

## ABSTRACT

PU, YAN. Auto-hydrolysis and Acid-catalyzed Prehydrolysis of Woody Biomass to Produce Value with Fermentable Sugars Prior to Combustion. (Under the direction of Richard Venditti, Hasan Jameel, Hou-min Chang and Sunkyu Park).

The main steps of producing bioethanol from the lignocellulosic biomass include pretreatment, enzymatic hydrolysis and fermentation. Biomass pretreatment is a means to remove most of the hemicellulose and a small portion of the cellulose and lignin from the woody matrix into the aqueous phase and to leave a comparatively open structure of the solid for further enzymatic hydrolysis. The overall objective of the present study is to investigate the possible optimal sugar yield by means of either auto-hydrolysis or acid-prehydrolysis pretreatment of woody biomass, and the economic feasibility of the so called “VPC” (value prior to combustion) technology. This concept was established for a process of extracting sugar from lignocellulosic biomass to produce bioethanol, as well as combustion of the solid residue to recover the heating value.

**In Chapter 3**, mixed hardwood chips were auto-hydrolyzed at different conditions. The tradeoff between fermentable sugar yield and caloric value of the residual solids was studied for the VPC process. Material balances were performed to evaluate the role of temperature and residence time on sugar production and residual solid heating value. The maximum total sugar was obtained from auto-hydrolysis at 160 °C for 2 hours. The solid balance closure became more open as the pretreatment temperature increased and retention time prolonged. Byproducts generation also increased as temperature and retention time

increased. The heating values that could be recovered after the hot-water extraction varied from 74% to 95%.

**In Chapter 4**, a similar auto-hydrolysis study as discussed in Chapter 3 was carried out with mixed softwood chips. For mixed softwood pretreatment, a better solid balance was observed compared with hardwood. The optimal condition for sugar extraction was found to be at 170 °C for 2 hours. A linear relationship between the pH of prehydrolyzate and temperature was demonstrated. The heating value that can be recovered from solid residue was ranging from 87% to 99%.

**In Chapter 5**, a comparison study of auto-hydrolysis and acid-prehydrolysis of mixed hardwood chips was conducted to understand their sugar yield difference in the liquid extract and their effect on the enzymatic hydrolysis of solid residues. Acetic acid and formic acid were selected for the acid-prehydrolysis. Enzymatic hydrolysis was performed for all the solid residues. A mechanical refining treatment was carried out on all the pulps. As a comparison, enzymatic hydrolysis of pulps without the mechanical refining treatment was also conducted. Auto-hydrolysis at 180 °C resulted in the most open solid balance closure, the highest amount of byproducts generated in the filtrate, and the best enzymatic hydrolysis performance of the solid residue. Acid will facilitate the removal of hemicellulose from the biomass, increase the content of byproducts generated and enhance the enzymatic hydrolysis of solid residues. Formic acid showed better catalytic ability compared with acetic acid. The mechanical refining treatment of the substrate increased the sugar conversion of the residual solids during the enzymatic hydrolysis by at least 10%.

A technical economic evaluation of the VPC technology was established in **Chapter 6** to evaluate whether integrating an ethanol production plant to an existing power generation plant will be feasible and profitable. Mass and energy balances of different proposed cases were created by using Excel spreadsheets populated with laboratory data (from the hot-water extraction of mixed hardwood and softwood studies) along with appropriate assumptions. Capital cost, operating costs and income statement and sensitivity analysis were established. It was determined that economic feasibility was highly dependent on the power selling price, ethanol selling price, and ethanol yield. The proposed VPC cases seemed not promising with the current status of this technology.

© Copyright 2011 by Yan Pu

All Rights Reserved

Auto-hydrolysis and Acid-catalyzed Prehydrolysis of Woody Biomass to Produce Value with  
Fermentable Sugars Prior to Combustion

by  
Yan Pu

A dissertation submitted to the Graduate Faculty of  
North Carolina State University  
in partial fulfillment of the  
requirements for the degree of  
Doctor of Philosophy

Forest Biomaterials

Raleigh, North Carolina

2012

APPROVED BY:

---

Dr. Richard Venditti  
Co-Chair of Advisory committee

---

Dr. Hasan Jameel  
Co-Chair of Advisory committee

---

Dr. Hou-min Chang

---

Dr. Sunkyu Park

## **BIOGRAPHY**

Yan Pu was born in Chengdu, Sichuan Province, China. Yan was raised and educated in the same city until 2006. Yan received her Bachelor degree in Chemical Engineering and graduated first out of all 134 graduates from the Department of Chemical Engineering and Technology. On August 15<sup>th</sup>, 2006, Yan left her country and came to United State continuing her further education. In 2008 Yan received her Master degree in Paper Science & Engineering from Western Michigan University and decided to pursue her Ph. D degree in the Department of Forest Biomaterials from North Carolina State University. In June 2011, Yan was presented with an opportunity for a summer internship from RJ Reynolds Tobacco and was later offered a permanent position during the internship.

Yan Pu enjoys active life styles in her free time. Her hobbies include sightseeing, hiking and traveling to new and adventurous places. Yan is an avid badminton and racquetball player. One of Yan's favorite personal motto is "do your best; forget the rest" and she believes through hard working and staying focus, she will make a difference in the world.

## ACKNOWLEDGMENTS

The members of my dissertation committee, Richard Venditti, Hasan Jameel, Hou-min Chang, and Sunkyu Park have generously given their time and expertise to better my work. I sincerely thank them for their contributions and their good-natured supports. I would like to thank the North Carolina Biofuels Center for funding my work, Project 2008-552-G.

Many thanks to my group members: James Lee, Ronalds Gonzalez, Trevor Treasure and Douyong Min for their patient help in my research and paper review. I would like to express my appreciation to Dr. Fred Cabbage and Dr. Mike Boyette, who kindly offered to be my Graduate Representative.

I am especially grateful for my mother and father back in China, being my strong back up and providing their unconditional support throughout my studies. I am very thankful for my uncle and aunt in Michigan, for their unstoppable encouragement and love.

Special thanks to my boyfriend, who always helps me out through the tough time without asking anything back. I want to give my thanks to my close fellow graduate students and my dear friends in United State, as well as my friends in China who shared their memories and experiences and many laughs and tears.

Thank and praise God for giving me the internal strength and looking after me along the way.

## TABLE OF CONTENTS

LIST OF FIGURES .....	xiii
LIST OF TABLES .....	xviii
CHAPTER 1: INTRODUCTION .....	1
CHAPTER 2: RESEARCH OBJECTIVES .....	13
CHAPTER 3: Autohydrolysis Pretreatment of Mixed Hardwoods to Extract Value Prior to Combustion .....	16
3.1 Abstract .....	16
3.2 Introduction .....	17
3.3 Materials and methods .....	21
3.3.1 Feedstock .....	21
3.3.2 Hot-water extraction .....	21
3.3.3 Potential Process Configuration .....	23
3.3.4 Analysis of extracts .....	24



3.3.5 Analysis of original wood and extracted wood residues .....	26
3.3.6 Standard bomb calorimeter method for heat content of samples .....	27
3.4 Results and discussion.....	29
3.4.1 Solid content of extracts and residues .....	29
3.4.2 Autohydrolysis Byproducts .....	31
3.4.3 Sugars in the extract solution.....	33
3.4.4 Heat Content of Residues .....	37
3.5 Conclusions .....	41
3.6 References .....	42
 CHAPTER 4: Auto-hydrolysis Pretreatment of Mixed Softwood to Produce Value Prior to Combustion.....	 49
4.1 Abstract .....	49
4.2 Introduction .....	50
4.3 Materials and methods .....	55
4.3.1 Softwood material.....	55

4.3.2 Hot-water extraction .....	56
4.3.3 Analysis of extracts .....	56
4.3.4 Analysis of original wood.....	58
4.3.5 Standard bomb calorimeter method for heat content of samples .....	59
4.4 Results and discussion.....	60
4.4.1 Solid recovery yield of extracts and residues .....	60
4.4.2 Byproducts.....	63
4.4.3 pH .....	66
4.4.4 Sugars measurement.....	68
4.4.5 Sugar mass balance.....	72
4.4.6 Heat content .....	75
4.5 Summary .....	80
4.6 Conclusions .....	81
4.6 References .....	83

CHAPTER 5: Auto-hydrolysis and Acid-catalyzed Prehydrolysis of Mixed Hardwood to Extract Fermentable Sugars, and Their Effect on the Enzymatic Hydrolysis of the Solid Residues .....	91
5.1 Abstract .....	91
5.2 Introduction .....	92
5.3 Materials and Methods .....	95
5.3.1 Feedstock .....	95
5.3.2 Hot-water Extraction and Acid-catalyzed Prehydrolysis .....	96
5.3.3 Analysis of original wood and solid residues .....	98
5.3.4 Sugar analysis of extracts .....	99
5.3.5 Byproduct analysis of extracts.....	100
5.3.6 Higher heating value measurement .....	101
5.3.7 Enzymatic hydrolysis of residual solids and sugar analysis.....	101
5.4 Results and Discussion.....	103
5.4.1 Solid content in residual chips and filtrate .....	103

5.4.2 Sugars in the extract .....	107
5.4.3 Sugars in the solid residues .....	114
5.4.4 Byproduct analysis .....	115
5.4.5 Heat content of residues .....	118
5.4.6 Enzymatic hydrolysis .....	124
5.5 Conclusions .....	140
5.6 References .....	142
<b>CHAPTER 6: The Feasibility Analysis of Ethanol Production from Lignocellulosic Biomass before Energy Generation .....</b>	<b>146</b>
6.1 Abstract .....	146
6.2 Objective .....	148
6.3 Introduction .....	149
6.4 Methods .....	154
6.4.1 Base Case .....	154
6.4.2 Proposed Cases and Process Design .....	155

6.4.3 Feedstock .....	158
6.4.4 Hot-water Extraction .....	160
6.4.5 Acid-hydrolysis and Evaporation .....	164
6.4.6 Ion Exchange .....	166
6.4.7 Neutralization .....	167
6.4.8 Fermentation .....	168
6.4.9 Distillation .....	168
6.5 Results and Discussion.....	170
6.5.1 CAPEX.....	170
6.5.2 General Assumptions.....	174
6.5.3 Financial Indicators .....	177
6.5.4 Sensitivity Analysis .....	181
6.6 Conclusions and Recommendations.....	183
6.7 References .....	185
CHAPTER 7: OVERALL CONCLUSIONS.....	189

CHAPTER 8: RECOMMENDED FUTURE WORK .....	194
APPENDICES .....	198
APENDIX I - CHAPTER 9: Co-Production of Electricity and Ethanol, Economics of Value Prior Combustion .....	199
9.1 Abstract .....	199
9.2 Introduction .....	200
9.3 Materials and Methods .....	203
9.3.1 Feedstock .....	204
9.3.2 Basis for Evaluation.....	206
9.3.3 Proposed pathway.....	208
9.3.4 Mass balance of extract and residues .....	210
9.3.5 Process Simulation .....	214
9.3.6 Economic Analysis .....	217
9.4 Results and Discussions .....	219
9.4.1 Power production.....	220

9.4.2 Power production costs.....	220
9.4.3 Minimum selling revenue.....	221
9.4.4 Moisture content effect on power production and minimum wholesale price .....	222
9.4.5 Ethanol production cost .....	226
9.4.6 Minimum ethanol revenue, cash cost and production cost.....	229
9.4.7 Return on investment and payback.....	230
9.4.8 By-products .....	230
9.4.9 Sensitivity analysis .....	231
9.5 Conclusions .....	238
9.6 References .....	239
APENDIX II: Individual Equipment Cost Summary (Scenario I) .....	245
APENDIX II Continued.....	252
Appendix III. Individual Equipment Cost Summary (Scenario II) (Only the additional equipment compared with Scenario I is listed here, any other equipment are all the same as in Scenario I).....	253

Appendix IV. Individual Equipment Cost Summary (Scenario III) (All the equipment listed below have been scaled up accordingly due to the increased feedstock input) .....	254
Appendix V. The Comparison between Freeze Dry and Oven Dry for Solid Content Measurement of Filtrates (Chapter 4) .....	262
Appendix VI. Sugar Conversion Calculation Index (From mono-sugars to polymers) .....	264
Appendix VII. Higher Heating Value versus Lignin Content of the Solids .....	265
Appendix VIII. Sugar Calibrations by Ion Chromatography.....	267
Appendix IX. Sugar Calibration Chromatography by Ion Chromatography.....	269
Appendix X. Calibration Lines and Chromatography for Byproducts Measurement Obtained by HPLC (Chapter 5).....	270
Appendix XI. Chromatography for Byproducts Measurement of Filtrate Obtained by HPLC (Chapter 5) .....	273
Appendix XII. Standardization of Bomb Calorimeter .....	274



## LIST OF FIGURES

Figure 1- 1 Mass balance of main wood components before and after hot-water extraction of sugar maple woodchips (Amidon, et al., 2008) .....	4
Figure 3- 1 Autohydrolysis extraction integrated in a facility coproducing power and ethanol.....	23
Figure 3- 2 Percentage of total heating value recovered from original wood. ....	40
Figure 4- 1 pH values of filtrate for each autohydrolysis temperature.....	67
Figure 4- 2 Higher heating value vs. the lignin content (based on solid) .....	78
Figure 4- 3 Percentage of heating value recovered from original wood.....	79
Figure 5- 1 The sum of all kinds of sugars that were present in the filtrate in the form of mono-sugars, oligo-sugars and total sugars (after breaking down oligo-sugars into mono-sugars), respectively, for each condition (a. Auto-hydrolysis at 160 °C; b. Auto-hydrolysis at 180 °C; c. 2% of acetic acid addition at 160 °C; d. 6% of acetic acid addition at 160 °C; e. 2% of formic acid addition at 160 °C; f. 6% of formic acid addition at 160 °C).....	113
Figure 5- 2 Higher heating value of the original woody biomass and solid residues (a) and total heating value recovered from the solid residues (b).....	120

Figure 5- 3 Lignin content in the original material and solid residues (based on o.d. solids) ..... 122

Figure 5- 4 The relationship between higher heating value and lignin content of the solid. 123

Figure 5- 5 Sugar fractional conversion (based on total sugars in the original wood) from enzymatic hydrolysis of solid residue (P.F.I treated) from each pretreatment condition at different enzyme loadings: (a) 5 FPU/gram of o.d. substrate, (b) 10 FPU/ gram of o.d. substrate, (c)15 FPU/ gram of o.d. substrate..... 125

Figure 5- 6 Sugar fractional conversion (based on sugars in the residue) from enzymatic hydrolysis of solid residue (P.F.I treated) from each pretreatment condition at different enzyme loadings: (a) 5 FPU/gram of o.d. substrate, (b) 10 FPU/ gram of o.d. substrate, (c)15 FPU/ gram of o.d. substrate. .... 129

Figure 5- 7 Solid weight loss (lines) and sugar yield (dots) versus enzyme charge in FPU/g from the enzymatic hydrolysis of solid residues..... 134

Figure 5- 8 Sugar yield vs. weight loss (all based on o.d. substrate) after enzymatic hydrolysis for 96 hours at different enzyme charge levels ..... 135

Figure 5- 9 Comparison of enzymatic hydrolysis of substrate with and without P.F.I. treatment (Sugar fractional conversion based on original total sugars in the wood; graph showing enzymatic hydrolysis with 5 FPU enzyme loading level for 48 hours and 96 hours).	137
Figure 5- 10 Comparison of enzymatic hydrolysis of substrate with and without P.F.I. treatment (Sugar fractional conversion based on sugars in the residue; graph showing enzymatic hydrolysis with 5 FPU enzyme loading level for 48 hours and 96 hours).	138
Figure 5- 11 Total sugars recovery (sugars from both prehydrolyzate and enzymatic hydrolysis) at different enzyme charge levels for each condition after 96 hours	139
Figure 6- 1 Base case process flow graph	154
Figure 6- 2 Hot-water extraction for 1 hour flow sheet, no catalyst added	156
Figure 6- 3 Acid-catalyzed prehydrolysis under 160°C for 1 hour flow sheet	157
Figure 6- 4 Composition of lignocellulosic materials and their potential hydrolysis products (Taherzadeh, et al., 2007)	162
Figure 6- 5 Steam requirements ethanol stripper ( (Jacquies, et al., 2003)	169
Figure 6- 6 Breakdown of installed equipment cost for Scenario I (Total CAPEX is \$80,000,000).	172

