9.07/gal of MF and there are no techno-economic
results performed so far to the best of our knowledge to produce MF using an electrolyzer or similar approach that we can compare with. The full DCFROR is provided in APPENDIX C.

Table 5-5: Annualized cost of producing MF from furfural via electrochemical process.

<table>
<thead>
<tr>
<th>Operating costs</th>
<th>$ MM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfural</td>
<td>82.07</td>
</tr>
<tr>
<td>Water</td>
<td>0.08</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>68.39</td>
</tr>
<tr>
<td>Sulfuric acid for first year</td>
<td>3.44</td>
</tr>
<tr>
<td>Sulfuric acid second year and beyond</td>
<td>0.03</td>
</tr>
<tr>
<td>Renewable electricity</td>
<td>1.06</td>
</tr>
<tr>
<td>Other utilities</td>
<td>0.15</td>
</tr>
<tr>
<td>Total Salaries</td>
<td>0.87</td>
</tr>
<tr>
<td>Overhead</td>
<td>0.82</td>
</tr>
<tr>
<td>Maintenance</td>
<td>7.44</td>
</tr>
<tr>
<td>Insurance &amp; Taxes</td>
<td>7.44</td>
</tr>
<tr>
<td>Total annual operating costs</td>
<td>171.79</td>
</tr>
<tr>
<td>Minimum Product Selling Price ($/gal)</td>
<td>9.07</td>
</tr>
</tbody>
</table>

5.4.2 Sensitivity Analysis Results

The sensitivity analysis results were computed with ±20% range for all parameters that were thought to have the most influence on the MPSP and are presented Figure 5-2. With a ±20% of MF yield, the MPSP is in the range of $7.56/gal to $11.34/gal of MF yield with a difference of $3.78/gal and is the most influential factor whereas the second influential factor, furfural price, fluctuates the MPSP between $8.37/gal to $9.77/gal with a difference of $1.40/gal and third influential parameter, fixed capital investment fluctuates the MPSP in the range of $8.46/gal to $9.68/gal with a difference of $1.22/gal. Other influential factors are acetonitrile price, internal rate of return (IRR), and income tax rate. The least influential factors to the MF MPSP include water and sulphuric acid prices.
Figure 5-2: Sensitivity analysis results of MF production from furfural vial electrochemical processing.

5.5 Conclusions

In this study, a techno-economic analysis was performed to access the feasibility of producing MF from furfural using electrochemical processing (electrolyzer). This approach is promising because it requires room temperature, ambient pressure and no hydrogen source is required because the system can generate itself the required hydrogen. Another advantage of using an electrolyzer is that it utilizes renewable electricity from sources such as solar and wind that are assumed to experience a storage challenge thus storing electrical energy into chemical energy. The electrochemical process is a promising technology.
The minimum product selling price is $9.07/gal of 2-methyfuran with a total capital investment of $433 MM. The investment cost might reduce with time since this process is under development. The MPSP is mostly influenced by MF yield, fixed capital investment, furfural price, and acetonitrile price.

5.6 References


6.1 Abstract

Electrochemical conversion of CO$_2$ into bioproducts such as biofuels is an alternative to CO$_2$ sequestration and/or its release into the atmosphere which causes global warming. This paper analyzed a 2000 metric tonnes per day (MTPD) CO$_2$ biorefinery producing Fischer Tropsch biofuels (gasoline gallon equivalent, GGE). It was estimated that the biorefinery can produce 70.7 MM gal/yr. GGE (1236 MTPD, C$_8$ and C$_{16}$ hydrocarbons) and 253 MTPD of byproduct (CH$_4$ – C$_3$ hydrocarbon mixture). Estimated investments are $388 MM as total purchased equipment cost (TPEC), $1.2 BB for total installed costs (TIC), $1.8 BB as a fixed capital investment (FCI), and $2.1 BB as the total investment cost. The estimated MPSP is $4.69/gal and is mostly influenced by F-T GGE yield ($3.91 – 5.86/GGE), fixed capital investment ($3.86 – 5.53/GGE), IRR ($4.11 – 5.28/GGE), and income tax rate ($$4.51-4.91/GGE). Electrochemical conversion of CO$_2$ is a promising technology to combat global warming however more research is needed to ascertain the electrolyzer functionality in converting CO$_2$ and its commercial price should be established since it influences mostly the MPSP.

Keywords: Carbon dioxide, Fischer-Tropsch, electrolyzer, electrolyzer, biorefinery
6.2 Introduction

Global warming of the earth has been so much linked with carbon dioxide (CO$_2$) released into the atmosphere and is ranked as the most influential greenhouse gas. Carbon dioxide sequestration alternatives other than carbon capture and storage/sequestering (CCS) are being researched on and one of them is through the electrochemical pathway of producing syngas from captured CO$_2$, water, and renewable electricity [1–4]. Electrochemical processing of CO$_2$ can be carried out for different purposes such as storing renewable electricity, producing hydrocarbon fuels, and reducing CO$_2$ emissions.

Carbon dioxide emissions occur in the globe with China, United States, and Europe being the largest energy users and emitting countries. In 2016, over 32.1 Gt (gigatons) of CO$_2$ were emitted worldwide which is the same amount emitted in 2015 and 2014 whereas the economy of the world grew by 3.1% [5]. The USA emissions in 2016 dropped by 3% and the economy grew by 1.6% due to decreased supplies of shale gas and the use of renewable power instead of coal. In particular, the US emitted 5171 MMt (million metric tons) of CO$_2$ of which 1821 MMt or 35% were from the electric power sector [6].

As energy demand increases there is expected increasing fossil fuel use that will strain the environment greater [7]. Different technologies that can mitigate CO$_2$ include chemical conversion [8,9], electrochemical reduction reaction (ECRR), and sequestration [10]. The ECRR approach has the following advantages in converting CO$_2$ to fuels and chemicals; by adjusting the electrode potential directly electrochemical conversion can be controlled, the process occurs almost at room temperature, it has a comparatively slight footprint, chemical
input necessity is minimal, and can be scaled-up easily [11]. Recycling of CO$_2$ through electrocatalytic reduction into useful fuels would positively impact the global carbon balance and this effort will meet the energy demands of the increasing human population sustainably without degrading the environment. However, since CO$_2$ is an extremely stable molecule, energy-efficient CO$_2$ electro-reduction that can operate near thermodynamic potentials with high reaction rate remains a major scientific challenge. Carbon-based catalysts can electrochemically convert CO$_2$ to syngas [12] (CO from CO$_2$ and H$_2$ coproduction from water). Examples of carbon-based catalysts are carbon nanotubes and N-doped graphene. Carbon-based catalysts are of low price and their reaction rate is compatible with industrial syngas production compared to metal-based catalysts that are at a disadvantage of being not friendly to the environment, have poor durability, are vulnerable to gas poisoning, have low selectivity, there are limited precious metal’s available and being expensive [12].

The published process model by Ou et al., [13] and Swanson et al., [14] were adapted and changed accordingly to investigate the replacement of a gasification reactor with the CO$_2$ electrolyzer technology to produce syngas and upgrade it to Fischer-Tropsch (F-T) fuels thus the objective of this study was to investigate the feasibility of processing CO$_2$ using an electrolyzer/electrochemical reactor into F-T fuels by computing the minimum fuel selling price (MFSP) and the required capital investment.

6.3 Materials and Method

The Aspen Plus and techno-economic analysis major assumptions are listed below. An nth biorefinery plant design was assumed for most of the hierarchy blocks except for the
electrolyzer block which is significant for a detailed process engineering project that is being considered on a commercial scale for the first time.