Figure 6- 7 Breakdown of installed equipment cost for Scenario II (Total CAPEX is \$84,000,000).	173
Figure 6- 8 Breakdown of installed equipment cost for Scenario III (Total CAPEX is \$102,000,000).	174
Figure 6- 9 Ethanol and unleaded gasoline rack prices. Source: (Official Nebraska Government Website, May 2011)	177
Figure 6- 10 NPV for all the scenarios (at the discount rate of 12%)	178
Figure 6- 11 Incremental NPV for all the cases (at the discount rate of 12%)	179
Figure 6- 12 Ethanol yield and wholesale price in order to achieve 12% IRR (Yield “as it” refers to the ethanol yield as simulated in our economic analysis; ethanol yield that “after matching” refers to the target ethanol yield in order to get a 12% IRR)	180
Figure 9- 1 Distribution of feedstock delivered cost in US\$ dollars per BDT, (1 dry metric ton = 1.1023 BDT)	206
Figure 9- 2 Proposed integrated system for power and cellulosic ethanol production	210
Figure 9- 3 Power production cost using softwood as feedstock	222
Figure 9- 4 Minimum revenue per MWh of electricity at different values of internal rate of return (IRR)	224

Figure 9- 5 Effect of moisture content on electricity production for 500,000 BDT and minimum revenue (to achieve 6% and 12% IRR). ..... 225

Figure 9- 6 Percentage of ethanol production costs (Softwood 170°C), 1 gallon = 3.785 liters. .... 227

Figure 9- 7 Ethanol production, wood to hydrolysis, excess of wood purchased and total wood input for each autohydrolysis condition..... 228

Figure 9- 8 Minimum ethanol revenue (12% IRR), cash cost and production cost for each autohydrolysis condition..... 229

Figure 9- 9 Sensitivity of minimum ethanol revenue (12% IRR) with variation of +/-25% for CAPEX, yield, biomass cost and enzyme cost (Case: Softwood 170°C). ..... 232

Figure 9- 10 Ethanol price FOB Omaha (Nebraska, U.S.) in the period Jan 2002 – Jul 2011 ..... 234

Figure 9- 11 Historic ethanol and regular gasoline price FOB Omaha, Nebraska, U.S. .... 235

Figure 9- 12 Probability distribution of the NPV value of the project (discount rate 12%). 237

## LIST OF TABLES

Table 3- 1 Autohydrolysis Solid Yield at Various Temperatures and Residence Times * ....	29
Table 3- 2 Dissolved Solid Content in the Extract after Auto-Hydrolysis Treatment under Each Condition * .....	31
Table 3- 3 Acetic Acid, Furfural, HMF and Formic Acid in the Filtrate Measured by HPLC (based on 100 grams of original OD wood).....	32
Table 3- 4 Summarized Dissolved Solid Content in the Solid Residue and Extract after Auto-Hydrolysis Treatment under Different Conditions as Grams based on 100 Grams of OD Original Wood .....	33
Table 3- 5 Sugar Composition in the Autohydrolysis Extracts under Each Condition Before (Mono) and After Acid-hydrolysis (Total) by 3% H <sub>2</sub> SO <sub>4</sub> as Grams of Mono-sugar Recovered from 100 grams of OD Original Wood.....	35
Table 3- 6 Sugar Composition of the Raw Material and of the Auto-hydrolysis Residue from Each Condition as Grams Recovered from 100 Grams of OD Original Wood.....	36
Table 3- 7 High Heating Value of the Original Wood and of the Residues under Each Condition. Average and range indicated for the duplicates.....	38

Table 3- 8 Lignin Content in the Residues (Based on oven dry residues, range of duplicate reported).....	39
Table 4- 1 Solid recovery yield in the centrifuged residues after auto-hydrolysis treatment. The mean value and standard deviation of triplicate experiments are reported.....	60
Table 4 - 2 Solid recover yield in the filtrate after auto-hydrolysis treatment*.....	62
Table 4 - 3 Other identified components in the filtrate by using HPLC (based on 100 grams of original OD wood).....	64
Table 4 - 4 Summarized solid recovery yield in the residue and filtrate after auto-hydrolysis treatment under different conditions as grams based on 100 grams of o.d original wood .....	66
Table 4 - 5 Sugar composition in the auto-hydrolysis extracts under each condition before and after acid-hydrolysis by 3% H <sub>2</sub> SO <sub>4</sub> as of grams of mono-sugar recovered from 100 grams of OD original wood. ....	71
Table 4 - 6 Sugar mass balance of starting materials, solid residues and extracts before and after hot-water extraction.....	72
Table 4 - 7 Heat of combustions of original wood and residues under different conditions. Range of duplicate experiments was reported. ....	76
Table 4 - 8 Lignin Content in the Residues (Based on oven dry residues).....	77

Table 5- 1 Solid yield in the residual chips from different conditions. Range of duplicate measurements was reported. .... 105

Table 5- 2 Solid yield in filtrate from different conditions. Range was reported for duplicate measurements..... 106

Table 5- 3 Solid content in the filtrate and solid residue after auto-hydrolysis or acid-catalyzed prehydrolysis. Results based on 100 grams of o.d. original wood ..... 107

Table 5- 4 Sugar composition in the extract under each condition before (Mono) and after (Total) acid-hydrolysis by 3% H<sub>2</sub>SO<sub>4</sub> as grams of mono-sugar based on 100 grams of o.d. original wood. .... 111

Table 5- 5 Sugar composition of the raw material and of the solid residues from each condition as grams recovered from 100 grams of o.d. original material ..... 114

Table 5- 6 Byproducts identified in the filtrate by using HPLC (All results are in grams based on 100 grams of original o.d. wood. This data reflects both the additional acetic acid and formic acid that was produced during the pretreatment and the acetic acid and formic acid that was initially charged to the reactor.)..... 116

Table 5- 7 Fractional conversion of each sugar component during enzymatic hydrolysis of solid residues from different conditions (based on 100 grams of original individual sugar in the wood) ..... 133



Table 6- 1 Advantages of lignocellulose-based liquid biofuels (Hahn-Hagerdal, et al., 2006) .....	150
Table 6- 2 U.S. fuel ethanol production and imports (2000-2010) (Millions of U.S. liquid gallons) Source: (Gnansounou, et al., 2005).....	152
Table 6- 3 Main assumptions for the base case .....	155
Table 6- 4 Hardwood and softwood feedstock composition .....	158
Table 6- 5 Feedstock price assumption for the increasing scale case.....	160
Table 6- 6 Key design data for hot-water extraction reactor .....	161
Table 6- 7 Sugar partitioning ratios and byproducts produced for all the scenarios (Hardwood) .....	163
Table 6- 8 Sugar partitioning ratios and byproducts produced for all the scenarios (Softwood) .....	164
Table 6- 9 The number of effects vs. steam economy .....	165
Table 6- 10 Sugar conversion efficiency and stoichiometry in the fermentation process ....	168
Table 6- 11 Chemical Engineering Plant Cost Index (2011).....	171
Table 6- 12 Major assumptions used in the economic analysis.....	176

Table 6- 13 Sensitivity analysis with variation of +/-25% for CAPEX, ethanol selling price, power price, feedstock price, sulfuric acid price and ethanol yield (Scenario I 170°C, 1 hour for softwood).....	182
Table 9- 1 Chemical composition of softwood and hardwood feedstocks.....	205
Table 9- 2 Alternative cases in power and ethanol production.....	208
Table 9- 3 Extract and residues mass balance for hardwood after autohydrolysis.....	212
Table 9- 4 Extract and residues yield for softwood after autohydrolysis (change name dissolve).....	213
Table 9- 5 Capital investment for an ethanol biorefinery producing 7 million gallons per year (Softwood 170 °C). Source: [8, 36-38].....	216
Table 9- 6 Power plant assumption.....	217
Table 9- 7 Biorefinery assumptions.....	219
Table 9- 8 Formation of acetic acid, formic acid, furfural and hydroxymethylfurfural for each autohydrolysis condition.....	231

## CHAPTER 1: INTRODUCTION

As the global environmental issues and the growing cost of nonrenewable fuels caught more and more attentions, a lot of efforts have been put into exploring alternative energy products that could be obtained from sustainable and renewable resources (Amidon, et al., 2008) (Persson, et al., 2006). The lignocellulosic materials have been selected as one of the biggest candidates, due to their abundant, green, price friendly and readily available nature (Tunc and Heiningen, 2008; Stocker et al., 2008). Woody materials and/or wastes have been widely used either in the pulping industry or for power generation purpose (Westbye, et al., 2008). However, depending on their inherent composition, there were tremendous interests placed to study their value-added chemical products potential (Ragauskas, et al., 2006; Tunc, et al., 2010). Lignocellulosic biomasses are basically composed of three components: cellulose, hemicelluloses and lignin (Willfor, et al., 2005; Willfor, et al., 2008). Cellulose is a linear homopolymer (one-dimensional polymer) with the structure of six-carbon glucose unit connected end to end. It provides the biomass with structure and strength (Amidon, et al., 2008). Hemicelluloses is a heteropolymer built up with five- and six- carbon sugars with short branched side connection, thus is a two-dimensional polymer with lower molecular weight than cellulose. Lignin is an amorphous heteropolymer with tree-dimensional structure mainly consists of phenylpropylene alcohol. It

has a carbon to oxygen ratio nearly 1, thus is more energy dense substance with the highest heating value, compared with other components (Amidon, et al., 2008). Depending on its inertia and stability in the present of corrosive chemicals, lignin acts as a natural barrier to biological degradation to biomass (Stocker, et al., 2008).

Among those three components, hemicellulose can be selectively extracted by a variety of pretreatments to further produce value-added products such as polymers, ethanol and other chemicals (Li, et al. 2010; Li, et al., 2005; Rughani and McGinnis, 1989). The hot-water extraction process, which is also known as autohydrolysis or autocatalytic, can partially extract hemicellulose oligomers (mainly xylo-oligomers with different degree of polymerization) from wood chips (mainly hardwoods), with water as the medium under high temperature and pressure (Leschinsky, et al., 2009; Taherzadeh and Karimi, 2008). The extracted xylose and other hemicelluloses sugars can undergo fermentation to be converted to ethanol by microorganisms, thus hemicelluloses can be deemed as a potential renewable resource for bio-based fuels (Stoutenburg, et al. 2008; Hess, et al., 2007). Hemicellulosic sugars can also be used in the field of producing biodegradable plastics and chemicals that are currently derived from petroleum (Amidon, et al., 2008; Willfor, et al., 2005; Liu, et al., 2006; Lundqvist, et al., 2003). Moreover, the heating value of the residues after hot-water extraction can be recovered by simply combustion or burning, as well as can be utilized in the paper production process.

During the process of hot-water extraction, acids are produced by the hydrolysis of hemicellulose (Amidon and Liu, 2009). Those acids, for example acetic acid formed from degradation of acetyl groups in hemicelluloses, coupled with the dissolution of extractives in the biomass, lead the liquor pH to drop and consequently effectively self-catalyzes the whole process. That is the reason why the hot-water extraction process is also known as auto-hydrolysis or auto-catalytic.

Compared with other chemical added pretreatment, auto-hydrolysis has the advantages (Garrote, et al., 2001) of: comparatively environmentally friendly due to no additional chemical added (Garrote, et al., 2003; Garrote, et al., 1999); less corrosion problems could be caused (Garrote, et al., 2001); less undesired sugar degradation occurs due to mild operational conditions; more value-added chemicals can be recovered and some other economic related benefits. With proper conditions under which auto-hydrolysis carried out, hemicellulose (mostly xylooligosaccharides) can be successfully isolated from lignocellulosic biomass to the most extent and further utilized in the field of ethanol production, pharmaceutical, agriculture, or even food industry (Tunc and Heiningen, 2008; Garrote and Parajo, 2002).

A lot of research has been placed on auto-hydrolysis to study the possibility to obtain high sugar yield from lignocellulosic material, as well as the kinetic behavior of this process.

Amidon and Wood (Amidon, et al., 2008; Amidon and Liu, 2009) reported the detailed mass balance (Figure 1) of both the solid and liquid phase before and after autohydrolysis for maple woodchips at 160°C for 2 hour with water to solid ratio of 4:1. According to their results, most of the components expect cellulose and lignin were effectively extracted into the liquid phase. The solid residue retained most of the cellulose and lignin. The total sugar yield in the liquor they obtained was approximately 15% out of the original o.d. material. The fermentable sugar yield (glucose and xylose) was about 11% based on the starting materials.

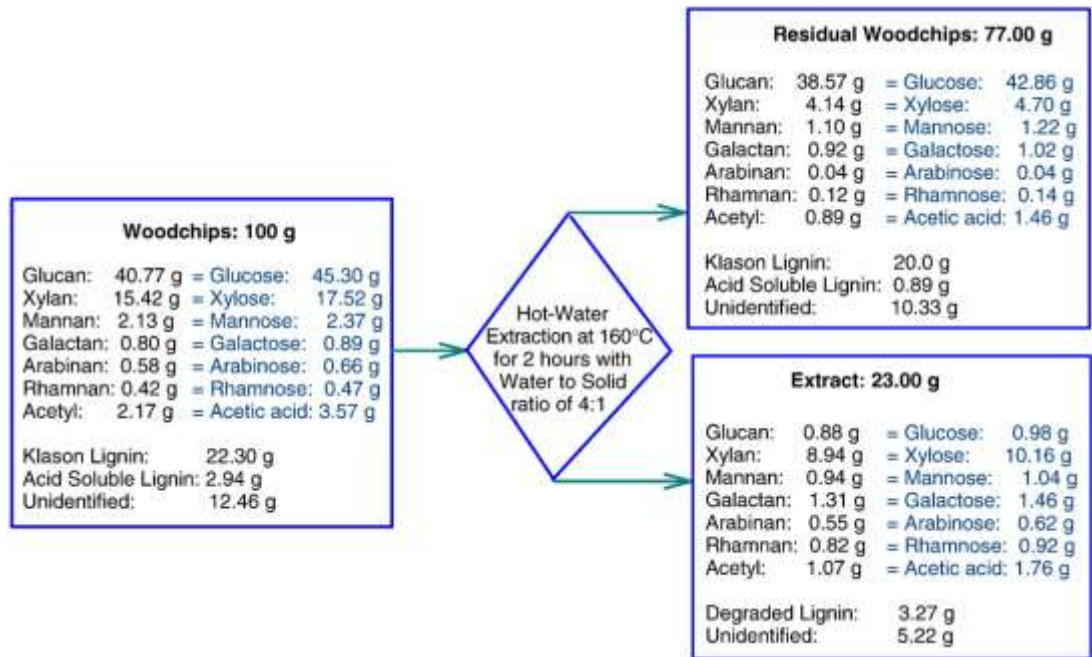


Figure 1- 1 Mass balance of main wood components before and after hot-water extraction of sugar maple woodchips (Amidon, et al., 2008)

Another study about the hot-water extraction of galactoglucomannan (GGM) from both spruce woodchips and ground wood at the temperature from 100 to 180 °C (Song, et al., 2008) revealed that chips yielded lower sugar compared with ground wood did. The highest yield of GGM was about 80-90%, which corresponding to 13-15% of the starting dry material. Such optimal GGM yield for ground wood was observed under 170°C and 1 hour or 100 min, and at 180°C for 20 min and 60 min. They also found that after 100 min at 180°C, the carbohydrate yields apparently dropped by approximately 40% due to the sugar degradation, especially for arabinose and xylose.

Haiming and Abrar (Li, et al., 2010) studied the effects of several parameters on the auto-hydrolysis of mixed hardwood chips, such as time, temperature, the addition of acetic acid and raw material species. They regarded that the maximum temperature at which the reaction carried out was the most important parameter for the hemicellulose extraction, and the optimal temperature they found out for the extraction was 170 °C, which contributed to relatively low byproduct formation. They also reported that the auto-hydrolysis is a complicated dynamic process that includes several simultaneous processes including breakage of hemicellulose to oligomers; formation of acetic acid; hydrolysis of oligomers to monomers; degradation of monomers to HMF and furfural. The longer the reaction carried out and the higher the temperature of the reaction, the more acetic acid will be formed and

more oligomers will be converted to monomers. In addition, it was found that by adding acetic acid into the system can actually speed up the extraction of hemicellulose and its conversion to monomers. Therefore, either adding acetic acid or recycling of the hydrolysate was proposed in this study.

The major products obtained in the autohydrolysis of xylan-rich lignocellulosics are xylooligomers, which cannot be directly fermented to sugars. In order to further use the auto-hydrolysis products as a carbon source for fermentation, it is necessary to convert the oligomers to monomers by a posthydrolysis step either catalyzed by acid or enzymes (Garrote, et al., 2001). It is believed that acid hydrolysis has the advantages over enzymatic hydrolysis due to its shorter reaction time and cheaper cost (Willfor, et al., 2005). However, carefully selection of the operational conditions including time, temperature and the amount of acid is required to obtain the minimal inhibitor generation during the hydrolysis of xylooligosaccharides into monomeric sugars. Gil and Herminia (Garrote, et al., 2001) established the kinetic pattern that governing the posthydrolysis step by using selected temperatures and concentrations of acid to carry out the post acid-hydrolysis reactions of xylooligosaccharide-containing liquors. They interpreted their results by means of a kinetic model that allowed a close reproduction of the experimental data and found that the first-order, kinetic coefficient for xylooligosaccharide hydrolysis varied with temperature and



concentration of the sulphuric acid. They provided the kinetic equations that correlated the kinetic coefficients for the acid hydrolysis of xylooligosaccharide and acetyl groups with both temperature and acid concentration. Almost at the meanwhile, Gil and Herminia (Garrote, et al., 2001) presented their results for the kinetic modeling of xylan degradation by means of a mechanism involving sequential, first order, pseudohomogeneous kinetics. They calculated the values of the kinetic coefficients and established their dependence on temperature with Arrhenius-type equations. Their model provided a desirable interpretation of the experimental data and allowed the selection of optimal operational conditions.

## REFERENCES

- Amidon, Thomas E., and Shijie Liu. "Water- based woody biorefinery." *Biotechnology Advances* 27, 2009: 542-550.
- Amidon, Thomas E., Christopher D. Wood, Alan M. Shupe, Yang Wang, Michell Graves, and Shijie Liu. "Biorefinery: Conversion of woody biomass to chemicals, energy and materials." *Journal of Biobased Materials and Bioenergy* 2, 2008: 100-120.
- Andersson, Alexandra, Tobias Persson, Guido Zacchi, Henrik Stalbrand, and Ann S. Jonsson. "Comparison of diafiltration and size-exclusion chromatography to recover hemicelluloses from process water from thermomechanical pulping of spruce." *Applied Biochemistry and Biotechnology*, 2007: 971-983.
- Garrote, G., and J. C. Parajo. "Non-isothermal autohydrolysis of Eucalyptus wood." *Wood Science and Technology*, 2002: 111-123.
- Garrote, G, JM Cruz, H Dominguez, and JC Parajo. "Valorisation of waste fractions from autohydrolysis of selected lignocellulosic materials." *Journal of Chemical Technology and Biotechnology*, 2003: 392-398.
- Garrote, Gil, Herminia Dominguez, and Juan Carlos Parajo. "Generation of xylose solutions from Eucalyptus globulus wood by autohydrolysis-posthydrolysis processes: posthydrolysis kinetics." *Bioresource Technology*, 2001: 155-164.

- Garrote, Gil, Herminia Dominguez, and Juan Carlos Parajo. "Kinetic modelling of corncob autohydrolysis." *Process Biochemistry*, 2001: 571-578.
- Garrote, Gil, Herminia Dominguez, and Juan Carlos Parajo. "Mild autohydrolysis: an environmentally friendly technology for xylooligosaccharide production from wood." *Journal of Chemical Technology and Biotechnology*, 1999: 1101-1109.
- Hess, J. Richard, Christopher T. Wright, and Kevin L. Kenney. "Cellulosic biomass feedstocks and logistics for ethanol production." *Biofuels, Bioproduct and biorefining* 1, 2007: 181-190.
- J.Taherzadeh, Mohammad, and Keikhosro Karimi. "Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: A review." *International Journal of Molecular Science*, 2008: 1621-1651.
- Leschinsky, Moritz, Herbert Sixta, and Rudolf Patt. "Detailed mass balances of the autohydrolysis of Eucalyptus Globulus at 170°C." *Bioresources*, 2009: 687-703.
- Li, Haiming, Abrar Saeed, M. Sarwar Jahan, Yonghao Ni, and Adriaan van Heiningen. "Hemicellulose removal from hardwood chips in the pre-hydrolysis step of the kraft-based dissolving pulp production process." *Journal of Wood Chemistry and Technology*, 2010: 48-60.

- Li, Jiebing, Gunnar Henriksson, and Goran Gellerstedt. "Carbohydrate reactions during high-temperature steam treatment of aspen wood." *Applied Biochemistry and Biotechnology*, 2005: 175-188.
- Liu, Shijie, Thomas E. Amidon, Raymond C. Francis, Bandaru V. Ramarao, Yuan Z. Lai, and Gary M. Scott. "From forest biomass to chemicals and energy." *Industrial Biotechnology*, 2006: 113-121.
- Lundqvist, Jon, Anna Jacobs, Magnus Palm, n Guido Zacchi, Olof Dahlman, and Henrik Stalbrand. "Characterization of galactoglucomannan extracted from spruce(*Picea abies*) by heat-fractionation at different conditions." *Carbohydrate Polymers*, 2003: 203-211.
- Persson, Tobias, Anna K. Nordin, Guido Zacchi, and Ann S. Jonsson. "Economic evaluation of isolation of hemicelluloses from process streams from thermomechanical pulping of spruce." *Applied Biochemistry and Biotechnology*, 2007: 741-752.
- Persson, Tobias, Mikael Matusiak, Guido Zacchi, and Ann-Sofi Jonsson. "Extraction of hemicellulose from process water from the production of masonite." *Desalination*, 2006: 411-412.
- Pettersen, Roger C. "Wood sugar analysis by anion chromatography." *Journal of Wood Chemistry and Technology*, 1991: 495-501.

- Ragauskas, Arthur J., Charlotte K. Williams, Brian H. Davison, George Greitovsek, and John Cairney. "The path forward for biofuels and biomaterials." *Science*, 2006: 484-489.
- Rughani, Jagdish, and Gary D. McGinnis. "Combined rapid-steam hydrolysis and organosolv pretreatment of mixed souther hardwoods." *Biotechnology and Bioengineering*, 1989: 681-686.
- Song, Tao, Andrey Pranovich, Ivan Sumerskiy, and Bjarne Holmbom. "Extraction of galactoglucomannan from spruce wood with pressurised hot water." *Holzforschung*, 2008: 659-666.
- Stocker, Michael. "Biofuels and biomass-to-liquid fuels in the biorefinery: catalytic conversion of lignocellulosic biomass using porous materials." *Angewandte Chemie*, 2008: 9200-9211.
- Stoutenburg, Rosanna M., Joseph A. Perrotta, Thomas E. Amidoon, and James P. Nakas. "Ethanol production from a membrane purified hemicellulosic hydrolysate derived from sugar maple by *Pichia Stipitis* NRRL Y-7124." *Bioresources* 3(4), 2008: 1349-1358.
- Taherzadeh, Mohammad J., and Keikhosro Karimi. "Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: A review." *International Journal of Molecular Sciences* 9, 2008: 1621-1651.

- Thipse, Sukrut S., Chad Sheng, Michael R. Booty, Richard S. Magee, and Joseph W. Bozzelli. "Chemical makeup and physical characterization of a synthetic fuel and methods of heat content evaluation for studies on MSW incineration." *Fuel* 81, 2002: 211-217.
- Tunc, M. Sefik, and Adriaan R. P. van Heiningen. "Hemicellulose extraction of mixed southern hardwood with water at 150 C: Effect of time." *Industrial Engineering Chemistry Resources*, 2008: 7031-7037.
- Tunc, Mehmet Sefik, Martin Lawoko, and Adriaan van Heiningen. "Understanding the limitations of removal of hemicelluloses during autohydrolysis of a mixture of southern hardwoods." *Bioresources*, 2010: 356-371.
- Westbye, Peter, Tobias Kohnke, and Paul Gatenholm. "Fractionation and characterization of xylan rich extracts from birch." *Holzforschung*, 2008: 31-37.
- Willfor, S., J. Hemming A. Sundberg, and B. Hlmbom. "Polysaccharides in some industrially important softwood species." *Wood Science Technology* 39 (2005): 245-258.
- Willfor, Stefan, Kenneth Sundberg, Maija Tenkanen, and Bjarne Holmbom. "Spruce-derived mannans - A potential raw material for hydrocolloids and novel advanced natural materials." *Carbohydrate Polymers* 72, 2008: 197-210.

## **CHAPTER 2: RESEARCH OBJECTIVES**

Auto-hydrolysis of woody biomass has been studied over a variety of conditions for both mixed hardwood chips and mixed softwood chips. Further studies of acid-catalyzed prehydrolysis of hardwood were also performed as a comparison to the auto-hydrolysis. The purpose of this study is to understand the critical factors in the pretreatment process of woody biomass in order to obtain the highest fermentable sugar yield, and to study the economic feasibility of implementing the VPC technology into practical bioethanol production.

In the first study, hot-water extraction was used to pretreat mixed hardwood chips to obtain an understanding of the extraction of hemicelluloses and other components from hardwood under different conditions. The heating value measurements of original wood and solid residues obtained for each treatment were also determined to evaluate the amount of heat in the wood that could be recovered after the auto-hydrolysis treatment. The objective was to understand the tradeoff between fermentable sugar yield and caloric value of the residual solids. This process layout will be referred to as “value prior to combustion” or VPC. The study develops a clear understanding of some of the tradeoffs that occur under different temperature, time conditions and can be used for economic modeling of the proposed process.

In the second study, hot-water extraction was performed for a mixed softwood to obtain a fundamental understanding of the extraction of hemicelluloses and other components from softwood under different conditions. The caloric value of the solid residues was also performed to see how much heating energy can be recovered after the extraction of softwood chips. The results from this study along with the results from the first study will be applied in an economic analysis to investigate the feasibility of integrating the auto-hydrolysis process into a power generation facility, from a greenfield stand point of view.

The objective of the third study is to compare the sugar yield in the prehydrolyzate from auto-hydrolysis and acid-catalyzed prehydrolysis of mixed hardwood chips and their effect on further enzymatic hydrolysis of the solid residues. Enzymatic hydrolysis of the prehydrolyzate is not in the scope of the present study; instead, an acid-hydrolysis treatment of the prehydrolyzate was conducted to see how much fermentable sugars could be recovered from the liquid phase. One of the innovative aspects of this work is to use mechanical refining to treat the pulp that generated from the solid residues, to obtain a substrate that is believed to be more easily approachable by enzymes. Comparison was carried out for enzymatic hydrolysis of substrates prepared with or without the mechanical refining treatment. The acids employed in the acid prehydrolysis pretreatment were found in the prehydrolyzate from auto-



hydrolysis: acetic acid and formic acid. As they are the acids self-generated during the auto-hydrolysis and have the function of self-catalyze the reaction process, it would be interesting to see how the presence of each acid at the beginning of the reaction will affect the sugar yield in the liquid as well as the enzymatic hydrolysis performance for the resulting residues.

The aim of the fourth study is to present the economics of co-producing power and cellulosic ethanol in an integrated process using southern mixed hardwood and southern yellow pine as feedstocks. The economics of standalone power production from biomass in a greenfield plant is explored first and represents a base case analysis. The following economic indicators were determined to gauge the economic performance of the base case and proposed cases: internal rate of return (IRR), net present value (NPV), payback period and minimum power selling price (to achieve a specific internal rate of return). After developing the base case, the proposed case involving biomass auto-hydrolysis and sugar extraction to produce ethanol while burning the residual solids, was developed and analyzed.

The objective of the fifth study is to establish a technical economic evaluation of the VPC technology to evaluate whether integrating an ethanol production plant to an existing power generation plant will be feasible and profitable. Ethanol is a low-value product, therefore to consider adding an ethanol plant to an existing power plant needs rigorous process modeling and economic evaluations with regard to the profitability concerns.

Paper published in BioResources 6(4), 4856-4870, 2011. "AUTOHYDROLYSIS PRETREATMENT OF MIXED HARDWOODS TO EXTRACT VALUE PRIOR TO COMBUSTION" Yan Pu, Trevor Treasure, Ronalds Gonzalez, Richard Venditti, and Hasan Jameel

## **CHAPTER 3: Autohydrolysis Pretreatment of Mixed Hardwoods to Extract Value Prior to Combustion**

### **3.1 Abstract**

Biomass pretreatment by autohydrolysis uses hot-water to extract soluble components from wood prior to converting the woody residuals into paper, wood products, or fuel, etc. Mixed hardwood chips were autohydrolyzed in hot-water at 150, 160, 170, and 180 °C, for 1 and 2 h. The tradeoff between fermentable sugar yield and caloric value of the residual solids was studied for a process that will be referred to as "value prior to combustion". The extracted liquid was treated with dilute sulfuric acid to break down sugar oligomers into fermentable monomers. Material balances were performed around autohydrolysis to evaluate the role of temperature and residence time on sugar production and residual solid heating value. The composition (sugars and byproducts) of the extracted liquid was determined. It was found that autohydrolysis at 160 °C for two hours resulted in the highest total fermentable sugars (9.96 grams out of 100 o.d. starting wood) in the prehydrolyzate. As the autohydrolysis temperature increased, the material balance closure became more open,

presumably due to more volatile byproducts being formed that were not quantified. More hemicelluloses were extracted from the wood by the hot water extraction process under higher temperature and longer residence time, but a greater degree of sugar degradation was also observed. After hot-water extraction the heating value of the solid residues was higher than the original wood due to increased concentration of lignin. The total energy content of the residual solid after extraction ranged from 74 to 95% of the original energy content of the feed.

### **3.2 Introduction**

Motivated by the urgency to discover alternative sources of sustainable and environmentally friendly energy, cellulosic ethanol has received increasing attention from private and public research sectors. Biofuels produce much lower greenhouse gas emissions and might potentially provide more employment in rural and industrial areas (Von Blottnitz et al. 2007; Bai et al. 2010; Cherubini et al. 2010). Conversion of biomass to ethanol and chemicals may be able to sustain our way of life, since woody biomass (lignocellulosic) can be replenished. Unlike fossil fuel energy sources whose natural replenishment is in the time scale of 200 million years (regarded as nonrenewable), biomass can be regenerated in the time scale ranging from 3 months to 80 years and is therefore considered renewable (Liu et al. 2006), moreover, lignocellulosic biomass is the most abundant organic source on earth with approximately 170 billion metric tons annual production (Sticklen 2006; Kumar et al. 2009).

Lignocellulosic feedstocks are basically composed of three components: cellulose, hemicelluloses and lignin (Amidon et al. 2008; Willför et al. 2008). Cellulose is a linear

homopolymer composed of D-glucose units connected by a  $\beta$  (1,4) linkage. Cellulose provides structure and strength for the plant or tree. Hemicelluloses are a heteropolymer composed of five and six carbon sugars with short branched side connections. Lignin is an amorphous heteropolymer with three-dimensional structure synthesized from three phenyl propylene alcohol units. Lignin has a carbon to oxygen ratio of nearly 1 and is more energy dense compared to cellulose and hemicelluloses (White 1987; Amidon et al. 2008).

In bioenergy conversion processes, biomass is the major cost driver accounting for 35 to 50% of total productions costs (Gonzalez et al. 2008; Gonzalez et al. 2011b; Gonzalez et al. 2011d). Though technical/economic analyses of several bioenergy conversion processes (with special emphasis on cellulosic ethanol) have highlighted the importance of recovering all major lignocellulosic components to offset high feedstock cost (Gregg et al. 1996a; Gregg et al. 1996b; Gonzalez et al. 2011c), commercial byproducts of lignocellulosic ethanol processes are minimal thus far. Researchers are working to find possible uses of hemicelluloses in the manufacture of polymers (Salam et al. 2011) and identifying more profitable uses of lignin other than heat-steam-power generation (Pan et al. 2005a; Pan et al. 2005b; Janssen et al. 2008; Janssen et al. 2010; Gonzalez et al. 2011a; Gonzalez et al. 2011c). The production of marketable byproducts is of great importance for the economy of the

biorefinery. The need to utilize all parts of the biomass is the basis for this study. The technology examined here could be deployed as a front end/pretreatment for many different pathways that use biomass to produce fuels, chemicals, and materials.

The hot-water extraction process, which is also known as autohydrolysis, can partially extract hemicellulose oligomers (mainly xylo-oligomers with different degrees of polymerization) from wood while leaving other components intact (White 1987; Amidon et al. 2008; Taherzadeh et al. 2008; Amidon et al. 2009; Leschinsky et al. 2009). The extracted xylose and other hemicellulose sugars can undergo fermentation to ethanol and can be considered a potential renewable resource for bio-based fuels (Hess et al. 2007; Stoutenburg et al. 2008). Hemicellulosic sugars can also be used to produce biodegradable plastics and chemicals that are currently derived from petroleum (Amidon et al. 2008; Amidon et al. 2009; Salam et al. 2011). The residues after hot water extraction can be burned to produce steam and electricity or alternatively can be used as a raw material for wood and paper products.