- Continuous operation of the plant.
- Current efficiency of over 90% at a superficial current density greater than 1 kA/m².
- Gas space velocity greater than 100 h⁻¹.
- Operating period of over 4000 h (based on metal-free carbon catalyst).
- Feed gas composition of greater than 90 vol% CO₂ (dry basis).
- Trace impurities of less than 0.1 vol% were assumed and have no effect on process performance.
- Average renewable electricity price is $0.055/kWh [15] and is assumed to be from a non-fossil based resource.
- CO₂ conversion/pass over 10%, can be absorbed & recovered by passing an alkali.
- The biorefinery is built near a CO₂ emitting plant with no transportation costs to incur.
- A trickle-bed continuous electrochemical reactor with N-S-doped porous carbon as cathode was assumed.

6.3.1 Process Model Description

The model design considered a 2000 MTPD CO₂ biorefinery producing Fischer-Tropsch fuels (biodiesel (C_{16}), biogasoline (C₈), and CH₄ and C₃ products). Biodiesel and biogasoline
products were converted into gasoline gallon equivalent (GGE) while CH\textsubscript{4} and C\textsubscript{3} stream was assumed to an equivalent of propane (LPG). The model consists of the following hierarchy blocks, electrolyzer (A100), water gas shift (WGS) (A200), Fischer-Tropsch (FT) (A300), and hydroprocessing (A400) and the detailed process flow diagram is as shown in Figure 6-1. Areas 200, 300, and 400 represent an nth design of these sections meaning that operating, significant design, and engineering knowledge has been accomplished.

The electrolyzer area (A100) consists of handling of the carbon dioxide before being channeled to the reactor and water that is pumped into the reactor too. The electrolyzer was modeled using a stoichiometric reactor (RStoic) at room temperature and ambient pressure with the reactants being carbon dioxide and water and the products being hydrogen, carbon monoxide, and oxygen. Renewable electricity is used in the electrochemical process. From the Renewable Electricity Future Study (RE Futures) [16], it is possible to have the U.S. electricity system dominated by renewable resources with a supply of more than 80% of which 50% can be produced from solar PV and wind based on commercially available technologies today in conjunction with a more flexible electric system by 2050. The products from the reactor were separated using a separator into two streams, one being oxygen and the other being hydrogen and Carbon monoxide (H\textsubscript{2} + CO) (syngas) with 1:1 mole fractions. The produced syngas from A100 is assumed to be clean that requires no further cleaning and the separated oxygen is assumed to be used within the plant. The WGS area (A200) main purpose is to increases the H\textsubscript{2}:CO ratio by reacting the produced syngas from A100 with water for optimal synthesis of F-T fuels. Area 300 can be referred to as the fuel synthesis area in which syngas is converted into a range of liquid fuels. The first step in the A300 is to compressor the syngas to 26 bar and
then the temperature is leveled to 200°C through a heat exchanger. A fraction (5%) of the main flow stream is forwarded to the pressure swing adsorption (PSA) processing unit to separate hydrogen in pure form from the rest of the compounds so as to be used in the hydroprocessing area and an 85% removal efficiency was assumed according to Swanson et al., [14]. The separated stream from PSA rejoins the mainstream that is mixed and then forwarded to the Fischer Tropsch reactor that operates at 25 bars and 200°C with cobalt catalysts in accordance with equation 1.

\[ CO + 2.1H_2 \rightarrow -(CH_2) - +H_2O \]  
Equation 1

Anderson-Schulz-Flory alpha distribution is followed for the product distribution and chain growth is dependent on reactor temperature and carbon monoxide and hydrogen partial pressures for the cobalt catalyst. Leaning towards the of production F-T fuels, also wax is produced that requires hydrocracking and more detailed explanation can be read from Swanson et al., [14]. The products from F-T reactor pass through a heater exchanger to be cooled from 200°C to 35°C. The hydrocarbons and liquid water are then separated through three separators using a liquid-gas knock out separator (both the flash and decanter operate at 35°C and 23 bar, and separator units were used in the Aspen plus model). During hydroprocessing, high molecular compounds are cracked down into low molecular hydrocarbons using hydrogen which is also assumed to be recycled within the area. The A400 comprises of the wax hydrocracker and a distillation subsection to separate the products. Byproduct distribution considered are propane and methane mixture which were assumed as an equivalent of liquefied propane gas (LPG) that is sold as a byproduct. Hydroprocessing area was modeled as a “black box”. 
Table 6-1: Percentage of different components in the hydroprocessing section [17].

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biodiesel (C_{16})</td>
<td>61.67</td>
</tr>
<tr>
<td>Biogasoline (C_{8})</td>
<td>26.10</td>
</tr>
<tr>
<td>Propane (LPG)</td>
<td>8.77</td>
</tr>
<tr>
<td>Methane</td>
<td>3.46</td>
</tr>
</tbody>
</table>

6.3.2 Economic Analysis Methodology

Total capital investment was determined by computing the total purchased equipment cost (TPEC) and operating costs whereas the minimum product selling price was estimated using a discounted cash flow rate of return (DCFROR) for a 30-year period of the biorefinery. TPEC was used as the basis to compute other requirements such as instrumentation and controls, electrical systems, construction, only to mention a few. The main techno-economic assumptions are listed in Table 6-2.

Aspen process economic analyzer V9 software was used to size and cost some equipment by uploading in there the Aspen plus model. Costing of equipment such as electrolyzer, the F-T reactor was estimated using literature external sources. The electrolyzer cost and required electricity were estimated by using the sixth-tenth factor rule (Equation 2) basing on Colin and Li’s [15] estimates. The F-T reactor, water gas shift catalyst, pressure swing adsorption packing, and F-T catalyst costs were estimated using an approach well
Figure 6-1: Detailed process flow diagram of CO₂ electrochemical conversion into Fischer-Tropsch fuels.
Table 6-2: CO$_2$ electrochemical conversion economic assumptions.

<table>
<thead>
<tr>
<th>Description</th>
<th>Assumption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cost year of consideration</td>
<td>2011</td>
</tr>
<tr>
<td>Internal rate of return (IRR)</td>
<td>10%</td>
</tr>
<tr>
<td>Income tax rate</td>
<td>39%</td>
</tr>
<tr>
<td>Equity</td>
<td>40%</td>
</tr>
<tr>
<td>Biorefinery life</td>
<td>30 years</td>
</tr>
<tr>
<td>CO$_2$ feedstock capture cost</td>
<td>$35/MT [18]</td>
</tr>
<tr>
<td>Propane wholesale price</td>
<td>$0.83/gal [19]</td>
</tr>
<tr>
<td>Overhead</td>
<td>95% of labor and supervision</td>
</tr>
<tr>
<td>Maintenance excluding</td>
<td>2% of FCI</td>
</tr>
<tr>
<td>Insurance and taxes</td>
<td>0.7% of FCI</td>
</tr>
<tr>
<td>Working capital</td>
<td>15% of FCI</td>
</tr>
<tr>
<td>Water gas shift catalyst, pressure swing adsorption packing, and F-T catalyst</td>
<td>Costed after every three years</td>
</tr>
</tbody>
</table>

outlined by Swanson et al., [14]. The hydroprocessing area cost was obtained as an overall cost from literature by modeling it as a “black box”.

Total Purchased Equipment Cost (TPEC) is calculated followed by Fixed Capital Investment (FCI) and then Total Project Investment (TPI) using Peters and Timmerhaus factors
[20]. FCI and TPI estimates are done by manipulating TPEC as a percentage of different parameters.

\[ \text{New equipment cost} = \text{Old equipment cost} \times \left( \frac{\text{New size}}{\text{Old size}} \right)^{0.6} \]  

Equation 2

6.3.3 Sensitivity Analysis

During the operation of biorefinery plants, process parameters change and thus raising a need to evaluate parameters that might impact the MPSP. Sensitivity analysis is done by varying one parameter while holding the others constant to assess their impact on MPSP. Some of the parameters considered in this analysis included CO₂ feedstock cost, product yield, internal rate of return (IRR), FCI, income tax rate, and others. All Process key parameters are varied within a ±20% range whereas that of CO₂ as the feedstock was varied within $±1000/MT considering carbon credit and non-carbon credit scenario.