During the process of hot-water extraction, acids are produced by the hydrolysis of hemicelluloses (Amidon et al. 2009). These acids coupled with the dissolution of extractives in the biomass cause the liquor pH to drop and effectively self-catalyze the process. That is the reason why the hot-water extraction process is also known as auto-catalytic. Previous studies have demonstrated that hot-water extraction (160°C) of sugar maple wood chips largely removed extractives and hemicellulose while most of the lignin and cellulose

remained with the residual wood structure (Amidon et al. 2008). The residual solids are then processed for production of pulp and paper, wood products or power.

In this study, hot-water extraction was used to pretreat mixed hardwood chips at 150, 160, 170 and 180 °C and two residence times (1 and 2 hours) to obtain an understanding of the extraction of hemicelluloses and other components under different conditions. The heating value measurements of original wood and solid residues obtained for each treatment were also determined to evaluate the amount of heat in the wood that could be recovered after the autohydrolysis treatment. The objective was to understand the tradeoff between fermentable sugar yield and caloric value of the residual solids. This process layout will be referred to as “value prior to combustion” or VPC. The study develops a clear understanding of some of the tradeoffs that occur under different temperature, time conditions and can be used for economic modeling of the proposed process.

### **3. 3 Materials and methods**

#### **3.3.1 Feedstock**

Hardwood chips (obtained from a North Carolina pulp and paper mill) with dimensions of 30 mm length, 20 mm width and 3 mm thickness were used as raw material for hot-water extraction. This feedstock is composed of several hardwood species naturally growing in the Southeastern U.S. Some of the species commonly found in this mix are maple, birch and oak (USDA 2011). Wood chips were stored in a cold room at 4 °C and air dried for two days prior to use. Moisture content of the air-dried chips was measured by oven drying at 105 °C until constant weight was achieved. Composition of the original biomass was determined using klason lignin standards, values are presented as follows: lignin 27%, glucan 41%, hemicellulose 20%, and identified others 12%

#### **3.3.2 Hot-water extraction**

Hot-water extraction was performed with a digester (M/K Systems Inc., Danvers, MA). 800 g wood chips was employed for each trial and the oven dry weight was calculated based on the moisture content obtained from parallel chips measurement. A 4:1 water to solid

ratio was used throughout all the extraction trials. Extraction conditions: 150 °C, 160 °C, 170 °C and 180 °C for 1 and 2 hours each. The water extract was collected after each extraction and the solid content of extract was measured by standard oven drying at 105 °C. pH of extracts was measured shortly after the extraction at the room temperature.

The remaining residues after extraction was washed in the running tap water for 1 hour and subsequently settled in still water for 16 hours. The soaked chips were centrifuged in a centrifugal until no more water was dripping from the reject. A small amount of such obtained centrifuged residues were put into oven at 105 °C for moisture content measurement until constant weight was achieved. A part of centrifuged residues were air dried for composition analysis.



### 3.3.3 Potential Process Configuration

The overall process flow is illustrated Figure 3-1, where an integrated hemicellulose extraction is seen to be part of an ethanol biorefinery and a power plant. In this system, wood

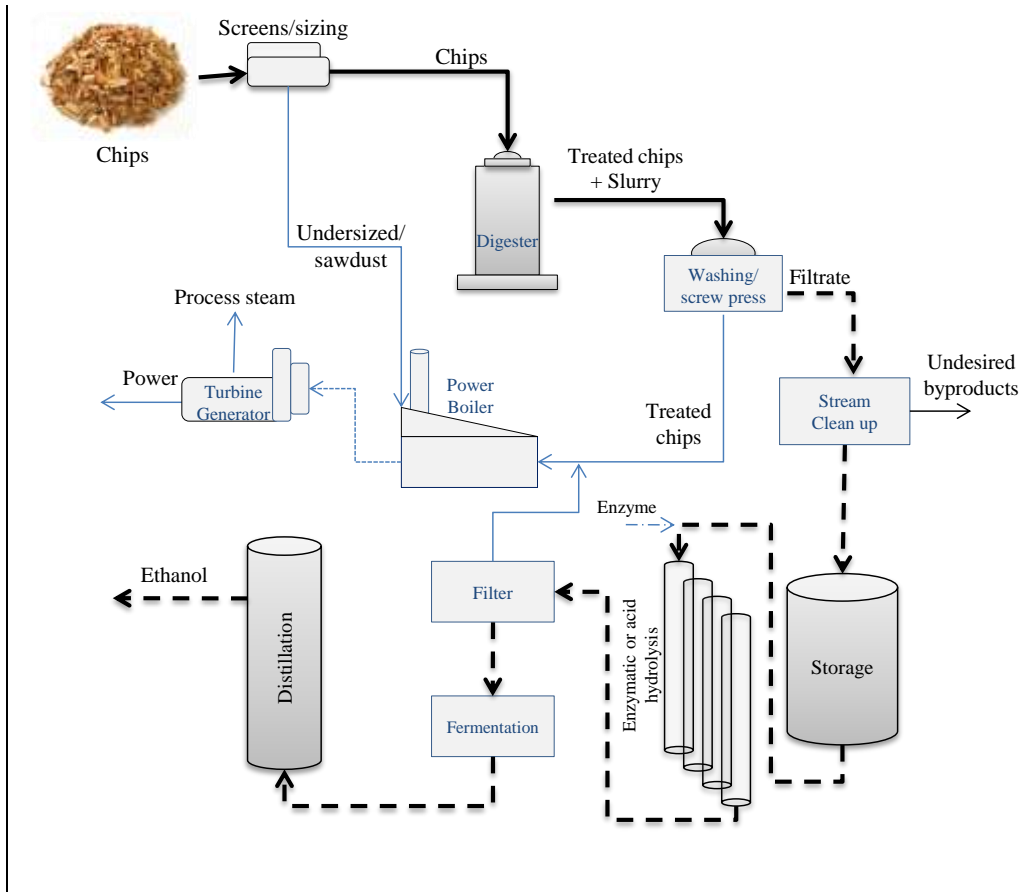


Figure 3- 1 Autohydrolysis extraction integrated in a facility coproducing power and ethanol

chips are fed into a digester for hot-water extraction, then the slurry is screw pressed and two streams are generated, one stream with low solid content (filtrate) and one stream with high solid content (extracted residues). Another alternative for the screw press can be a washing

system to reduce sugar carryover with residues. The extracted solid residues are sent to combustion for generation of power and process steam. The filtrate needs to be cleaned up to remove agents that might interfere with hydrolysis and fermentation (White 1987; Amidon et al. 2008; Amidon et al. 2009). After stream clean up the stream is hydrolyzed (by means of acid or enzymes) in order to reduce oligomer sugars into fermentable monomeric sugars. Then fermentation and distillation processes take place for alcohol production. With respect to oligomer hydrolysis, as previously noted, it can be done by means of acid or enzymes. Acid hydrolysis will require addition of more capital investment for chemical recovery so that the process can be profitable and also avoid downstream contamination problems in fermentation; also additional cost is required in equipment for acid resistant metallurgy. An economic analysis comparing clean up options may assess the economic potential and risk of the different options.

#### **3.3.4 Analysis of extracts**

The solid content of extract was determined gravimetrically by standard oven drying under 105 °C to a constant weight. Triplicate treatments were carried out for each sample. The sugar monosaccharides of the extract were determined by an ion chromatography system (Dionex ICS-3000, Sunnyvale, CA) before and after acid hydrolysis (3% sulfuric acid, 122°C, 1.5 hour in the autoclave) that converts sugar oligomers to monosaccharides. The monomeric

sugar content difference before and after the acid hydrolysis represents the oligo- and polysaccharide content in the sample (Persson, et al. 2007; Andersson, et al. 2007). The chromatograph was equipped with an autosampler, a dual pump (model DP-1), an eluent generator (model EG-2) and a detector/chromatography module (model DC-1). Milli-Q water and 400mN sodium hydroxide (NaOH) solution were used as the eluents at the flow rate of 1.1mL/min. Fucose was added to each sample as an internal standard. D-fucose, D-arabinose, D-rhamnose, D-galactose, D-glucose, D-xylose and D-mannose were used as calibration standards to make the sugar calibration curve (Pettersen 1991).

Acid soluble lignin (ASL) in the extract was measured by UV absorption at a wavelength of 205 nm (Westbye, et al., 2008). A 3% sulfuric acid was employed as the background. The extract sample was diluted with DI water to appropriate times (10-500) to bring the absorbance into the range of 0.1-1. The quantity of ASL was calculated by the following equation:

$$ASL (g) = \frac{A \times t \times V}{b \times a \times 1000}$$

where,

- A absorbance obtained by the UV measurement,
- b light path (cm),
- a absorptivity ( $L \cdot g^{-1} \cdot cm^{-1}$ ),
- t dilution times of the original sample
- V total volume of sample (mL)

Furfural, hydroxymethyl furfural (HMF), formic acid and acetic acid were determined by a Dionex high-performance liquid chromatography. Standard curves were made for each byproduct by using a 6 point calibration and all the standard samples were dissolved in the ACS grade methanol. The 4-tert-butylphenoxyacetic acid was used as the internal standard. Both methanesulfonic acid and acetonitrile were used as the eluents, with a flow rate of 1mL/min.

### 3.3.5 Analysis of original wood and extracted wood residues

Original wood chips and air-dried extracted wood residues were ground to 40-60 meshes. A certain amount of such ground wood powder was subjected to an acid hydrolysis by adding 1.5 mL 72% sulfuric acid and thoroughly stirring every 15 minutes at the room

temperature. After 1.5 hours, the resulting sample was carefully transferred to a serum bottle by washing with 56 mL DI water to bring the acid concentration to 3%. The serum bottle was sealed and autoclaved for 90 minutes at 122 °C. The autoclaved hydrolysis solution was vacuum filtered through a previously weighed filtering crucible and collected. This sample was used to determine acid soluble lignin as well as sugar composition, as described above. Deionized water was used to quantitatively transfer all remaining solids in the serum bottle into the filtering crucible (medium porosity) after the filtrate had been collected. The crucible accompanied with acid insoluble residue was dried by standard oven drying at 105 °C until a constant weight was achieved. Acid insoluble lignin (AISL), which is also known as Klason lignin was calculated after the gravimetric analysis described above.

### **3.3.6 Standard bomb calorimeter method for heat content of samples**

All samples were subjected to a standard bomb calorimeter (1341 Oxygen Bomb Calorimeter, Parr Instrument Company, Moline, IL) measurement. Samples were first ground to pass a 20 mesh screen and then compressed into pellets using a pellet press (Perkin Elmer 15.011, Britain) prior to being weighed.

Heat content was determined by burning the samples with excess of oxygen at a pressure of 30 atmospheres in a sealed steel bomb, which is regarded as a near-adiabatic system. The steel bomb was submerged in a certain amount of water, whose temperature changes during the combustion process were monitored by a thermometer. Time versus water

temperature over the entire combustion process was recorded. The total temperature rise and other pertinent thermochemical corrections, which included correction for heat in formation of nitric acid, sulfuric acid and heat of combustion of fuse wire, were determined and used in the final heating value calculations. Before the heat of combustion measurement, four trials were carried out combusting standard benzoic acid pellets provided by Parr Instrument Company to obtain the energy equivalent of the calorimeter (ASTM 2011). The procedure was strictly performed following the procedure from the Instruction Sheet No. 204M (Operating Instruction Manual, Parr Instrument Company). All samples were first ground into powder form by Wiley Mill and then pressed into pellets, to facilitate a slow and complete combustion in the bomb.

### 3.4 Results and discussion

#### 3.4.1 Solid content of extracts and residues

The solid yield after the autohydrolysis treatment decreased from 90% to 70% as the treatment temperature increased from 150°C to 180°C and the residence time increased from 1 to 2 hours (Table 3-1). The effect of residence time on yield was greater at lower temperatures. At higher temperatures and longer residence times the moisture content of wet residues after centrifugation was higher. A possible explanation for this may be a more open structure of the wood chips, which absorbs and holds more water. This phenomenon may have implications for subsequent pressing or drying operations if the chips are used for fuel.

Table 3- 1 Autohydrolysis Solid Yield at Various Temperatures and Residence Times \*

Temp (°C)	Time (hour)	Original Wood (OD g)	Solid Residue after Autohydrolysis (OD g)	Yield (%)	Moisture Content (%)
150	1	721.0±1.6	658.6	91.3	54.7±0.6
	2	721.0±1.6	625.7	86.8	55.4±0.9
160	1	713.7±1.1	557.1	78.1	58.9±0.7
	2	721.0±1.6	539.4	74.8	60.0±0.8
170	1	713.7±1.1	540.9	75.8	60.8±0.3
	2	713.7±1.1	520.5	73.0	62.4±0.9
180	1	713.7±1.1	504.6	70.8	62.0±0.9
	2	713.7±1.1	501.4	70.3	63.7±1.0

\* The mean value and deviation of duplicate experiments are reported

The dissolved solid content of the extract solution increased with increasing temperature from 150°C to 160°C and by increasing the residence time from 1 to 2 hours

(Table 3- 2). However, higher temperature (greater than 170°C) and longer residence times resulted in lower sugar recovery in the extract solution. This can be explained by higher temperature and longer extraction times promoting the formation of furfural and hydroxyl-methyl furfural (HMF) when pentose and hexose sugars are degraded by the elevated temperatures (Jeoh 1998; Jeoh et al. 2001; Sun et al. 2002; Yang et al. 2007). When the dissolved solid content was measured by atmospheric oven drying, the volatile components such as furfural, HMF, methanol, and other light organics are evaporated, causing a lower solid content measurement.



Table 3- 2 Dissolved Solid Content in the Extract after Auto-Hydrolysis Treatment under Each Condition \*

Temp (°C)	Time (hour)	Original o.d wood <sup>a</sup> (g)	Total extract <sup>b</sup> (g)	Total extract <sup>c</sup> (ml)	Solid content <sup>d</sup> (%)	Oven dried solids <sup>e</sup> (g)	Yield <sup>f</sup> (%)
150	1	721.0±1.6	2,911.4	2,850.1	1.9±0.0	53.8	7.5
	2	721.0±1.6	2,944.3	2,910.1	2.8±0.0	84.4	11.7
160	1	713.7±1.1	3,007.9	2,904.7	3.7±0.1	111.1	15.6
	2	721.0±1.6	3,030.6	2,992.8	4.7±0.0	142.1	19.7
170	1	713.7±1.1	3,027.3	2,993.9	4.0±0.0	120.2	16.8
	2	713.7±1.1	3,047.8	2,961.1	3.4±0.1	102.2	14.4
180	1	713.7±1.1	3,060.4	2,973.6	2.7±0.0	83.3	11.7
	2	713.7±1.1	3,066.9	3,006.7	2.1±0.1	63.4	8.9

<sup>a</sup> Calculated by weight of air-dried wood chips times consistency measured gravimetrically

<sup>b</sup> Calculated by subtracting OD solids of the residue from total raw material (wood + water)

<sup>c</sup> Calculated from extract weight with known volume

<sup>d</sup> Weight percentage, measured gravimetrically, calculated by (oven dried solid weight in the filtrate / weight of extract\*100)

<sup>e</sup> Total solids in the extract, calculated by (solid content (w/w%) times total grams of extract)

<sup>f</sup> Weight percentage, calculated by (total solids in the extract / total original solid weight\*100)

\* The mean value and the range of duplicate experiments are reported.

### 3.4.2 Autohydrolysis Byproducts

Other identified components present in the extract solution were analyzed by HPLC. The amount of acetic acid, which is the degradation product from the acetyl groups of hemicelluloses, increased with temperature and time (Table 3- 3). Furfural and HMF have

the same increasing trend as acetic acid as the temperature and extraction time increased. High temperature and longer extraction time favor the formation of furfural and HMF as xylose and glucose are formed in the wood extract during the extraction process. This fact is in good agreement with the previous discussion of the solid recovery yield.

Table 3- 3 Acetic Acid, Furfural, HMF and Formic Acid in the Filtrate Measured by HPLC (based on 100 grams of original OD wood)

Temperature (°C)	150		160		170		180	
Time (hour)	1	2	1	2	1	2	1	2
Acetic Acid (g)	1.3±0.1	1.5±0.2	1.5±0.1	3.1±0.4	2.7±0.0	4.0±0.4	5.4±0.0	6.2±0.6
Furfural (g)	0.1±0.0	0.2±0.0	0.2±0.0	0.6±0.0	0.4±0.0	1.0±0.1	1.1±0.1	1.2±0.0
HMF (g)	0.0±0.0	0.0±0.0	0.0±0.0	0.1±0.0	0.1±0.0	0.2±0.0	0.4±0.0	0.5±0.0
Formic acid (g)	2.5±0.0	1.4±0.1	1.7±0.2	1.7±0.2	1.5±0.1	1.4±0.3	1.7±0.0	1.8±0.2

Table 3- 4 shows the summarized solid recovery yield in both solid residues and extract solutions after auto-hydrolysis. As temperature increased, the total solid recovery yield was steadily decreased from nearly 99% at 150 °C to about 80% at 80 °C. There was a similar solid decline trend with the extension of reaction time when the temperature approached over 170 °C. The increasing total lost solid can contribute to the increasing volatile components listed in the Table 3 formed during the extraction. When the solid recovery yield measurements were carried out in the oven, those components evaporated and thus caused the solid loss.

Table 3- 4 Summarized Dissolved Solid Content in the Solid Residue and Extract after Auto-Hydrolysis Treatment under Different Conditions as Grams based on 100 Grams of OD Original Wood

Temp (°C)	150		160		170		180	
Time (hour)	1	2	1	2	1	2	1	2
Solid in residue (g)	91.3	86.8	78.1	74.8	75.8	73.0	70.8	70.3
Solid in filtrate (g)	7.5	11.7	15.6	19.7	16.8	14.4	11.7	8.9
Total (g)	98.8	98.5	93.7	94.5	92.6	87.3	82.5	79.2

### 3.4.3 Sugars in the extract solution

During the auto-hydrolysis process, water under high temperature and high pressure penetrates into the wood, causes partial hydrolysis of cellulose, dissolving of hemicellulose and removal of a portion of lignin (Taherzadeh et al., 2008). The hemicellulose is extracted from the wood chips in the form of liquid-soluble oligosaccharides with various degree of polymerization. The oligosaccharides can be further hydrolyzed to monosaccharides by using acid with proper concentration. The monomeric sugars formed during the auto-hydrolysis can further degraded into furfural and HMF. In the present study, monomeric sugars, formed during auto-hydrolysis and the afterward acid hydrolysis (using 4% H<sub>2</sub>SO<sub>4</sub>), were analyzed by a Dionex ICS 3000 system. All results are presented in Table 3- 5. The total carbohydrates amounted to almost 10 grams out of 100 grams of oven dried starting material under 170 °C for 2 hours. The carbohydrate yields clearly dropped after the temperature approached to 180 °C. The decrease was extensive for arabinose and xylose under severer conditions that went beyond 170 °C, 2 hour, mainly due to their acidic degradation to furfural.

Arabinose was mostly extracted in the monomeric form under all the conditions, while rhabinose was in the form of monomer only under higher temperature (170 °C and 180 °C). A major portion of xylose remained in the polymeric form until a higher extraction severities was achieved (180 °C). Xylose in the auto-hydrolysis filtrate was a maximum of 4.1g under 180 °C, 1 hour pretreatment condition, which is the highest yield of mono-sugar in the filtrate compared with other sugars. Glucomannan kept mostly in the polymeric form even under higher temperature and longer retention time, since after the acid treatment there was still a significant increase can be observed in the amount of monomeric glucose and mannose under severer conditions, comparing with other sugars. Most of the monomeric glucose formed in the extract was derived from glucomannan, while the other fraction was a result of dissolving and hydrolysis of cellulose.

Table 3- 5 Sugar Composition in the Autohydrolysis Extracts under Each Condition Before (Mono) and After Acid-hydrolysis (Total) by 3% H<sub>2</sub>SO<sub>4</sub> as Grams of Mono-sugar Recovered from 100 grams of OD Original Wood

Temp		150°C		160°C		170°C		180°C	
Time (hour)		1	2	1	2	1	2	1	2
Arabinan (g)	Mono <sup>a</sup>	0.27	0.34	0.55	0.37	0.33	0.32	0.27	0.13
	Total <sup>b</sup>	0.37	0.40	0.54	0.40	0.29	0.26	0.15	0.04
Rhamnan (g)	Mono <sup>a</sup>	0.04	0.05	0.14	0.17	0.13	0.24	0.22	0.12
	Total <sup>b</sup>	0.11	0.16	0.28	0.28	0.20	0.24	0.16	0.10
Galactan (g)	Mono <sup>a</sup>	0.07	0.11	0.21	0.30	0.30	0.49	0.55	0.41
	Total <sup>b</sup>	0.34	0.51	0.61	0.58	0.69	0.63	0.46	0.34
Glucan (g)	Mono <sup>a</sup>	0.03	0.04	0.05	0.07	0.02	0.20	0.34	0.43
	Total <sup>b</sup>	0.15	0.19	0.25	0.24	0.33	0.42	0.44	0.54
Xylan (g)	Mono <sup>a</sup>	0.11	0.24	1.10	2.10	2.61	3.84	4.10	2.40
	Total <sup>b</sup>	1.90	3.76	7.56	7.84	7.26	7.45	5.29	2.54
Mannan (g)	Mono <sup>a</sup>			0.05	0.09	0.10	0.33	0.52	0.46
	Total <sup>b</sup>	0.24	0.31	0.57	0.63	0.59	0.83	0.76	0.60
Sum (g)	Mono <sup>a</sup>	0.52	0.78	2.10	3.09	3.49	5.42	6.00	3.93
	Total <sup>b</sup>	3.10	5.34	9.81	9.96	9.35	9.82	7.27	4.15
Yield (%)	Extract <sup>c</sup>	41.48	45.67	62.95	50.57	55.51	68.62	62.22	46.66
	Lost <sup>d</sup>	35.78	40.43	44.66	40.53	38.64	36.26	24.77	13.92

<sup>a</sup> The amount of monosaccharides formed in the extracts during auto-hydrolysis

<sup>b</sup> The total amount of monosaccharides in the extracts after acid-hydrolysis by 3% H<sub>2</sub>SO<sub>4</sub>

<sup>c</sup> Sugar yield per solid in the extract, calculated by (total sugar / total solid yield in the extract \*100)

<sup>d</sup> Sugar yield out of solid loss of original OD wood material, calculated by (total sugar / (100 – solid recovery yield of solid residue after hot-water extraction)\*100)

After 60 min pretreatment at 180 °C, 6.0g of mono-sugars was contained in the autohydrolysis filtrate. All the filtrate was subjected to an acid hydrolysis with 4% H<sub>2</sub>SO<sub>4</sub>,

after that totally 9.9g sugar was recovered from the extract under 170 °C for 2 hours, which accounted for 66.79% of the total solid recovered from the extract solution and 36.86% out of the total solid loss during the extraction. Hot-water extraction under 160 °C for 1 hours seemed like have the highest sugar recovery yield from the total solid loss: totally 9.81 g sugar was recovered, which is 62.95% of the total solid in the extract and 44.66% of the solid loss.

Table 3- 6 Sugar Composition of the Raw Material and of the Auto-hydrolysis Residue from Each Condition as Grams Recovered from 100 Grams of OD Original Wood

Temp		150°C		160°C		170°C		180°C	
Time (hour)	Raw	1 hour	2 hour	1 hour	2 hour	1 hour	2 hour	1 hour	2 hour
Arabinan (g)	0.8	-	-	-	-	-	-	-	-
Rhamnan (g)	0.5	-	-	-	-	-	-	-	-
Galactan (g)	1	0.5	0.4	-	-	-	-	-	-
Glucan (g)	41.2	43.8	42.6	38.4	43.1	42	42.3	39.3	40.1
Xylan (g)	16.2	12.7	11	7.4	5.1	5.1	3.7	3.1	2.4
Mannan (g)	1.6	1.2	1.2	1.1	0.6	0.8	0.5	0.3	0.2
Sum (g)	61.2	58.3	55.2	46.9	48.8	47.8	46.6	42.7	42.6
% of sugar <sup>a</sup>		63.8	63.6	60	53.5	63	63.9	60.3	60.7

<sup>a</sup> Percentage of total sugar out of solid recovery yield of solid residue after auto-hydrolysis

The high yield of xylose was verified by the analysis of sugar content in the solid residues after extraction (Table 3- 6). The amount of xylose in the solid residues decreases

continuously from almost 13g at 150 °C for 1 hour to only 2-3 g at 180 °C for 2 hours, which means that more xylose was removed under harsher condition and longer retention time. Arabinose, rhamnose and galactose were efficiently removed under higher reaction temperature and longer reaction time, while there was a significant amount of glucose found in the residues. This is probably due to the partial degradation of cellulose in the course of 4% H<sub>2</sub>SO<sub>4</sub> treatment applied in this study (Song, et al., 2008).

#### **3.4.4 Heat Content of Residues**

The heating values of all the residues from different auto-hydrolysis treatment conditions as well as from the original wood sample were determined by a standard bomb calorimeter method. The heating value determined was the “high heating value” (HHV), which includes the latent heat given up when newly formed water vapor condenses and cools to the temperature of the bomb (Thipse et al. 2002). Table 3- 7 shows all the heating value results obtained in duplicate for each sample.

Table 3- 7 High Heating Value of the Original Wood and of the Residues under Each Condition. Average and range indicated for the duplicates.

		Heat of combustion (calories/gram)
From Reference <sup>a</sup>		4,630
Original wood		4,377±20
150°C	1 hour	4,557±12
	2 hour	4,628±1
160°C	1 hour	4,410±14
	2 hour	4,502±29
170°C	1 hour	4,494±20
	2 hour	4,534±1
180°C	1 hour	4,627±1
	2 hour	4,616±56

<sup>a</sup> Data obtained from a reference (Thipse et al. 2002).

The heating value of the original wood sample was about 4,400 calories per gram (oven dry), which was the lowest value compared with all other extracted samples. As the extraction temperature increased, the corresponding heating values of the residues steadily increased. This is a reasonable tendency, since the higher the temperature the more extensive the hemicellulose and cellulose extraction. As a result, the residues after the hot-water extraction had a higher concentration of lignin (Table 3- 8), which has a higher heating value than the carbohydrates in woody material (White 1987; Demirba 2001, 2002). However, this



did not mean that a higher extraction temperature will always achieve a higher total energy content, since higher temperatures resulted in a dramatic weight loss of the solid residues (Table 3- 4). Figure 3- 2 shows the percentage of total energy remaining in the solid residues, compared with the original starting material. At 150 °C and 1 hour treatment the energy content of the solid residues was 95% of the original wood. As the extraction temperature increased to 160 °C, 75% of the total energy was retained in the residue.

Table 3- 8 Lignin Content in the Residues (Based on oven dry residues, range of duplicate reported)

Temp (°C)	Residence time (hours)	Lignin <sup>a</sup> (%)
150	1	26.8±1.0
	2	27.0±0.5
160	1	27.8±1.2
	2	27.9±0.3
170	1	28.9±0.8
	2	29.7±1.1
180	1	34.4±0.5
	2	34.5±0.8

<sup>a</sup> Including both acid soluble lignin and acid insoluble lignin

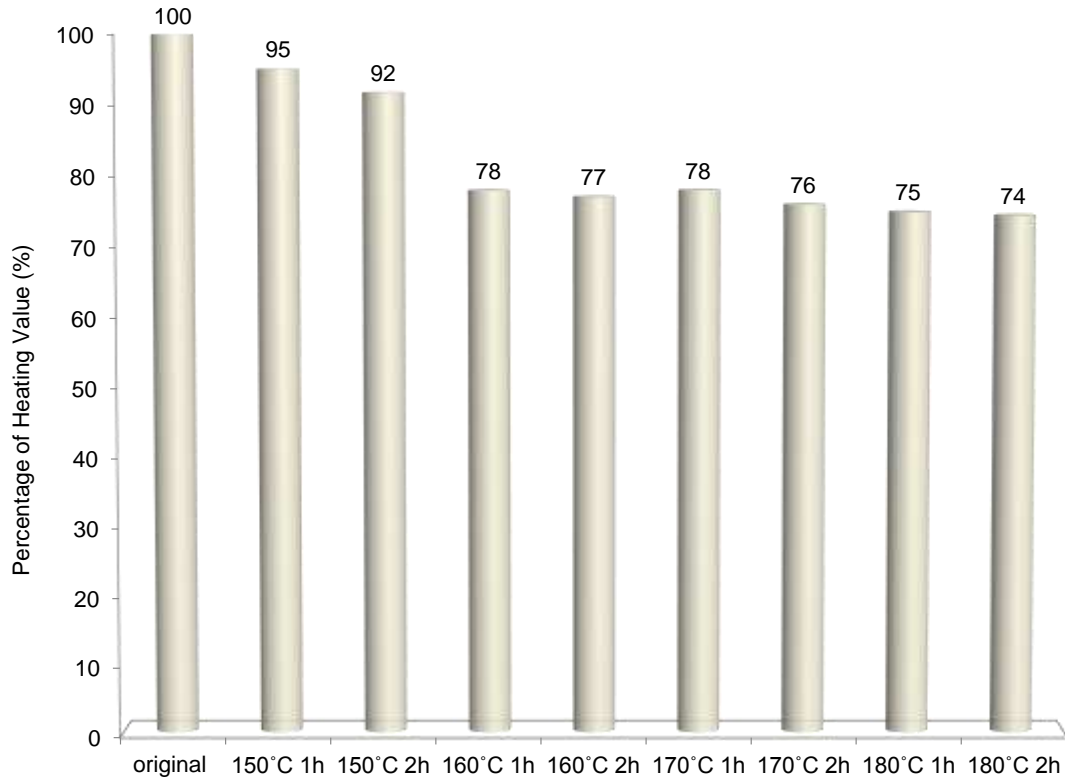


Figure 3- 2 Percentage of total heating value recovered from original wood.

When considering the use of the solid residues for energy content in a combustion process and the use of the extracted carbohydrates as feedstock for ethanol production, a careful analysis of the overall net benefit of the system versus extraction temperature and time needs to be evaluated. A subsequent paper on the relative economics of the proposed “value prior to combustion” process will use these results as modeling inputs.

### 3.5 Conclusions

The hot-water extraction of mixed hardwood was carried out from 150 °C to 180 °C, with 1 and 2 hours residence time. By examining the solid content in both the extraction liquid and solid residues, a significant weight loss was found for the higher temperature and longer reaction time treatment, which correlated to a greater amount of volatile byproducts formed during the extraction process. Acetic acid, furfural, and HMF formed during the hot-water extraction were found to steadily increase with increasing extraction temperature and reaction time. There were four “optimal” conditions found for sugar extraction, in terms of different criteria: 180 °C, 1 hour had the highest mono-sugars (6.00 grams) in the filtrate without acid hydrolysis treatment; 160 °C, 2 hours had the highest sugar monomers after breaking down all the oligo-sugars to mono-sugars (9.96 grams); 170 °C, 2 hours resulted in the highest yield of sugar per unit of solid in the extract (68.6%); and 160 °C, 1 hour ended up with the highest sugar yield per unit of solid that supposed to be dissolved in the filtrate (44.7%). Xylose had the highest yield out of all extracted sugars. Xylose was primarily extracted in a polymeric form. The composition analysis of the solid residues verified that most of the hemicelluloses were effectively extracted into the liquid, while the cellulose remained in the residue. As the extraction temperature increased, more material was dissolved, leaving higher proportions of lignin in the residues and thus higher heating values of the residues. The total energy that could be recovered in the residue after the hot-water extraction was approximately 75% after extraction of the hemicelluloses.

### 3.6 References

- Amidon, T., and Liu, S. (2009). "Water-based woody biorefinery," *Biotechnology advances* 27(5), 542-550.
- Amidon, T., Wood, C., Shupe, A., Wang, Y., Graves, M., and Liu, S. (2008). "Biorefinery: Conversion of woody biomass to chemicals, energy and materials," *Journal of Biobased Materials and Bioenergy* 2(2), 100-120.
- Andersson, A., Persson, T., Zacchi, G., Stålbrand, H., and Jönsson, A. (2007). "Comparison of diafiltration and size-exclusion chromatography to recover hemicelluloses from process water from thermomechanical pulping of spruce," *Applied Biochemistry and Biotechnology* 136(140), 971-983.
- ASTM (2011). "Standard test method for gross calorific value of coal and coke by the adiabatic bomb calorimeter," Retrieved 06/17, 2011, from <http://www.astm.org/Standards/D2015.htm>.
- Bai, Y., Luo, L., and van der Voet, E. (2010). "Life cycle assessment of switchgrass-derived ethanol as transport fuel," *The International Journal of Life Cycle Assessment* 15(5), 468-477.