6.4 Results and Discussion

6.4.1 Process Results

With a 2000 MTPD CO₂ input, the biorefinery produces 70.7 MM gal/yr GGE (1236 MTPD, C₈ and C₁₆ hydrocarbons) and 253 MTPD of the byproduct (CH₄ – C₃ hydrocarbon mixture) as shown in Table 6-3 and the electricity required is 800 MW.
Table 6-3: CO$_2$ electrochemical conversion model results.

<table>
<thead>
<tr>
<th>Description</th>
<th>Quantity</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Major inputs</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO$_2$</td>
<td>2000</td>
<td>MTPD</td>
</tr>
<tr>
<td>Water</td>
<td>3000</td>
<td>MTPD</td>
</tr>
<tr>
<td>Process yields</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH$_4$ &amp; C$_3$ -LPG</td>
<td>253</td>
<td>MTPD</td>
</tr>
<tr>
<td>Gasoline gallon equivalent (GGE)</td>
<td>1236</td>
<td>MTPD</td>
</tr>
<tr>
<td>Required electricity</td>
<td>800</td>
<td>MW</td>
</tr>
</tbody>
</table>

6.4.2 Techno-Economic Results

The investment requirements are shown in Table 6-4 with $388$ MM estimated for total purchased equipment cost (TPEC), $1.2$ BB for total installed costs (TIC), $1.8$ BB as fixed capital investment (FCI), and $2.1$ BB as the total investment cost. The breakdown of TPEC is shown in Figure 6-2 with $244$ MM, $0.2$ MM, $57$ MM, and $86$ MM estimates for electrolyzer, water-gas shift, Fischer-Tropsch, and Hydroprocessing areas respectively accounting for 63%, 0.06%, 15%, and 22% respectively of TPEC. To our knowledge, there is limited literature of techno-economics for CO$_2$ electrochemical conversion. Oloman and Li [15] reported a 100 MTPD CO$_2$ plant producing formate/ formic acid. They assumed 80% current efficiency, 100% selectivity of formate, 100% conversion, negative carbon credit ($10-1000$/metric tonne), and electricity price of 0.01 to 0.10 $/kWh. They estimated $80.62$ MM in 2011-dollar value (SMM 70 in 2005-dollar value) for the electrolyzer alone installed cost and $195.80$ MM in 2011-dollar value (SMM 170 in 2005-dollar value) as the installed plant cost and 40 MW of required electricity.
Comparing this analysis with that of Oloman and Li [15], the plant capacity is twenty times (20X) larger, the electrolyzer cost estimate is approximately three times (3X) higher, and the installed cost is six times (6X) higher. The high cost of the electrolyzer could be attributed to the high installation cost factor used to develop a more conservative estimate. The electrolyzer costing and full equipment list is provided in APPENDIX D.

![Figure 6-2: Total purchased equipment cost of CO2 electrochemical conversion to F-T fuels.](image)

The operating costs and minimum product selling price are shown in The estimated MPSP for this analysis is $4.69/GG and the estimates from Swanson et al., [14] using gasification to produce F-T fuel were $4.30/GGE for high-temperature (1300°C) scenario and $4.80/GGE for low-temperature scenario (870°C) with a capital investment of $610 MM and $500 MM respectively. The difference with Swanson et al., [14] scenarios was attributed to difference in yields and carbon efficiency. Swanson et al., [14] went ahead to estimate the capital
requirement as $1.4 \text{ BB}$ and $1.1 \text{ BB}$ and MPSP of $7.60/\text{GGE}$ and $8.10/\text{GGE}$ of a pioneer plant for high temperature and low-temperature scenarios respective.

Table 6-5. General maintenance, insurance and taxes, CO$_2$ capture price, and renewable electricity annual operating costs are $14 \text{ MM}$, $13 \text{ MM}$, $11 \text{ MM}$ and $7 \text{ MM}$ respectively. WGS-catalyst, FT catalyst, and pressure swing adsorption packing costs are $4 \text{ MM}$, $5 \text{ MM}$, $0.07 \text{ MM}$ respectively and these are incurred in the first year and thereafter every three years [21].

Table 6-4: Investment requirement of CO$_2$ electrochemical conversion to F-T fuels.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Assumption</th>
<th>Cost ($\text{MM}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total purchased equipment cost (TPEC)</td>
<td>1</td>
<td>388</td>
</tr>
<tr>
<td>Purchased equipment installation</td>
<td>0.39</td>
<td>151</td>
</tr>
<tr>
<td>Instrumentation and controls</td>
<td>0.26</td>
<td>101</td>
</tr>
<tr>
<td>Piping</td>
<td>0.1</td>
<td>39</td>
</tr>
<tr>
<td>Electrical systems</td>
<td>0.31</td>
<td>120</td>
</tr>
<tr>
<td>Buildings (including services)</td>
<td>0.29</td>
<td>112</td>
</tr>
<tr>
<td>Yard improvements</td>
<td>0.12</td>
<td>47</td>
</tr>
<tr>
<td>Service facilities</td>
<td>0.55</td>
<td>213</td>
</tr>
<tr>
<td>Total installed cost (TIC)</td>
<td>3.02*TPEC</td>
<td>1170</td>
</tr>
<tr>
<td>Engineering</td>
<td>0.32</td>
<td>124</td>
</tr>
<tr>
<td>Construction</td>
<td>0.34</td>
<td>132</td>
</tr>
<tr>
<td>Legal and contractor’s fees</td>
<td>0.23</td>
<td>89</td>
</tr>
<tr>
<td>Indirect cost (IC)</td>
<td>0.89*TPEC</td>
<td>345</td>
</tr>
<tr>
<td>Total direct and indirect costs (TDIC)</td>
<td>TIC + IC</td>
<td>1515</td>
</tr>
<tr>
<td>Contingency</td>
<td>20% of TDIC</td>
<td>303</td>
</tr>
<tr>
<td>Fixed capital investment (FCI)</td>
<td>TDIC + Contingency</td>
<td>1818</td>
</tr>
<tr>
<td>Working capital (WC)</td>
<td>15% of FCI</td>
<td>273</td>
</tr>
<tr>
<td>Land use</td>
<td>6% of TPEC</td>
<td>23</td>
</tr>
<tr>
<td>Total capital investment (with land)</td>
<td>FCI + WC + Land</td>
<td>2114</td>
</tr>
</tbody>
</table>
The estimated MPSP for this analysis is $4.69/GG and the estimates from Swanson et al., [14] using gasification to produce F-T fuel were $4.30/GGE for high-temperature (1300°C) scenario and $4.80/GGE for low-temperature scenario (870°C) with a capital investment of $610 MM and $500 MM respectively. The difference with Swanson et al., [14] scenarios was attributed to difference in yields and carbon efficiency. Swanson et al., [14] went ahead to estimate the capital requirement as $1.4 BB and $1.1 BB and MPSP of $7.60/GGE and $8.10/GGE of a pioneer plant for high temperature and low-temperature scenarios respective.

Table 6-5: Operating costs and MPSP of CO₂ electrochemical conversion to F-T fuels.

<table>
<thead>
<tr>
<th>Operating costs</th>
<th>$MM</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>11.20</td>
</tr>
<tr>
<td>Water</td>
<td>0.76</td>
</tr>
<tr>
<td>WGS-catalyst</td>
<td>3.66</td>
</tr>
<tr>
<td>FT-catalyst</td>
<td>4.75</td>
</tr>
<tr>
<td>Pressure swing adsorption (PSA) packing</td>
<td>0.07</td>
</tr>
<tr>
<td>Renewable electricity</td>
<td>7.04</td>
</tr>
<tr>
<td>Other utilities</td>
<td>0.39</td>
</tr>
<tr>
<td>Wastewater</td>
<td>0.06</td>
</tr>
<tr>
<td>Total Salaries</td>
<td>2.99</td>
</tr>
<tr>
<td>Overhead</td>
<td>2.84</td>
</tr>
<tr>
<td>Maintenance (other areas)</td>
<td>13.43</td>
</tr>
<tr>
<td>Maintenance (electrolyzer area)</td>
<td>0.23</td>
</tr>
<tr>
<td>Insurance &amp; Taxes</td>
<td>12.73</td>
</tr>
<tr>
<td>Minimum Product Selling Price ($/gal GGE)</td>
<td>4.69</td>
</tr>
</tbody>
</table>

6.4.3 Sensitivity Analysis Results

The sensitivity analysis on the minimum product selling price (MPSP) results are as shown in Figure 6-3. The MPSP computed is $4.69/ gal of GGE (The estimated MPSP for this analysis is $4.69/GG and the estimates from Swanson et al., [14] using gasification to produce
F-T fuel were $4.30/GGE for high-temperature (1300°C) scenario and $4.80/GGE for low-temperature scenario (870°C) with a capital investment of $610 MM and $500 MM respectively. The difference with Swanson et al., [14] scenarios was attributed to difference in yields and carbon efficiency. Swanson et al., [14] went ahead to estimate the capital requirement as $1.4 BB and $1.1 BB and MPSP of $7.60/GGE and $8.10/GGE of a pioneer plant for high temperature and low-temperature scenarios respective.

Table 6-5) assuming 160 days in a year of operation. The MPSP drops to $2.21/gal when the days of operation are increased to 350 days/year. The MPSP is mostly influenced by F-T GGE yield that makes MPSP fluctuate in the range of $3.91/GGE to $5.86/GGE, FCI fluctuates the MPSP in the range of $3.86/GGE to $5.53/GGE, IRR makes MPSP fluctuate in the range of $4.11/GGE to $5.28/GGE, and CO2 capture price makes MPSP fluctuate in the range of $4.66/GGE to $4.72/GGE. The least influential parameters are water price, pressure swing adsorption packing, and electricity cost.
Figure 6-3: Sensitivity analysis results of CO₂ electrochemical conversion to F-T fuels.

6.5 Conclusions

This analysis considered a 2000 MTPD CO₂ biorefinery producing Fischer-Tropsch fuel (GGE) requiring $388 MM as total purchased equipment cost (TPEC), $1.2 BB for total installed costs (TIC), $1.8 BB as fixed capital investment (FCI) and $2.1 BB as the total investment cost.

The estimated MPSP is $4.69/gal of GGE and is mostly influenced by F-T GGE yield, fixed capital investment (FCI), internal rate of return (IRR), CO₂ capture price whereas the least influential parameters are water price, pressure swing adsorption packing, and electricity cost. The number of operating hour/year also affect the MPSP.
Electrochemical conversion of CO\(_2\) is a promising technology still in the early stages of development with promising results to be used to produce fuels instead of causing global warming and/or its sequestration. More research is needed to ascertain electrolyzer use on a commercial scale.

### 6.6 References


CHAPTER 7. GENERAL CONCLUSIONS

A bioeconomy based on biofuels and biochemicals is the best approach to protect the environment, have energy independence, have energy security, minimize global warming, avoid energy politics, and to have a sustainable energy supply. These reasons are why this dissertation aimed at analyzing the feasibility of producing biofuels and biochemicals. The objectives of this dissertation were; 1) to review literature about the subject matter and to identify missing gaps 2) to evaluate the techno-economics of integrating ethanol biorefineries with hydrothermal liquefaction of lignin to produce biochemicals 3) to assess the techno-economics of biorefineries producing 2,5-dimethylfuran (DMF) using an electrolyzer/electrochemical reactor 4) assess the techno-economics of producing 2-methylfuran (MF) from furfural via electrochemical conversion and, 5) to evaluate the techno-economic analysis of electrochemically converting CO₂ into syngas using renewable electricity and further processing it into Fischer-Tropsch fuels.

The project about integrating bioethanol plants with hydrothermal liquefaction processing of lignin into biochemicals yielded promising results of ethanol minimum selling price, but the production of lignin-derived biochemicals using HTL and separation of the produced chemicals are in the early stages of development. Thus, more investment in terms of fixed and operating cost might be required for future commercial biorefinery plants than those obtained in this analysis. The ethanol yield was the most influential factor affecting the minimum ethanol selling price. Producing biochemicals with ethanol is hypothesized to make
ethanol more competitive in the future with fossil-based fuels as efficient production and separation of biochemicals from lignin improves.

The project to produce 2,5-dimethylfuran (DMF) using an electrochemical reactor/electrolyzer technology is a promising approach to produce chemicals that have been referred to as “sleeping giants”. The technology utilizes renewable electricity from sources such as wind and solar energy that encounter the challenge of storage and this would be one way of storing the electrical energy into chemical energy. This process is carried out at near ambient temperature and atmospheric pressure thus eliminating the need for high pressure and temperature reactor vessels.

Furfural is among the most widely produced platform biochemical from biomass and thus its hydrogenation into 2-methylfuran (MF) is considered a promising approach to produce a biofuel that can be used in the transportation section and more particular in ignition engines. This approach is among the few ways in which to convert overproduced electrical energy from renewable resources such as solar panels and wind turbines into chemical energy. There was no TEA work we came across by the time this analysis was done for comparison and thus this TEA can be used as a bench mark for future TEA analysis.

The concept of converting CO\textsubscript{2} into syngas using an electrochemical process is also a promising technology. The syngas produced from CO\textsubscript{2} electrochemical conversion is upgraded into biofuels using the Fischer-Tropsch process. This technology utilizes a greenhouse gas that is causing most of the global warming. From the sensitivity analysis results, the price of F-T fuels from CO\textsubscript{2} via electrochemical process can be improved by increasing the product yield
and lowering the fixed capital investment and probably also the economics can be improved by considering carbon credits for CO$_2$ input material.

The set of studies in this dissertation sought to contribute a better understanding of how novel technologies of biomass conversion into biofuels and biochemicals via hydrothermal liquefaction and electrochemical conversion could contribute to the bioeconomy. By using TEA, we have been able to evaluate these technologies and identify some of their opportunities.
CHAPTER 8. RECOMMENDATIONS FOR FUTURE WORK

The techno-economic analysis research done in this dissertation is of novel biofuels and biochemicals production pathway approaches. Several intriguing factors might be included into the future analysis such as life-cycle analysis, potential location of the suggested technologies, and the effects of government policies and incentives. More innovations are expected in different areas such as in the HTL sector i.e. reactor designs, separation of lignin-derived biochemicals, catalysts that can be used to speed up the reactions and that are selective or favor the production of particular chemicals, cathode and anode materials and electrochemical reactor designs. All these innovations will aim at reducing cost thus lowering minimum product selling price.

Lignin-derived chemicals using HTL and separation are in the early stages of development with a need to research about the HTL reactor in terms of experiments and simulation. Also, research should be done about the pumps to investigate if they can handle the lignin slurry. Research about the HTL reactor will ascertain if it can handle the liquefaction temperature and pressures that are needed for the process and which material could be the best.

DMF production as an alternative to gasoline is still in the early stages of development with more research being needed to document and confirm its selectivity and conversion rates for commercialization. Also, DMF compatibility and performance with existing engines should be done before commercial production can commence. Higher selectivity and conversion rates will increase production that will lower the minimum product (DMF) selling price.
For MF production from furfural using electrochemical processing (electrolyzer), future work can be done to ascertain the performance of an electrochemical reactor at room temperature, ambient pressure, and no use of hydrogen. This future analysis will document and provide data that the suggested approach can eliminate the use of high temperature and pressure columns that are required in conventional pathways.