- Chen, S. F., Mowery, R. A., Castleberry, V. A., Walsum, G., and Chambliss, C. K. (2006). "High-performance liquid chromatography method for simultaneous determination of aliphatic acid, aromatic acid and neutral degradation products in biomass pretreatment hydrolysates," *Journal of Chromatography A* 1104(1-2), 54-61.
- Cherubini, F., and Jungmeier, G. (2010). "LCA of a biorefinery concept producing bioethanol, bioenergy, and chemicals from switchgrass," *The International Journal of Life Cycle Assessment* 15(1), 53-66.
- Demirba, A. (2001). "Relationships between lignin contents and heating values of biomass," *Energy conversion and management* 42(2), 183-188.
- Demirba, A. (2002). "Relationships between heating value and lignin, moisture, ash and extractive contents of biomass fuels," *Energy, Exploration & Exploitation* 20(1), 105-111.
- Gatenholm, P. (2008). "Fractionation and characterization of xylan rich extracts from birch," *Holzforschung* 62, 31-37.
- Gonzalez, R., Jameel, H., Chang, H., Treasure, T., Pirraglia, A., and Saloni, D. (2011a). "Thermo-mechanical Pulping as a Pretreatment for Agricultural Biomass for Biochemical Conversion," *BioResources* 6(2), 1599-1614.

- Gonzalez, R., Phillips, R., Saloni, D., Jameel, H., Abt, R., Pirraglia, A., and Wright, J. (2011b). "Biomass to energy in the Southern United States: Supply chain and delivered cost," *BioResources*. 6(3), 2954-2976.
- Gonzalez, R., Saloni, D., Dasmohapatra, S., and Cubbage, F. (2008). "South America: industrial roundwood supply potential," *BioResources* 3(1), 255-269.
- Gonzalez, R., Treasure, T., Phillips, R., Jameel, H., and Saloni, D. (2011c). "Economics of cellulosic ethanol production: Green liquor pretreatment for softwood and hardwood, greenfield and repurpose scenarios," *BioResources* 6(3), 2551-2567.
- Gonzalez, R., Treasure, T., Phillips, R., Jameel, H., Saloni, D., Abt, R., and Wright, J. (2011d). "Converting Eucalyptus biomass into ethanol: Financial and sensitivity analysis in a co-current dilute acid process. Part II," *Biomass and Bioenergy* 35(2), 767-772.
- Gregg, D., and Saddler, J. (1996a). "Factors affecting cellulose hydrolysis and the potential of enzyme recycle to enhance the efficiency of an integrated wood to ethanol process," *Biotechnology and Bioengineering* 51(4), 375-383.
- Gregg, D., and Saddler, J. (1996b). "A techno-economic assessment of the pretreatment and fractionation steps of a biomass-to-ethanol process," *Applied biochemistry and Biotechnology* 57(1), 711-727.

- Hess, J., Wright, C., and Kenney, K. (2007). "Cellulosic biomass feedstocks and logistics for ethanol production," *Biofuels, Bioproducts and Biorefining* 1(3), 181-190.
- Janssen, M., Chambost, V., and Stuart, P. (2008). "Successful partnerships for the forest biorefinery," *Industrial Biotechnology* 4(4), 352-362.
- Janssen, M., and Stuart, P. (2010). "Sustainable product portfolio and process design of the forest biorefinery," Proceedings of the Canadian Engineering Education Association.
- Jeoh, T. (1998). "Steam explosion pretreatment of cotton gin waste for fuel ethanol production," Master Thesis. Virginia Polytechnic Institute and State University.
- Jeoh, T., and Agblevor, F. (2001). "Characterization and fermentation of steam exploded cotton gin waste," *Biomass and Bioenergy* 21(2), 109-120.
- Kumar, S., Singh, S. P., Mishra, I. M., and Adhikari, D. K. (2009). "Recent advances in production of bioethanol from lignocellulosic biomass," *Chemical Engineering & Technology* 32(4), 517-526.
- Lee, J., Venditti, R., Jameel, H., and Kenealy, W. (2010). "Detoxification of woody hydrolyzates with activated carbon for bioconversion to ethanol by the thermophilic anaerobic bacterium *Thermoanaerobacterium saccharolyticum*," *Biomass and Bioenergy* 35(1), 626-636.

- Leschinsky, M., Sixta, H., and Patt, R. (2009). "Detailed mass balances of the autohydrolysis of Eucalyptus globulus at 170 C," *BioResources* 4(2), 687-703.
- Liu, S., Amidon, T., Francis, R., Ramarao, B., Lai, Y., and Scott, G. (2006). "From forest biomass to chemicals and energy... Biorefinery initiative in New York State," *Industrial Biotechnology* 2(2), 113-120.
- NREL (2005). "Biomass analysis technology team laboratory analytical procedure."US Department of Energy, National Renewable Energy Laboratory.
- Pan, X., Arato, C., Gilkes, N., Gregg, D., Mabee, W., Pye, K., Xiao, Z., Zhang, X., and Saddler, J. (2005a). "Biorefining of softwoods using ethanol organosolv pulping: Preliminary evaluation of process streams for manufacture of fuel-grade ethanol and co-products," *Biotechnology and Bioengineering* 90(4), 473-481.
- Pan, X., Xie, D., Gilkes, N., Gregg, D., and Saddler, J. (2005b). "Strategies to enhance the enzymatic hydrolysis of pretreated softwood with high residual lignin content," *Applied Biochemistry and Biotechnology* 124(1), 1069-1079.
- Persson, T., Nordin, A., Zacchi, G., and Jönsson, A. (2007). "Economic evaluation of isolation of hemicelluloses from process streams from thermomechanical pulping of spruce," *Applied Biochemistry and Biotechnology* 136(140), 741-752.



- Pettersen, R. (1991). "Wood sugar analysis by anion chromatography," *Journal of Wood Chemistry and Technology* 11(4), 495-501.
- Salam, A., Venditti, R., Pawlak, J., and El-Tahlawy, K. (2011). "Crosslinked hemicellulose citrate-chitosan aerogel foams," *Carbohydrate Polymers* 84(4), 1221-1229.
- Song, T., Pranovich, A., Summerskiy, I., and Holmbom, B. (2008). "Extraction of galactoglucomannan from spruce wood with pressurised hot water," *Holzforschung* 62(6), 659-666.
- Sticklen, M. (2006). "Plant genetic engineering to improve biomass characteristics for biofuels," *Current Opinion in Biotechnology* 17(3), 315-319.
- Stoutenburg, R., Perrotta, J., Amidon, T., and Nakas, J. (2008). "Ethanol production from a membrane purified hemicellulosic hydrolysate derived from sugar maple by *Pichia stipitis* NRRL Y-7124," *BioResources* 3(4), 1349-1358.
- Sun, Y., and Cheng, J. (2002). "Hydrolysis of lignocellulosic materials for ethanol production: A review," *Bioresource Technology* 83(1), 1-11.
- Taherzadeh, M., and Karimi, K. (2008). "Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: A review," *International Journal of Molecular Sciences* 9(9), 1621-1651.

- Thipse, S., Sheng, C., Booty, M., Magee, R., and Bozzelli, J. (2002). "Chemical makeup and physical characterization of a synthetic fuel and methods of heat content evaluation for studies on MSW incineration," *Fuel* 81(2), 211-217.
- USDA (2011). "Forest Inventory and Analysis National Program," Retrieved 06/14, 2011, from <http://fia.fs.fed.us/>.
- Von Blottnitz, H., and Curran, M. A. (2007). "A review of assessments conducted on bio-ethanol as a transportation fuel from a net energy, greenhouse gas, and environmental life cycle perspective," *Journal of Cleaner Production* 15(7), 607-619.
- White, R. (1987). "Effect of lignin content and extractives on the higher heating value of wood," *Wood and Fiber Science* 19(4), 446-452.
- Willför, S., Sundberg, K., Tenkanen, M., and Holmbom, B. (2008). "Spruce-derived mannans-A potential raw material for hydrocolloids and novel advanced natural materials," *Carbohydrate Polymers* 72(2), 197-210.
- Yang, H., Yan, R., Chen, H., Lee, D. H., and Zheng, C. (2007). "Characteristics of hemicellulose, cellulose and lignin pyrolysis," *Fuel* 86(12-13), 1781-1788.

Paper submitted to Bioenergy Research. “AUTO-HYDROLYSIS PRETREATMENT OF MIXED SOFTWOOD TO PRODUCE VALUE PRIOR TO COMBUSTION” Yan Pu, Trevor Treasure, Richard A. Venditti, Hasan Jameel, Ronalds Gonzalez

## **CHAPTER 4: Auto-hydrolysis Pretreatment of Mixed Softwood to Produce Value Prior to Combustion**

### **4.1 Abstract**

Auto-hydrolysis is a pretreatment that uses hot-water to extract soluble components from wood prior to converting the woody residuals into paper, wood products, fuel, or other goods. In this study, mixed softwood chips were auto-hydrolyzed in hot-water at 150, 160, 170 and 180 °C, for 1 and 2 hour residence times. The objective was to understand the tradeoff between the extraction of fermentable sugar and the residual solid total energy of combustion. This process strategy will be referred to as “value prior to combustion”. For each condition a material balance was performed around autohydrolysis to realize the role of temperature and residence time on sugar production and residual solid heating value. The extracted liquid was treated with dilute sulfuric acid to break down sugar oligomers for compositional analysis. High Performance Liquid Chromatography (HPLC) was used to determine composition (sugars and byproducts such as acetic acid, furfural, and

hydroxymethylfurfural) of the extracted liquid. The composition of the raw material and residual solid was determined by a conventional Klason lignin assay. A bomb calorimeter was used to measure the heating value of original wood and solid residue. As the autohydrolysis temperature increased, the material balance closure decreased, presumably due to more volatile byproducts being formed that were not quantified. More hemicelluloses were solubilized by the hot water extraction process at higher temperatures and longer residence times, and a greater degree of sugar degradation was also observed. After hot-water extraction the heating value of the solid residues was greater than the original wood. The total energy content of the solid residual after extraction ranged from 85-98% of the original energy content of the feed with higher temperatures reducing the total energy content.

## **4.2 Introduction**

As global environmental issues and the growing cost of nonrenewable fuels garner more attention, significant effort has been put into exploring alternative energy products that could be obtained from sustainable and renewable resources. Lignocellulosic materials have been recognized as one of the most promising candidates feedstocks, due to their availability in nature, low cost, and positive environmental attributes (Gonzalez, et al., 2011a; Gonzalez, et al. 2011b; Gonzalez, et al., 2011c; Stocker, 2008; Tunc, et al., 2010) . Woody materials

and/or wastes have already been widely used either in the pulping industry or for power generation (Westbye, et al., 2008). There is tremendous interest to study their value-added chemical byproducts potential (Tunc, et al., 2010; Ragauskas, et al., 2006).

Lignocellulosic feedstocks are basically composed of three components: cellulose, hemicelluloses and lignin (Willfor, et al., 2005; Willfor, et al. 2008). Cellulose is a linear homopolymer (one-dimensional polymer) composed of D-glucose units connected by a  $\beta(1,4)$  linkage. It provides the biomass with structure and strength. Hemicelluloses are heteropolymer built up with five- and six- carbon sugars with short branched side connections, thus a two-dimensional polymer with lower molecular weight than cellulose. Cellulose and hemicellulose both have a carbon to oxygen atom ratio about 1:1 (Amidon, et al., 2008). Lignin is an amorphous heteropolymer with a three-dimensional structure mainly consisting of phenylpropylene alcohol. It has a carbon to oxygen atom ratio higher than 2:1, thus is a more energy dense substance relative to cellulose and hemicellulose. Lignin acts as a natural barrier to biological degradation to biomass (Stocker, 2008).

Among the three major components of wood, hemicellulose can be selectively extracted by a variety of pretreatments to subsequently produce value-added products such as polymers, ethanol and other chemicals (Li, et al., 2010; Li, et al., 2005; Salam, et al., 2011;

Rughani and McGinnis, 1989). The hot-water extraction process, which is also known as autohydrolysis or autocatalytic, can partially extract hemicellulose oligomers (mainly xylo-oligomers with different degrees of polymerization) from wood chips at high temperature and pressure (Leschinsky, et al., 2009; Taherzadeh and Karimi, 2008). The extracted xylose and other hemicellulose sugars can undergo fermentation by microorganisms to produce chemicals such as ethanol. Thus, hemicelluloses can be deemed a potential renewable resource for bio-based fuels (Hess, et al., 2007; Stoutenburg, et al., 2008). Hemicellulosic sugars can also be used to produce biodegradable plastics and chemicals that are currently derived from petroleum (Amidon, et al., 2008; Liu, et al., 2006; Lundqvist, et al., 2003; Salam, et al., 2011; Willfor, et al., 2005). Moreover, the residual solid material after extraction can be burned to produce heat and power or further processed to produce paper products (Amidon and Liu, 2009; Caparros, et al., 2008; Lavoie, et al., 2010; Li, et al., 2010; San Martin, et al., 1995) or wood products.

During the process of hot-water extraction, acids are produced by the hydrolysis of hemicellulose and degradation of sugars (Amidon and Liu, 2009). Organic acids, for example, acetic acid formed from hydrolysis of acetyl groups in hemicelluloses (Ligero, et al., 2011; Mills, et al., 2009; Zhang, et al., 2010), coupled with the dissolution of extractives in the biomass, lead to a decrease in liquor pH. Decreases in pH enhance the solubility of the

hemicelluloses, which is the reason that the hot-water extraction process is also known as auto-hydrolysis or auto-catalytic.

Compared with other chemical pretreatments, auto-hydrolysis has the advantages of: being comparatively environmentally friendly due to no inorganic chemical use and recovery (Garrote, et al., 2003; Garrote, et al., 1999; Garrote, et al., 2001); having no organic solvent use; being less corrosive (Garrote, et al., 2001); having fewer undesired sugar degradation products when compared with inorganic acid pretreatments; and having more value-added chemicals that can be recovered and some other economic related benefits. Under optimum autohydrolysis conditions, hemicelluloses (mostly xylo-oligosaccharides) can be successfully extracted from lignocellulosic biomass and utilized to produce ethanol, pharmaceuticals, agricultural raw materials, and food additives (Tunc, et al., 2008).

Hemicellulose extraction from woody biomass can be employed in either a biorefinery scheme that targets extracting and producing value-added chemicals before power generation (FitzPatrick, et al., 2010; Ligeró, et al., 2011), or in the pulp and paper industry in which ethanol and pulp is simultaneously produced (Amidon and Liu, 2009; Caparrós, et al., 2008; Lavoie, et al., 2010; San Martín, et al., 1995; Garrote, et al., 2003; Vila, et al., 2011). Unlike the production of pulp from pre-extracted biomass, the physical and chemical properties of pre-extracted biomass for combustion are not as critical. In the

value prior to combustion concept, hemicellulose extraction before the combustion of biomass will positively enhance the heating value density, due to a higher lignin concentration being generated (Pu, et al., 2011). Since the purpose of utilizing all parts of the biomass is the basis of the present study, the technology examined here could be deployed as a front-end pretreatment for many different pathways that use biomass to produce fuels, chemicals, and other materials.

In this study, hot-water extraction was applied to pretreat mixed softwood chips at temperatures ranging from 150 °C to 180 °C for 1 hour and 2 hours. The optimal condition, in terms of the highest sugar yield is presented. The heating value and total energy content of the residual material after the hemicellulose extraction is shown. A previous study by Pu et al. (2011) of auto-hydrolysis of mixed hardwood describes the tradeoff between water extractable sugar yield and energy content of the solid residue. This process configuration has been previously termed “value prior to combustion” or VPC. According to this study, there were four “optimal” conditions found for sugar extraction in terms of different criteria: the highest mono-sugars in the hydrolyzate; the highest sugar monomers after breaking down all the oligo-sugars to mono-sugars; the highest sugar yield per unit of solid in the extract and the highest sugar yield per unit of original oven dry material lost. Xylose was found primarily extracted in polymeric form and had the highest yield compared with other sugars. About 75%



of the total energy content could be recovered after the extraction of hardwood. Compared with hardwood, the predominant hemicellulose in softwoods is mannose, which is fermentable by using normal baker's yeast rather than a five carbon sugar fermenting organism that needs to be used in the hardwood case (Galbe and Zacchi, 2002). Additionally, softwood is known as being much more recalcitrant than hardwood due to its more rigid structure and higher content of lignin as well as types of lignin (Galbe and Zacchi, 2002).

### **4.3 Materials and methods**

#### **4.3.1 Softwood material**

Softwood chips collected from Eastern North Carolina with dimensions approximately 30 mm long, 30 mm wide and 2.5 mm thick were used as the raw material for the hot-water extraction. These chips were stored in a cold room at 4 °C and air dried for two days before use. Moisture content of air-dried chips was measured by standard oven drying at 105 °C until constant weight was achieved. Composition of the original biomass was determined using Klason lignin standards; values are as follows: lignin 29%, cellulose 41%, hemicellulose 21%, and unidentified others 9%.