The CO$_2$ electrochemical conversion approach will need to further assess the performance of electrochemical reactor/electrolyzer, and the life-cycle analysis to quantify if CO$_2$ electrochemical conversion reduces the amount emitted into the atmosphere. This research will evaluate if it is worth to convert CO$_2$ into bioproducts and how much is eliminated to be released into the atmosphere by using electrochemical approach. It was out of scope for this TEA work on CO$_2$ electrochemical conversion to consider gas cleaning, but this might affect the economics of the process.
Figure A1-1: General economic assumptions and base case values for the ethanol and lignin-derived chemicals production manuscript
Material Costs

<table>
<thead>
<tr>
<th>Raw Materials</th>
<th>Prices</th>
<th>Usage</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfuric Acid</td>
<td>500.00</td>
<td>50.00</td>
<td>g/day</td>
</tr>
<tr>
<td>“Ammesa”</td>
<td>50.00</td>
<td>5.00</td>
<td>g/day</td>
</tr>
<tr>
<td>“Corn Steep Liquor”</td>
<td>51.50</td>
<td>27.25</td>
<td>g/day</td>
</tr>
<tr>
<td>“Lignosol”</td>
<td>800.00</td>
<td>80.00</td>
<td>g/day</td>
</tr>
<tr>
<td>“Lignosol”</td>
<td>1.00</td>
<td>1.00</td>
<td>g/day</td>
</tr>
<tr>
<td>“Purchased enzyme”</td>
<td>0.00</td>
<td>0.00</td>
<td>g/day</td>
</tr>
<tr>
<td>“Glucose”</td>
<td>520.00</td>
<td>520.00</td>
<td>g/day</td>
</tr>
<tr>
<td>“Purchased enzyme”</td>
<td>0.00</td>
<td>0.00</td>
<td>g/day</td>
</tr>
<tr>
<td>“Test nutrients”</td>
<td>250.00</td>
<td>250.00</td>
<td>g/day</td>
</tr>
<tr>
<td>“Sulfur dioxide”</td>
<td>275.00</td>
<td>275.00</td>
<td>g/day</td>
</tr>
<tr>
<td>“Catalyst”</td>
<td>130.00</td>
<td>130.00</td>
<td>g/day</td>
</tr>
</tbody>
</table>

Figure A1-2: Material costs for the ethanol and lignin-derived chemicals production.
Capital Costs

```
getEquipmentCosts[] :=
{ "Area 100: Feedstock handling": 1.420689369^7,
  "Area 200: Pretreatment": 1.945512989^7,
  "Area 300: Neutralization": 1.535088804^7,
  "Area 300: Enzymatic Hydrolysis & Fermentation": 1.850578513^7,
  "Area 300: Recovery": 1.604816197^7,
  "Area 300: Wastewater": 1.110796954^7,
  "Area 700: Storage": 2.826565322^6,
  "Area 800: Boiler": 3.630787214^7,
  "Area 800: Utilities": 5.528212386^6
}
```

typFactors =
{ "Warehouse": 0.951,
  "Site Development": 0.962,
  "Additional Piping": 0.853,
  "Total Direct costs (Inc.)": 1.923,
  "Promotional Expenses": 0.160,
  "Preliminary Expenses": 0.160,
  "Project Office & Construction Fee": 0.326,
  "Project Contingency": 0.150,
  "Other costs (Startup, Permit, etc.)": 0.150,
  "Total Indirect Costs": 0.070,
  "Fixed Capital Investment (FCI)": 2.595,
  "Land": 0.082,
  "Working Capital": 0.530,
  "Total Capital Investment (TCl)": 2.750

Labor Costs

```
getSalaryCosts[] :=
{ "Plant Manager": 141509 1,
  "Plant Engineer": 65412 1,
  "Maintenance Super": 56404 1,
  "Maintenance Tech": 38522 12,
  "Lab Manager": 53923 1,
  "Lab Technician": 38522 2,
  "Lab Tech-Enzyme": 38522 1,
  "Shift Supervisor": 68522 6,
  "Shift Operators": 38522 20,
  "Shift Oper-Enzyme": 38522 8,
  "Yard Employees": 26956 4,
  "Clerks & Secretaries": 54070 5
}
```

getOtherCosts[equipmentCost, salaryCosts, fixedCapital_] := Module[{},
  land = 151246890 (*$/acre avg cost *);
  overhead = 0.3*salaryCosts;
  maintenance = 0.05*equipmentCost;
  insurance = 0.01*equipmentCost;
  overhead + maintenance + insurance
}
```

Figure A1-3: Capital and labor costs for the ethanol and lignin-derived chemicals production manuscript
Figure A1- 4: Other functions and fuel out for the ethanol and lignin-derived chemicals production
Figure A2- 1: Aspen plus process flow diagram (PFD) of DMF production from HMF

Table A2- 1: Mass flow rates of DMF production from HMF

<table>
<thead>
<tr>
<th>Description</th>
<th>Stream 2,5-BIS CHEMS D1-2-D2 DMF DMFBIS DMF/EHOH ETOH FULL ALL H2O-OUT H2SO4RY HMF-IN MIX MIX2PMP MIX-OUT OTH-IN RYIEL D1</th>
</tr>
</thead>
<tbody>
<tr>
<td>From</td>
<td>D4       D2       D1       D4       D3       DD1       D3       D2       DD1       D1       M1       M2       P1       M1       M1       D1       R1</td>
</tr>
<tr>
<td>To</td>
<td>DD1      D2       D4       D3       M1       P1       R1       M2       M1       D1       M1       D1</td>
</tr>
<tr>
<td>Phases</td>
<td>Liquid</td>
</tr>
<tr>
<td>Temperature</td>
<td>C</td>
</tr>
<tr>
<td>Pressure</td>
<td>bar</td>
</tr>
<tr>
<td>Molar Vapor</td>
<td>0</td>
</tr>
<tr>
<td>Molar Liquid</td>
<td>0</td>
</tr>
<tr>
<td>Molar Solid</td>
<td>0</td>
</tr>
<tr>
<td>Mass Vapor</td>
<td>0</td>
</tr>
<tr>
<td>Mass Liquid</td>
<td>0</td>
</tr>
<tr>
<td>Mass Solid</td>
<td>0</td>
</tr>
<tr>
<td>Molar Density</td>
<td>mol/cc</td>
</tr>
<tr>
<td>Mass Density</td>
<td>kg/cum</td>
</tr>
<tr>
<td>Enthalpy Flow</td>
<td>Gcal/hr</td>
</tr>
<tr>
<td>Average MW</td>
<td>180</td>
</tr>
<tr>
<td>Mole Flows</td>
<td>kmol/hr</td>
</tr>
<tr>
<td>Mass Flows</td>
<td>kg/hr</td>
</tr>
</tbody>
</table>
Table A2-2: DCFROR of DMF production from HMF - assumptions

<table>
<thead>
<tr>
<th>Assumptions</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed Capital Investment</td>
<td>$686,643,480</td>
<td></td>
</tr>
<tr>
<td>Equity</td>
<td>40%</td>
<td></td>
</tr>
<tr>
<td>Loan Interest</td>
<td>7.5%</td>
<td></td>
</tr>
<tr>
<td>Loan Term, years</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Annual Loan Payment</td>
<td>$60,014,058</td>
<td></td>
</tr>
<tr>
<td>General Plant</td>
<td>$686,643,480</td>
<td>Short et. al</td>
</tr>
<tr>
<td>Working Capital (% of FCI)</td>
<td>15.00%</td>
<td>Short et. al</td>
</tr>
<tr>
<td>General Plant</td>
<td>0 FBT</td>
<td></td>
</tr>
<tr>
<td>Steam Plant</td>
<td>0 FBT</td>
<td></td>
</tr>
<tr>
<td>Type of Depreciation</td>
<td>Double Declining Balance (DBD)</td>
<td>Short et. al</td>
</tr>
<tr>
<td>Steam Plant</td>
<td></td>
<td>Short et. al</td>
</tr>
<tr>
<td>Depreciation Period (Years)</td>
<td></td>
<td>Short et. al</td>
</tr>
<tr>
<td>General Plant</td>
<td>3 Short et. al</td>
<td></td>
</tr>
<tr>
<td>Steam Plant</td>
<td>3 Short et. al</td>
<td></td>
</tr>
<tr>
<td>Construction Period (Years)</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>% Spent in Year - 1</td>
<td>8.00%</td>
<td></td>
</tr>
<tr>
<td>% Spent in Year - 2</td>
<td>60.00%</td>
<td></td>
</tr>
<tr>
<td>% Spent in Year - 3</td>
<td>32.00%</td>
<td></td>
</tr>
<tr>
<td>Start-up Time (Years)</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Revenues (% of Normal)</td>
<td>50%</td>
<td></td>
</tr>
<tr>
<td>Variable Costs (% of Normal)</td>
<td>75%</td>
<td></td>
</tr>
<tr>
<td>Fixed Cost % of Normal</td>
<td>100%</td>
<td></td>
</tr>
<tr>
<td>Internal Rate of Return</td>
<td>10.00%</td>
<td>Short et. al</td>
</tr>
<tr>
<td>Income Tax Rate</td>
<td>10%</td>
<td>Short et. al</td>
</tr>
<tr>
<td>DCF Production Rate (Mg/d of HMF)</td>
<td>9.9</td>
<td></td>
</tr>
<tr>
<td>Operating Hours per Year</td>
<td>8,400</td>
<td>95.9%</td>
</tr>
<tr>
<td>Cost Year for Analysis</td>
<td>2011</td>
<td></td>
</tr>
<tr>
<td>Minimum Product Selling Price ($/gal)</td>
<td>$1.235</td>
<td>Manipulated Value</td>
</tr>
<tr>
<td>Feedback Cost Selling Price ($/gal)</td>
<td>$1.235</td>
<td>Targeted Value</td>
</tr>
<tr>
<td>Net Present Worth</td>
<td>$10,817,651</td>
<td></td>
</tr>
</tbody>
</table>

Table A2-3: DCFROR of DMF production from HMF (-3 to 10 years)
Table A2-4: DCFROR of DMF production from HMF (11 to 26 years)

<table>
<thead>
<tr>
<th>Year</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
<th>20</th>
<th>21</th>
<th>22</th>
<th>23</th>
<th>24</th>
<th>25</th>
<th>26</th>
</tr>
</thead>
<tbody>
<tr>
<td>Working Capital</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>Loan Payment</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>Loan Interest Payment</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>Loan Principal</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
</tr>
</tbody>
</table>

Table A2-5: DCFROR of DMF production from HMF (26 to 30 years)

<table>
<thead>
<tr>
<th>Year</th>
<th>27</th>
<th>28</th>
<th>29</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed Capital Investment</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>Working Capital</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>Loan Payment</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>Loan Interest Payment</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>Loan Principal</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
<td>$0</td>
</tr>
</tbody>
</table>

Other relevant tables and figures are present in the document, which provide detailed financial calculations and projections.
Table A2- 6: Electrolyzer cost computation for DMF production

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>HMF input</td>
<td>300 MTPD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HMF input</td>
<td>12500 Kg/hr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HMF molecular</td>
<td>126.11 kg/kmol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>HMF input</td>
<td>52.1528301 kmol/hr</td>
<td>6 electrons for dehydreation of HMF to DMF</td>
<td></td>
</tr>
<tr>
<td>Selectivity</td>
<td>80 %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMF output</td>
<td>41.7226408 kmol/hr</td>
<td>Assumed</td>
<td></td>
</tr>
<tr>
<td>DMF output-actual</td>
<td>37.3996587 kmol/hr</td>
<td>Aspen plus</td>
<td></td>
</tr>
<tr>
<td>Actual selectivity</td>
<td>0.717103149</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Time</td>
<td>8400 h/yr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DMF output-actual</td>
<td>314151.2531 kmol/yr</td>
<td>Assumed</td>
<td></td>
</tr>
<tr>
<td>Current efficiency</td>
<td>90%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Coulombs</td>
<td>1.63704E+14 C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amperes required</td>
<td>5,413,496.27 A</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Current density</td>
<td>1000 A/m²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrode area</td>
<td>5,413.50 m²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Module/Unit cell area</td>
<td>1</td>
<td>Assumed</td>
<td></td>
</tr>
<tr>
<td>Total cells</td>
<td>5,413.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cell stack</td>
<td>19 unit cells</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total cell stack</td>
<td>284.92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cost</td>
<td>10000 $/m²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total cost</td>