### **4.3.2 Hot-water extraction**

Hot-water extraction was performed with a lab scale batch digester capable of liquor circulation (M/K Systems Inc., Danvers, MA). Approximately 800 g air dried wood chips were extracted in each batch. A water to solid ratio of 4:1 was used for all of the extraction trials. Extraction conditions evaluated were 150 °C, 160 °C, 170 °C and 180 °C for both 1 and 2 hours residence time for each temperature. The water extract was collected and the solid content of the extract was measured. The pH value of each extract was measured shortly after the extraction at room temperature.

The residue after extraction was thoroughly washed with tap water for 1 hour and subsequently soaked in tap water for 16 hours. The soaked chips were centrifuged to approximately 40% consistency.

### **4.3.3 Analysis of extracts**

The solid content of the extract was determined gravimetrically by standard oven drying at 105 °C to a constant weight. Triplicate treatments were carried out for each sample.

The sugar monosaccharides of the extract were determined by an ion chromatography system (Dionex ICS-3000, Sunnyvale, CA) before and after acid hydrolysis (3% sulfuric acid,

122°C, 1.5 hour in the autoclave). The monomeric sugar content difference before and after the acid hydrolysis represents the oligo- and polysaccharide content in the sample (Andersson, et al., 2007; Persson, et al., 2007). The chromatograph was equipped with an autosampler, a dual pump (model DP-1), an eluent generator (model EG-2) and a detector/chromatography module (model DC-1). Milli-Q water and 400mN sodium hydroxide (NaOH) solution were used as the eluents at the flow rate of 1.1mL/min. Fucose was added to each sample as an internal standard. D-fucose, D-arabinose, D-rhamnose, D-galactose, D-glucose, D-xylose and D-mannose were used as calibration standards to produce the sugar calibration curves (Pettersen, 1991).

Furfural, hydroxymethyl furfural (HMF), formic acid and acetic acid were quantified by a Dionex high performance liquid chromatography, which was equipped with an eluent pump (P680 HPLC pump), an autosampler (ASI-100 Automated Sample Injector) and a UV detector (UVD170U). Standard curves were made for each byproduct by using a 6 point calibration and all the standard samples were dissolved in milli-Q water. The 4-tert-butylphenoxyacetic acid, which was dissolved in methanol, was used as the internal standard. Both methanesulfonic acid and acetonitrile were used as the eluents, with a flow rate of 1mL/min.

#### **4.3.4 Analysis of original wood**

Original wood chips and air-dried solid extracted residues were ground to pass through a 40 mesh screen and be retained on a 60 mesh screen. A certain amount (0.100 g) of such ground wood powder was subjected to an acid hydrolysis by adding 1.5 mL 72% sulfuric acid and thoroughly stirring every 15 minutes at room temperature. After 1.5 hours, the resulting sample was carefully transferred to a serum bottle by rinsing with 56 mL of DI water to bring the acid concentration to 3%. The serum bottle was sealed and autoclaved for 90 minutes at 122 °C. The autoclaved hydrolysis solution was vacuum-filtered through a previously weighed filtering crucible (medium porosity) and collected. This sample was used to determine acid soluble lignin as well as sugar composition, as described above. Deionized water was used to quantitatively transfer all remaining solids in the serum bottle into the filtering crucible after the filtrate had been collected. The crucible accompanied with acid insoluble residue was dried by standard oven drying at 105 °C until a constant weight was achieved. Acid insoluble lignin (AISL), also known as Klason lignin, was calculated after the gravimetric analysis described above.

#### **4.3.5 Standard bomb calorimeter method for heat content of samples**

All the samples to be subjected to a standard bomb calorimeter (1341 Oxygen Bomb Calorimeter, Parr Instrument Company, Moline, IL) measurement were first ground to 20 meshes particle and then compressed into pellet by using a pellet press (Perkin Elmer 15.011, Britain) prior to be weighed.

The heat content was determined by burning the samples with excess oxygen at a pressure of 30 atmospheres in a sealed steel bomb, which is regarded as a near-adiabatic circumstance. Time versus temperature over the whole combustion process was recorded to obtain the total temperature rising and other pertinent thermochemical corrections, which including correction for heat of formation of nitric acid, sulfuric acid and heat of combustion of fuse wire. Before the heat of combustion test, 4 trials of standardization of the calorimeter were carried out by combusting of standard benzoic acid pellets provided by Parr Instrument Company to obtain the energy equivalent of calorimeter (Appendix XII). The heat of combustion was then calculated from the temperature rise, energy equivalent of calorimeter, all the thermochemical corrections and the mass of sample.

## 4.4 Results and discussion

### 4.4.1 Solid recovery yield of extracts and residues

Table 4-1 shows detailed solid recovery of residues after hot-water extraction for each condition.

Table 4- 1 Solid recovery yield in the centrifuged residues after auto-hydrolysis treatment. The mean value and standard deviation of triplicate experiments are reported.

<b>Temp</b> (° C)	<b>Time</b> (hour)	<b>Original</b> <b>Solid</b> <sup>a</sup> (g)	<b>Total wet</b> <b>residues</b> <sup>b</sup> (g)	<b>Moisture</b> <b>content</b> <sup>c</sup> (%)	<b>Oven dried</b> <b>solid</b> <sup>d</sup> (g)	<b>% out of</b> <b>original</b> <sup>e</sup>
<b>150</b>	1	679.3±11.9	1520.2	57.1±0.73	651.5±11.0	95.9
	2	689.9±2.3	1412.9	56.3±0.15	618.0±2.1	89.6
<b>160</b>	1	679.3±11.9	1498.1	59.4±1.14	607.8±17.0	89.5
	2	689.9±2.3	1372.4	58.7±1.32	566.5±18.1	82.1
<b>170</b>	1	689.9±2.3	1415.7	59.5±0.50	574.1±7.1	83.2
	2	689.9±2.3	1417.3	62.6±0.91	530.2±12.8	76.9
<b>180</b>	1	689.9±2.3	1408.2	61.9±0.79	536.2±11.0	77.7
	2	689.9±2.3	1424.6	63.0±1.05	526.8±15.0	76.4

<sup>a</sup> Calculated by weight of air-dried wood chips times consistency measured gravimetrically

<sup>b</sup> Measured after centrifuging the rinsed and soaked residue

<sup>c</sup> Weight percentage, measured gravimetrically, calculated as (oven dried solid weight of residue / weight of wet residue\*100)

<sup>d</sup> Total oven dried solid in the residue, calculated as (1- moisture content%) times total weight of wet residue

<sup>e</sup> Weight percentage, calculated as (total oven dried solid in the residue divides total original solid\*100)

The lowest temperature (150 °C) and shortest reaction time (1 hour) resulted in the highest solid recovery from the residues (about 96%). As temperature and residence time increased, a lower solid recovery yield was obtained with a 24% loss for 180 °C for 2 hours. These results are expected, since higher temperature and longer residence time should cause more woody material to be dissolved into the liquid phase. A parallel expectation is that a more severe extraction condition will contribute to a higher solid content in the liquid phase. However, from Table 4-2 it can be observed that higher temperature and longer reaction time did result in higher solid recovery in the filtrate, but not under the “extreme” condition for longer residence time (180 °C, for 2 hours). At higher temperature (greater than 170 °C) and longer residence time, more volatile byproducts like furfural, HMF and other light organics were generated, causing evaporation of those compounds and a lower solid content when measured by atmospheric oven drying. It was observed that as temperature increased the moisture contents of the solid residues were also increased. A possible explanation for this was proposed by Pu (Pu, et al. 2011) that a more open structure of wood chips, which absorbs and holds more water, was created under more severe condition. The higher moisture content of solid residue obtained at higher temperature implies that more pressing or drying operations may be needed in order to maximize the efficiency of the subsequent heating generation.

Table 4 - 2 Solid recover yield in the filtrate after auto-hydrolysis treatment\*

Temp (°C)	Time (hour)	Original Solid <sup>a</sup> (g)	Total extract <sup>b</sup> (g)	Total extract <sup>c</sup> (ml)	Solid content <sup>d</sup> (%)	Oven dried solid <sup>e</sup> (g)	Yield <sup>f</sup> (%)
<b>150</b>	1	679.3±11.9	2745.5	2727.7	1.8±0.05	50.0	7.4
	2	689.9±2.3	2832.0	2751.3	2.5±0.00	70.4	10.2
<b>160</b>	1	679.3±11.9	2789.2	2755.6	3.1±0.02	85.3	12.6
	2	689.9±2.3	2883.5	2837.7	3.6±0.03	102.8	14.9
<b>170</b>	1	689.9±2.3	2875.9	2843.3	3.6±0.01	102.5	14.9
	2	689.9±2.3	2919.8	2877.4	4.0±0.01	115.7	16.8
<b>180</b>	1	689.9±2.3	2913.8	2843.9	4.0±0.00	116.9	17.0
	2	689.9±2.3	2923.2	2895.2	3.0±0.00	88.7	12.9

a Calculated by weight of air-dried wood chips times consistency measured gravimetrically

b Measured after centrifuging the rinsed and soaked residue

c Weight percentage, measured gravimetrically, calculated by (oven dried solid weight of residue / weight of wet residue\*100)

d Total oven dried solid in the residue, calculated by (solid content (w/w%) times total weight of wet residue

e Weight percentage, calculated by (total oven dried solid in the residue / total original solid weight\*100)

\* The mean value and range of duplicate experiments are reported

The highest solid recovery yield in the filtrate was about 17% of the starting o.d. material, obtained from either extraction at 170 °C for 2 hours or at 180 °C for 1 hour. It seems like that by increasing the temperature from 170 °C to 180 °C will shorten the time



that needed to achieve the same solid recovery yield in the filtrate. Nevertheless, the advantage of higher temperature will be written off by using longer reaction time, as higher temperature will not only facilitate the dissolving of material into water but also accelerating the degradation of dissolved sugar to form volatile components. As a consequence, lower solid recovery yield will be observed for the filtrate. In the practical application of hot-water extraction of cellulosic biomass, we must understand this tradeoff between extraction temperature, time and usable solid content in the liquid phase, as well as the associated cost issues. A relatively lower temperature and shorter retention time will lead to lower solid recovery in the hydrolyzate, which implies lower sugar yield, but will cost less energy and cause lower sugar degradation; higher temperature and longer retention time will contribute to higher solid content in the filtrate, at the meanwhile, is more energy/cost-consuming and may even result in higher sugar degradation.

#### **4.4.2 Byproducts**

The total amount of acetic acid, furfural, HMF and formic acid in the filtrate determined by HPLC is shown in Table 4 - 3. All the results are based on 100 grams of o.d. starting wood. Acetic acid is generated from hydrolysis of the acetyl groups in the

hemicellulose, and is normally observed at the highest concentration in the filtrate after the hot-water extraction, compared with all the other byproducts (Mills, Sandoval and Gill 2009). Furfural and HMF had comparatively lower concentration in the filtrate and they are sugar degradation products from pentoses and hexoses, respectively. Formic acid is a byproduct from further degradation of HMF and furfural and presented as the second highest byproduct concentration in the filtrate (Table 4 - 3).

Table 4 - 3 Other identified components in the filtrate by using HPLC (based on 100 grams of original OD wood)

Temp (°C)	150		160		170		180	
Time (hour)	1	2	1	2	1	2	1	2
Acetic Acid (g)	0.9±0.1	0.8±0.0	1.5±0.0	2.0±0.2	1.9±0.0	3.3±0.3	4.1±0.4	6.0±0.1
furfural (g)	0.02±0.0	0.1±0.0	0.1±0.0	0.4±0.0	0.4±0.0	0.7±0.0	0.9±0.1	1.4±0.1
HMF (g)	0.0±0.0	0.01±0.0	0.02±0.0	0.1±0.0	0.1±0.0	0.3±0.0	0.5±0.0	1.5±0.0
Formic acid (g)	2.3±0.0	1.9±0.1	2.1±0.1	1.3±0.1	2.0±0.1	1.2±0.1	1.5±0.1	1.6±0.1

Acetic acid, furfural and HMF contents in the filtrate increased as the temperature and reaction time increased. Higher temperatures and longer reaction times facilitate the generation of these byproducts. However, formic acid shows an opposite trend, that is, the

higher the temperature and the longer the residence time, the lower the formic acid concentration in the hydrolyzate. Previous research indicates that formic acid can undergo either decarboxylation or dehydration process to decompose into CO<sub>2</sub> and H<sub>2</sub>, or CO, under hydrothermal conditions (Yu and Savage, 1998), with or without oxidant and catalyst (Bjerre and Soerensen, 1992; McCart, et al., 1973). This may explain why under more severe conditions, the content of formic acid decreased.

In the previous section, the solid recovery yields in the filtrate and in the solid residues were discussed. Recall that, instead of obtaining a higher solid content in the filtrate at a higher temperature (180 °C) for 2 hours, a lower solid recovery yield was actually observed (Table 4-2). The solid yield measurement in the filtrate was carried out by an atmospheric oven-dried method at a temperature of 105 °C, under which most of the volatile byproduct compounds in the filtrate are expected to volatilize. Table 3 shows that at 180 °C, 2 hours of extraction resulted in the highest level of acetic acid, furfural and HMF. These compounds may not be accounted for in the solid content in the filtrate due to the solid measurement method employed. This may explain why less than 100% of the solids in the original wood were not accounted for in the solids of the filtrate and residues, especially for the harsher conditions. Note also that in some trials, more than 100% of the solids entering were detected in the output streams, indicating that the experimental error was no less than 2-3%.

Table 4 - 4 Summarized solid recovery yield in the residue and filtrate after auto-hydrolysis treatment under different conditions as grams based on 100 grams of o.d original wood

Temp (°C)	150		160		170		180	
Time (hour)	1	2	1	2	1	2	1	2
Solid in residue	95.9	89.6	89.5	82.1	83.2	76.9	77.7	76.4
Solid in filtrate	7.4	10.2	12.6	14.9	14.9	16.8	17.0	12.9
Total <sup>a</sup>	103.3	99.8	102.1	97.0	98.1	93.7	94.7	89.3
Volatiles <sup>b</sup>		0.2		3.0	1.9	6.3	5.3	10.7

<sup>a</sup> Sum of the solid in both residue and filtrate

<sup>b</sup> The gap between “Total” and 100 grams of starting material

#### 4.4.3 pH

Figure 4-1 shows the pH of the filtrate obtained from each condition. These pH values were measured shortly after the hot-water extraction under ambient temperature. It was very interesting to come up with two parallel, nearly straight trend lines when plot the pH values as a function of temperature. This implies us that Figure 4-1 may be used to predict the pH value of hydrolyzate attained by hot-water extraction of mixed softwood under certain temperature (in the unit of degree Celsius) for either 1 hour or 2 hours of extraction.

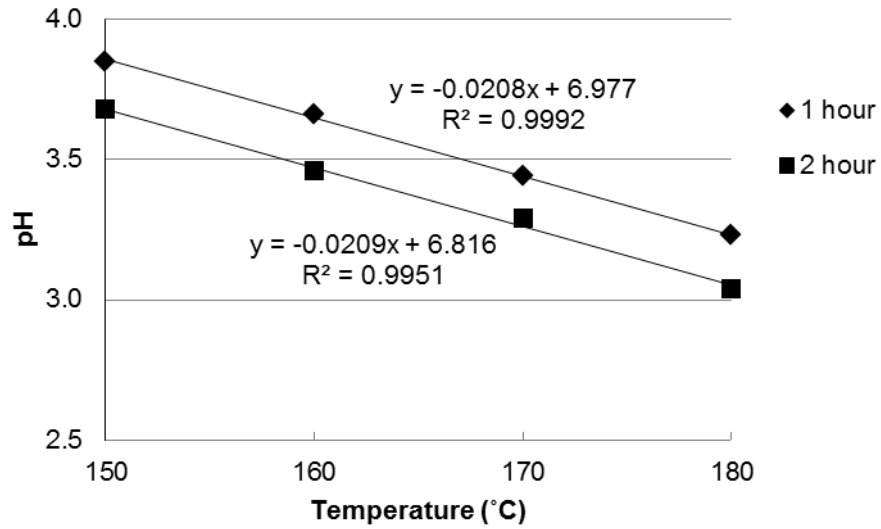


Figure 4- 1 pH values of filtrate for each autohydrolysis temperature

After 1 hour of hot-water extraction at 150 °C, the pH value of the filtrate was 3.9, Figure 4-1. For each 10 °C increase in autohydrolysis temperature, the pH value dropped approximately 5~6%. At 180 °C, the pH values of the filtrate for 1 and 2 hours were 3.2 and 3.0, respectively. Acids, i.e. acetic acid and formic acid, which generated during the hot-water extraction are the major contributors to the pH decreasing, which will consequently self-catalyze the extraction process and cause more starting material to dissolve and more amount of acids being released.