<td>54,134,992.72</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure A3-1: Aspen plus PFD of MF production from furfural

Table A3-1: Mass flow rates of MF production from furfural

<table>
<thead>
<tr>
<th>Description</th>
<th>Stream</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>6</th>
<th>ACETONI</th>
<th>DEC-OUT</th>
<th>FACID-OU</th>
<th>MF-OUT</th>
<th>MIXOUT</th>
<th>MXX</th>
<th>P2R</th>
<th>RYI-OUT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pressure (bar)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molar Vapor Fraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molar Liquid Fraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Molar Solid Fraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass Vapor Fraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass Liquid Fraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass Solid Fraction</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass Entropy</td>
<td>cal/gm-K</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Molar Density</td>
<td>kmol/cum</td>
<td>15</td>
<td>17</td>
<td>0</td>
<td>17</td>
<td>17</td>
<td>52</td>
<td>51</td>
<td>11</td>
<td>26</td>
<td>17</td>
<td>26</td>
<td>26</td>
</tr>
<tr>
<td>Mass Density</td>
<td>kg/cum</td>
<td>834</td>
<td>962</td>
<td>2</td>
<td>1175</td>
<td>711</td>
<td>1037</td>
<td>5466</td>
<td>943</td>
<td>959</td>
<td>889</td>
<td>959</td>
<td>934</td>
</tr>
<tr>
<td>Enthalpy Flow</td>
<td>Gcal/hr</td>
<td>-3</td>
<td>-11</td>
<td>2</td>
<td>-12</td>
<td>1</td>
<td>-42</td>
<td>-1</td>
<td>-3</td>
<td>-61</td>
<td>-18</td>
<td>-61</td>
<td>-60</td>
</tr>
<tr>
<td>Average MW</td>
<td></td>
<td>57</td>
<td>58</td>
<td>45</td>
<td>70</td>
<td>41</td>
<td>20</td>
<td>107</td>
<td>82</td>
<td>37</td>
<td>53</td>
<td>37</td>
<td>36</td>
</tr>
<tr>
<td>Mole Flows</td>
<td>kmol/hr</td>
<td>233</td>
<td>299</td>
<td>150</td>
<td>150</td>
<td>75</td>
<td>609</td>
<td>12</td>
<td>121</td>
<td>1192</td>
<td>598</td>
<td>1192</td>
<td>1208</td>
</tr>
<tr>
<td>Mole Fractions</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mass Flows</td>
<td>kg/hr</td>
<td>13161</td>
<td>17243</td>
<td>6804</td>
<td>10439</td>
<td>3084</td>
<td>12149</td>
<td>1261</td>
<td>9954</td>
<td>43750</td>
<td>31601</td>
<td>43750</td>
<td>43750</td>
</tr>
</tbody>
</table>
Table A3- 2: Equipment list for MF production from furfural

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>Block</td>
<td>756</td>
<td>546</td>
<td>451</td>
<td>546</td>
<td>$77,183</td>
<td>$5,839</td>
<td>1 year</td>
<td>5 year</td>
<td>$92,500</td>
<td>$32,415,000</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>Furfural input</td>
<td>300</td>
<td>MTPD</td>
<td>96500</td>
<td>0</td>
<td>$12,500</td>
<td>$96500</td>
<td>2 year</td>
<td>3 year</td>
<td>$120,875</td>
<td>$39,900,000</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>Furfural input</td>
<td>12500</td>
<td>Kg/hr</td>
<td>96500</td>
<td>0</td>
<td>$26,121</td>
<td>$20,977</td>
<td>2 year</td>
<td>3 year</td>
<td>$33,241</td>
<td>$11,100,000</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>Furfural input</td>
<td>53.0776945</td>
<td>kmol/hr</td>
<td>96500</td>
<td>0</td>
<td>$85,032</td>
<td>$68,026</td>
<td>2 year</td>
<td>3 year</td>
<td>$109,484</td>
<td>$36,100,000</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>Selectivity</td>
<td>80</td>
<td>%</td>
<td>Assumed</td>
<td></td>
<td>$0</td>
<td>$0</td>
<td>3 year</td>
<td>3 year</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>MF output</td>
<td>42.4621566</td>
<td>Kmol/hr</td>
<td>Assumed</td>
<td></td>
<td>$0</td>
<td>$0</td>
<td>3 year</td>
<td>3 year</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>7</td>
<td>0</td>
<td>MF output-actual</td>
<td>46.0566065</td>
<td>Kmol/hr</td>
<td>Assumed</td>
<td></td>
<td>$0</td>
<td>$0</td>
<td>3 year</td>
<td>3 year</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>8</td>
<td>0</td>
<td>Actual selectivity</td>
<td>0.867702643</td>
<td>A</td>
<td>Assumed</td>
<td></td>
<td>$0</td>
<td>$0</td>
<td>3 year</td>
<td>3 year</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>9</td>
<td>0</td>
<td>Tane</td>
<td>40h</td>
<td>h/yr</td>
<td>Assumed</td>
<td></td>
<td>$0</td>
<td>$0</td>
<td>3 year</td>
<td>3 year</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>10</td>
<td>0</td>
<td>MF output-actual</td>
<td>184222.662</td>
<td>kmol/yr</td>
<td>Assumed</td>
<td></td>
<td>$0</td>
<td>$0</td>
<td>3 year</td>
<td>3 year</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>11</td>
<td>0</td>
<td>Current efficiency</td>
<td>90</td>
<td>%</td>
<td>Assumed</td>
<td></td>
<td>$0</td>
<td>$0</td>
<td>3 year</td>
<td>3 year</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>12</td>
<td>0</td>
<td>Total Coulombs</td>
<td>6.399885E+13</td>
<td>C</td>
<td>Assumed</td>
<td></td>
<td>$0</td>
<td>$0</td>
<td>3 year</td>
<td>3 year</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>Amperes required</td>
<td>4,444,370.27</td>
<td>A</td>
<td>Assumed</td>
<td></td>
<td>$0</td>
<td>$0</td>
<td>3 year</td>
<td>3 year</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>14</td>
<td>0</td>
<td>Current density</td>
<td>1000</td>
<td>A</td>
<td>Assumed</td>
<td></td>
<td>$0</td>
<td>$0</td>
<td>3 year</td>
<td>3 year</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>15</td>
<td>0</td>
<td>Electode area</td>
<td>4,444.37</td>
<td>m²</td>
<td>Assumed</td>
<td></td>
<td>$0</td>
<td>$0</td>
<td>3 year</td>
<td>3 year</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>16</td>
<td>0</td>
<td>Module/Unit cell area</td>
<td>1</td>
<td>m²</td>
<td>Assumed</td>
<td></td>
<td>$0</td>
<td>$0</td>
<td>3 year</td>
<td>3 year</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>17</td>
<td>0</td>
<td>Total cells</td>
<td>4,444.37</td>
<td>Assumed</td>
<td></td>
<td>$0</td>
<td>$0</td>
<td>3 year</td>
<td>3 year</td>
<td>$0</td>
<td>$0</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>0</td>
<td>Cell stack</td>
<td>18</td>
<td>unit cells</td>
<td>Assumed</td>
<td></td>
<td>$0</td>
<td>$0</td>
<td>3 year</td>
<td>3 year</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>19</td>
<td>0</td>
<td>Total cell stack</td>
<td>233.91</td>
<td>m²</td>
<td>Assumed</td>
<td></td>
<td>$0</td>
<td>$0</td>
<td>3 year</td>
<td>3 year</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>20</td>
<td>0</td>
<td>Cost</td>
<td>10,000</td>
<td>per m²</td>
<td>Assumed</td>
<td></td>
<td>$0</td>
<td>$0</td>
<td>3 year</td>
<td>3 year</td>
<td>$0</td>
<td>$0</td>
</tr>
<tr>
<td>21</td>
<td>0</td>
<td>Total cost</td>
<td>44,443,702.74</td>
<td></td>
<td>Assumed</td>
<td></td>
<td>$0</td>
<td>$0</td>
<td>3 year</td>
<td>3 year</td>
<td>$0</td>
<td>$0</td>
</tr>
</tbody>
</table>

Table A3- 3: Electrolyzer cost computation for MF production from furfural

<table>
<thead>
<tr>
<th>Furfural input</th>
<th>300 MTPD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furfural input</td>
<td>12500 Kg/hr</td>
</tr>
<tr>
<td>Furfural input</td>
<td>53.0776945 kmol/hr</td>
</tr>
<tr>
<td>Selectivity</td>
<td>80 %</td>
</tr>
<tr>
<td>MF output</td>
<td>42.4621566 Kmol/hr</td>
</tr>
<tr>
<td>MF output-actual</td>
<td>46.0566065 Kmol/hr</td>
</tr>
<tr>
<td>Actual selectivity</td>
<td>0.867702643</td>
</tr>
<tr>
<td>Tane</td>
<td>40h</td>
</tr>
<tr>
<td>MF output-actual</td>
<td>184222.662 kmol/yr</td>
</tr>
<tr>
<td>Current efficiency</td>
<td>90 %</td>
</tr>
<tr>
<td>Total Coulombs</td>
<td>6.399885E+13 C</td>
</tr>
<tr>
<td>Amperes required</td>
<td>4,444,370.27 A</td>
</tr>
<tr>
<td>Current density</td>
<td>1000 A</td>
</tr>
<tr>
<td>Electode area</td>
<td>4,444.37 m²</td>
</tr>
<tr>
<td>Module/Unit cell area</td>
<td>1 m²</td>
</tr>
<tr>
<td>Total cells</td>
<td>4,444.37</td>
</tr>
<tr>
<td>Cell stack</td>
<td>18 unit cells</td>
</tr>
<tr>
<td>Total cell stack</td>
<td>233.91 m²</td>
</tr>
<tr>
<td>Cost</td>
<td>10,000 per m²</td>
</tr>
<tr>
<td>Total cost</td>
<td>44,443,702.74</td>
</tr>
</tbody>
</table>
APPENDIX D. SUPPORTING INFORMATION OF CHAPTER 6

Figure A4- 1: Aspen plus PFD for A100 of CO2 electrochemical conversion

Figure A4- 2: Aspen plus PDF for A200 (Water-gas shift) CO2 electrochemical conversion
Table A4- 1: DCFROR of CO$_2$ electrochemical conversion-assumptions

<table>
<thead>
<tr>
<th>Assumptions</th>
<th>Value</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fixed Capital investment</td>
<td>$1,818,311.605</td>
<td></td>
</tr>
<tr>
<td>Loan Interest</td>
<td>7.5%</td>
<td></td>
</tr>
<tr>
<td>Loan Term, years</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>Annual Loan Payment</td>
<td>$118,941.448</td>
<td></td>
</tr>
<tr>
<td>General Plant</td>
<td>$1,818,311.605</td>
<td></td>
</tr>
<tr>
<td>Steam Plant</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Working Capital (of FCI)</td>
<td>15.0%</td>
<td></td>
</tr>
<tr>
<td>Salvage value</td>
<td>0 P&amp;T</td>
<td></td>
</tr>
<tr>
<td>Steam Plant</td>
<td>0 P&amp;T</td>
<td></td>
</tr>
<tr>
<td>Depreciation Period</td>
<td>Short et al</td>
<td></td>
</tr>
<tr>
<td>General Plant</td>
<td>200 Short et al</td>
<td></td>
</tr>
<tr>
<td>Steam (Electricity System)</td>
<td>7 Short et al</td>
<td></td>
</tr>
<tr>
<td>Construction Period (% years)</td>
<td>0.00%</td>
<td></td>
</tr>
<tr>
<td>% spent in year -1</td>
<td>8.00%</td>
<td></td>
</tr>
<tr>
<td>% spent in year -2</td>
<td>12.00%</td>
<td></td>
</tr>
<tr>
<td>Start-up Time (Years)</td>
<td>6.3</td>
<td></td>
</tr>
<tr>
<td>Revenue (% of Normal)</td>
<td>73%</td>
<td></td>
</tr>
<tr>
<td>Fixed Cost (% of normal)</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>Internal Rate of Return</td>
<td>35% Short et al</td>
<td></td>
</tr>
<tr>
<td>Income Tax Rate</td>
<td>39.0%</td>
<td></td>
</tr>
<tr>
<td>Operating Hours per Year</td>
<td>4,800</td>
<td></td>
</tr>
<tr>
<td>Cost Year for Analysis</td>
<td>2011</td>
<td></td>
</tr>
<tr>
<td>Cost Year Increment</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>Annual Average Minimum Product Selling Price (after taxes)</td>
<td>$3.49 Manipulated Value</td>
<td></td>
</tr>
<tr>
<td>Net Present Worth</td>
<td>50 Targeted Value</td>
<td></td>
</tr>
</tbody>
</table>

Table A4- 2: DCFROR of CO$_2$ electrochemical conversion (upto 10 years)
Table A4- 3: DCFROR of CO$_2$ electrochemical conversion (11 to 26 years)

<table>
<thead>
<tr>
<th>Year</th>
<th>11</th>
<th>12</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
<th>18</th>
<th>19</th>
<th>20</th>
<th>21</th>
<th>22</th>
<th>23</th>
<th>24</th>
<th>25</th>
<th>26</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annual Depreciation</td>
<td>$17,850,000</td>
<td>$17,850,000</td>
<td>$17,850,000</td>
<td>$17,850,000</td>
<td>$17,850,000</td>
<td>$17,850,000</td>
<td>$17,850,000</td>
<td>$17,850,000</td>
<td>$17,850,000</td>
<td>$17,850,000</td>
<td>$17,850,000</td>
<td>$17,850,000</td>
<td>$17,850,000</td>
<td>$17,850,000</td>
<td>$17,850,000</td>
<td></td>
</tr>
<tr>
<td>Net Present Worth</td>
<td>$277,746,751</td>
<td>$277,746,751</td>
<td>$277,746,751</td>
<td>$277,746,751</td>
<td>$277,746,751</td>
<td>$277,746,751</td>
<td>$277,746,751</td>
<td>$277,746,751</td>
<td>$277,746,751</td>
<td>$277,746,751</td>
<td>$277,746,751</td>
<td>$277,746,751</td>
<td>$277,746,751</td>
<td>$277,746,751</td>
<td>$277,746,751</td>
<td></td>
</tr>
</tbody>
</table>

Table A4- 4: DCFROR of CO$_2$ electrochemical conversion (27 to 30 years)
Table A4- 5: Different costs of CO\textsubscript{2} electrochemical conversion catalyst

<table>
<thead>
<tr>
<th>Capacity (Ton/day)</th>
<th>Installed cost ($MM)</th>
<th>Year</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>422</td>
<td>2005</td>
<td>Using six-tenths factor rule</td>
</tr>
</tbody>
</table>

Table A4- 6: F-T reactor and PSA costing

<table>
<thead>
<tr>
<th>FT-reactor cost</th>
<th>Value</th>
<th>Unit</th>
<th>Remarks</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base size</td>
<td>2.52</td>
<td>MM scfh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sizing exponent</td>
<td>0.72</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Installed factor</td>
<td>3.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flow rate into FT-reactor</td>
<td>65741.3279</td>
<td>lbm/ft\textsuperscript{3}</td>
<td>Apen plus</td>
<td></td>
</tr>
<tr>
<td>Molar volume</td>
<td>22.4</td>
<td>L/mol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conversion ratio</td>
<td>38.32</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volumetric flow rate</td>
<td>147.28042</td>
<td>MM scfh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volumetric flow rate</td>
<td>5.2038165</td>
<td>MM scfh</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Installed cost of current FT-reactor</td>
<td>17.69471</td>
<td>$MM</td>
<td>2003 dollars installed cost</td>
<td></td>
</tr>
<tr>
<td>Uninstalled cost of current FT-reactor</td>
<td>9.317418</td>
<td>$MM</td>
<td>2003 dollars</td>
<td></td>
</tr>
<tr>
<td>PSA package cost</td>
<td>497.135</td>
<td>$3/yr</td>
<td>2009 dollars</td>
<td></td>
</tr>
<tr>
<td>Current design</td>
<td>0.458072</td>
<td>tonne/day</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Current design PSA package cost</td>
<td>52.138</td>
<td>$3/yr</td>
<td>2009 dollars</td>
<td></td>
</tr>
<tr>
<td>Current design PSA package cost</td>
<td>72.314</td>
<td>$3/yr</td>
<td>2011 dollars</td>
<td></td>
</tr>
</tbody>
</table>

Table A4- 7: Electrolyzer costing for CO\textsubscript{2} electrochemical conversion

<table>
<thead>
<tr>
<th>Capacity (Ton/day)</th>
<th>Installed cost ($MM)</th>
<th>Year</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000</td>
<td>422</td>
<td>2005</td>
<td>Using six-tenths factor rule</td>
</tr>
</tbody>
</table>
Table A4- 8: Equipment list for CO\textsubscript{2} electrochemical conversion

<table>
<thead>
<tr>
<th>Equipment</th>
<th>Number of</th>
<th>Brand</th>
<th>Model</th>
<th>Type</th>
<th>Power (kW)</th>
<th>Voltage (V)</th>
<th>Current (A)</th>
<th>Temperature (°C)</th>
<th>Pressure (bar)</th>
<th>Cost (USD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cooling</td>
<td>1</td>
<td>LG</td>
<td>2000</td>
<td>1</td>
<td>200</td>
<td>220</td>
<td>40</td>
<td>25</td>
<td>1</td>
<td>5000</td>
</tr>
<tr>
<td>Vacuum</td>
<td>2</td>
<td>Siemens</td>
<td>1200</td>
<td>1</td>
<td>400</td>
<td>380</td>
<td>25</td>
<td>15</td>
<td>1</td>
<td>7000</td>
</tr>
<tr>
<td>Generator</td>
<td>3</td>
<td>Mitsubishi</td>
<td>1500</td>
<td>1</td>
<td>750</td>
<td>440</td>
<td>30</td>
<td>10</td>
<td>1</td>
<td>9000</td>
</tr>
</tbody>
</table>

Note: All equipment is estimated based on current market price.

Table continued on the next page...