#### 4.4.4 Sugars measurement

Table 4 - 5 compiles all the sugars results of hydrolyzates before and after the acid-hydrolysis by using 3% sulfuric acid. In Table 4 - 5, “Mono” refers to the monosaccharides content that in the filtrate before the acid treatment, and “Total” shows the total sugar content after the acid treatment by breaking down all the sugar oligomers to monomer sugars. By subtracting the “mono” sugar results from the “total” sugars, one obtains the sugar oligomers that generated during the hot-water extraction. Those sugar oligomers cannot be directly converted to ethanol by the fermentation process, unless being broken down into their mono-form in order to be fermentable. From Table 4 - 5, the highest total carbohydrates content obtained was 13 grams out of 100 grams of o.d. starting material, at 170 °C for 2 hours. As temperature increased to 180 °C, the total sugar yield began to decrease somehow. For 2 hours extraction at 180 °C, the total sugars obtained were about 10 grams. Before the temperature reached 180 °C, all the sugar produced (for both monomers and oligomers) were increasing as the temperature increased and the reaction time prolonged. During the hot-water extraction process, water under high temperature and high pressure penetrates into the wood, causes partial hydrolysis of cellulose, dissolving of hemicellulose. The higher temperature and longer retention time will be favorable to this process and lead to a higher sugar yield. However, the sugar generation is coupled with the sugar degradation

simultaneously. By increasing the temperature and reaction time to a certain degree, the higher sugar yield will eventually be written off by the greater degree of byproduct generation (see Table 4 - 3). From Table 4 - 5, we know that this “breaking point” of sugar yield is around 180 °C.

A closer look at Table 4 - 5 reveals that arabinose was mostly extracted in the monomeric form throughout all the conditions. A majority of rhamnose, glucose, and xylose were in monomer forms only under higher temperature (170 °C and 180 °C), at lower temperatures these extracted sugars were mostly in their oligomer forms. A major portion of mannose and galactose remained in their polymeric form under all the conditions. Different from hardwood, mannose is the dominant hemicellulose sugar in the softwood mainly derived from (galacto)-glucomannan. Mannose in the filtrate had a maximum yield of 6.5 grams out of an original 100 grams of oven dry wood at 170 °C for 2 hours. This is the highest sugar yield achieved with respect to all the sugars present.

Xylose and arabinose had their highest yields of 2.8 grams and 1.5 grams, respectively for the extraction at 160 °C for 1 hour. These sugars are mainly generated from the arabino-glucuronoxylan. The yields of these sugars constantly decreased with increased temperature and longer residence time.

The sugar yield was expressed in two ways as shown in the last two rows of Table 5. Sugar yield in terms of “extract” refers to the portion of the solid that is measurable in the filtrate and can be accounted as carbohydrates. A higher value of this yield does not mean more total sugars were generated overall. As already mentioned above, analysis should also take into consideration how much solid was actually present in the hydrolyzate. For example, at 180°C, a 2 hours extraction resulted in 79% of sugar yield in terms of solid in the filtrate. However, from Table 4, the solid measured in this filtrate was only about 13 grams, which leads to a relatively higher yield in this case.

Another version of sugar yield (last row of Table 4 - 5) shows how many percentages of the solids that supposed to be dissolved in the liquid phase (back calculated from total solid in the residues after hot-water extraction) account for sugars. Notice that this yield has close correlation with the “volatiles” value shown in Table 4 - 4. Even though the condition of 170 °C for 2 hours achieved the highest total amount of sugars, a 56% sugar yield in terms of “solid loss” indicates that more volatiles were generated. In other words, the second sugar yield concept presented here may represent the sugar production “efficiency” with regard to both the total sugars and volatiles generated during the hot-water extraction. In a practical application, it is preferential to have as much a large yield of sugar with minimum volatiles to maximize feedstock use.



Table 4 - 5 Sugar composition in the auto-hydrolysis extracts under each condition before and after acid-hydrolysis by 3% H<sub>2</sub>SO<sub>4</sub> as of grams of mono-sugar recovered from 100 grams of OD original wood.

	Temp. Time (hr)	150°C		160°C		170°C		180°C	
		1	2	1	2	1	2	1	2
<b>Arabian (g)</b>	Mono <sup>a</sup>	1.15±0.01	1.15±0.11	1.17±0.04	0.89±0.03	0.92±0.03	1.03±0.03	0.51±0.01	0.21±0.01
	Total <sup>b</sup>	1.21±0.01	1.20±0.01	1.54±0.04	0.86±0.00	0.91±0.00	0.61±0.03	0.49±0.01	0.20±0.01
<b>Rhamnan (g)</b>	Mono	0.02±0.00	0.04±0.00	0.04±0.00	0.08±0.00	0.07±0.00	0.14±0.01	0.08±0.01	0.05±0.00
	Total	0.09±0.00	0.11±0.00	0.16±0.00	0.12±0.00	0.11±0.00	0.10±0.00	0.08±0.01	0.04±0.00
<b>Galactan (g)</b>	Mono	0.08±0.00	0.17±0.00	0.18±0.02	0.41±0.03	0.36±0.02	1.07±0.06	0.79±0.03	0.84±0.04
	Total	0.52±0.01	1.03±0.01	1.40±0.04	1.46±0.00	1.36±0.01	1.51±0.07	1.72±0.01	2.00±0.02
<b>Glucan (g)</b>	Mono	0.01±0.00	0.02±0.00	0.01±0.00	0.09±0.00	0.07±0.00	0.49±0.02	0.53±0.02	1.30±0.07
	Total	0.48±0.01	0.92±0.01	1.48±0.04	1.72±0.01	1.66±0.01	2.11±0.10	0.84±0.00	1.95±0.03
<b>Xylan (g)</b>	Mono	0.09±0.00	0.31±0.00	0.36±0.01	1.30±0.03	1.16±0.02	2.99±0.06	1.84±0.00	1.07±0.01
	Total	0.95±0.01	1.80±0.04	2.81±0.07	2.51±0.00	2.51±0.01	2.22±0.09	2.18±0.02	1.11±0.02
<b>Mannan (g)</b>	Mono	0.01±0.00	0.04±0.00	0.04±0.00	0.40±0.01	0.32±0.01	1.88±0.03	1.79±0.00	1.76±0.03
	Total	1.42±0.01	2.89±0.09	4.03±0.07	5.59±0.00	5.39±0.03	6.45±0.27	6.22±0.00	4.93±0.02
<b>Sum (g)</b>	Mono	1.36±0.00	1.73±0.11	1.80±0.07	3.16±0.09	2.90±0.08	7.60±0.20	5.53±0.05	5.23±0.14
	Total	4.66±0.05	7.96±0.16	11.41±0.26	12.26±0.02	11.94±0.06	13.00±0.56	11.53±0.21	10.23±0.17
<b>Yield (%)</b>	of extract <sup>c</sup>	63.2	77.9	90.8	82.3	80.3	77.5	67.8	79.3
	of lost <sup>d</sup>	113.8	76.4	108.0	68.6	71.1	56.1	51.7	43.3

<sup>a</sup> The amount of monosaccharides formed in the extracts during auto-hydrolysis

<sup>b</sup> The total amount of monosaccharides in the extracts after 3% acid-hydrolysis

<sup>c</sup> Sugar yield out of solid in the extract, calculated as (total mono-sugar / total solid yield in the extract \*100)

<sup>d</sup> Sugar yield out of solid loss of original o.d. wood after auto-hydrolysis, calculated as (total mono-sugar / (100 – solid recovery yield of solid residue after hot-water extraction) \* 100)

#### 4.4.5 Sugar mass balance

Table 4 - 6 Sugar mass balance of starting materials, solid residues and extracts before and after hot-water extraction

<b>Starting Materials (100g)</b>		<b>150°C Solids</b>		<b>160°C Solids</b>		<b>170°C Solids</b>		<b>180°C Solids</b>	
<b>Component</b>	<b>(g)</b>	<b>1 hr</b>	<b>2 hr</b>	<b>1 hr</b>	<b>2 hr</b>	<b>1 hr</b>	<b>2 hr</b>	<b>1 hr</b>	<b>2 hr</b>
Glu	41.0	39.8	39.6	39.5	39.0	38.9	39.0	38.6	38.1
Xyl	5.9	3.8	2.9	2.7	2.0	1.9	1.2	0.7	0.5
Gal	1.3	0.6	0.4						
Ara+Man	13.9	9.5	7.5	5.7	4.5	4.3	2.9	2.3	1.5
<b>Sugar Sum</b>	<b>62.1</b>	<b>53.7</b>	<b>50.4</b>	<b>47.9</b>	<b>45.5</b>	<b>45.1</b>	<b>43.0</b>	<b>41.6</b>	<b>40.1</b>

		<b>150°C Filtrate</b>		<b>160°C Filtrate</b>		<b>170°C Filtrate</b>		<b>180°C Filtrate</b>	
<b>Component</b>		<b>1 hr</b>	<b>2 hr</b>	<b>1 hr</b>	<b>2 hr</b>	<b>1 hr</b>	<b>2 hr</b>	<b>1 hr</b>	<b>2 hr</b>
Glu		0.5	0.9	1.5	1.7	1.7	2.1	0.8	2.0
Xyl		1.0	1.8	2.8	2.5	2.5	2.2	2.2	1.1
Gal		0.5	1.0	1.4	1.5	1.4	1.5	1.7	2.0
Ara+Man		2.6	4.1	5.6	6.5	6.3	7.1	6.7	5.1
<b>Sugar Sum<sup>a</sup></b>		<b>4.7</b>	<b>8.0</b>	<b>11.4</b>	<b>12.3</b>	<b>11.9</b>	<b>13.0</b>	<b>11.5</b>	<b>10.2</b>
Acetic Acid		0.9	0.8	1.5	2.0	1.9	3.3	4.1	6.0
Formic Acid		2.3	1.9	2.1	1.3	2.0	1.2	1.5	1.6
Furfural		0.02	0.1	0.1	0.4	0.4	0.7	0.9	1.4
HMF			0.01	0.02	0.1	0.1	0.3	0.5	1.5
<b>Byproduct Sum</b>		<b>3.2</b>	<b>2.8</b>	<b>3.7</b>	<b>3.8</b>	<b>4.4</b>	<b>5.5</b>	<b>7.0</b>	<b>10.5</b>
Volatiles <sup>b</sup>			0.2		3.0	1.9	6.3	5.3	10.7
<b>Total Sugar and Byproduct<sup>c</sup></b>		<b>61.6</b>	<b>61.2</b>	<b>63.0</b>	<b>61.6</b>	<b>61.4</b>	<b>61.5</b>	<b>60.1</b>	<b>60.8</b>

Table 4- 6 Continued

<sup>a</sup> Sugars sum including rhamnan, which is not shown in this table

<sup>b</sup> Calculated from 100g - Table 4 "Total" row; "volatiles" stands for the solids "lost" (short from 100g), after adding up the solids from both the residues and the filtrates

<sup>c</sup> Sum up of sugars in residues, filtrates and byproducts in the filtrates

Table 4 - 6 summarizes all the sugar results in the raw material, solid residues and filtrates, as well as all the byproduct results in the filtrate. Ideally, the total (shown in the last row of Table 4 - 6) sugars in the filtrates and residues, along with the total byproducts that generated should be equal to the sugars in the initial material. The sugars results in the solid residues show that after the temperature raised to above 160 °C, more than half of the hemicellulose has been removed from the raw material. The higher the temperature and the longer the reaction time, more hemicellulose will be removed. However, most of the cellulose stayed intact in the solid phase: at the most severe condition (180 °C, 2 hours), there was still about 93% cellulose left in the solid residue.

Reasonable sugar balances were determined for all the conditions. The “solid loss” (expressed as volatiles) can be attributed to the byproducts, but it reflects the performance of the overall mass balance (not just only the sugar mass balance). Again, the more severe the condition is, the more solid loss.

At 180 °C for 2 hours, the total sugar and the solid loss was 10.2% and 10.7%, out of the initial starting material, which means this condition is not desirable for the purpose of approaching recovering as much sugar as possible but at the same time causing the least solid loss. The highest sugar amount in the filtrate (13 grams) corresponded to a solid loss of 6.3 grams, at 170 °C 2 hours. About 12 grams of sugars were obtained at 170 °C for 1 hour, but with a relatively low solid loss (1.9 grams). Lower temperature (150 °C) resulted in much

lower total sugars (4.7 and 8.0 grams for 1 and 2 hours), but the solid loss was minimal. There are still substantial substances that were not identified preventing this analysis from closing the mass balance, as Amidon et. al observed in 2008. (Amidon, et al., 2008).

#### **4.4.6 Heat content**

The heating values of all the residues from different hot water extraction conditions as well as from the original softwood sample were determined by a standard bomb calorimeter method. The heating value determined was the “high heating value” (HHV), which includes the latent heat given up when newly formed water vapor condenses and cools to the temperature of the bomb (Thipse et al. 2002). Table 4 - 7 shows all the heating value results obtained in duplicate for each sample.

Table 4 - 7 Heat of combustions of original wood and residues under different conditions. Range of duplicate experiments was reported.

		Heat of combustion (calories/gram)
From Reference <sup>a</sup>		4,630
Original wood		4,283±56
150°C	1 hour	4,403±3
	2 hour	4,553±3
160°C	1 hour	4,558±38
	2 hour	4,682±3
170°C	1 hour	4,646±26
	2 hour	4,755±27
180°C	1 hour	4,802±33
	2 hour	4,895±38

<sup>a</sup> Data obtained from a reference (Thipse and Sheng, 2002)

The heating value of the original wood sample was about 4,283 calories per gram (oven dry), which was the lowest value compared with all other extracted samples. As the extraction temperature increased, the corresponding heating values of the residues steadily increased. This is a reasonable tendency since the higher the temperature the more hemicellulose and cellulose are being extracted. As a result, the residues after the hot-water

extraction had a relatively higher “concentration” of lignin, which has a higher heating value compared with the carbohydrates in woody material (White, 1987; Demirba, 2001; Demirba, 2002). Table 4 - 8 shows the lignin content of the solid residues obtained from each condition. However, the resulting higher lignin concentration does not mean that a higher extraction temperature will always achieve a higher total energy content since higher temperatures resulted in a dramatic weight loss of the solid residues (Table 4- 4).

Table 4 - 8 Lignin Content in the Residues (Based on oven dry residues)

Temp (°C)	Residence time (hours)	Lignin <sup>a</sup> (%)
150	1	28.4±0.4
	2	29.5±0.5
160	1	30.4±1.0
	2	31.2±0.7
170	1	36.6±1.1
	2	36.8±1.3
180	1	37.0±1.8
	2	37.2±0.7

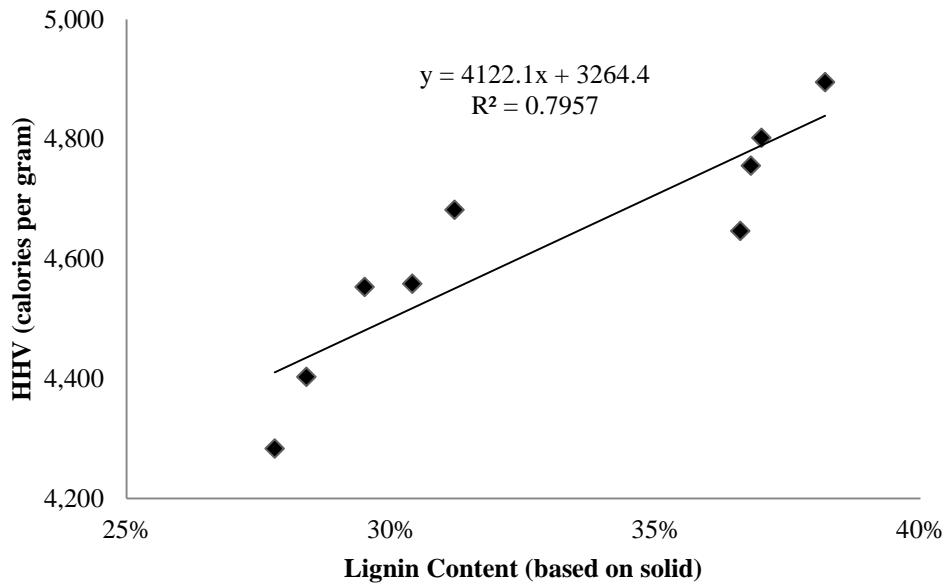


Figure 4- 2 Higher heating value vs. the lignin content (based on solid)

Figure 4- 2 demonstrates the relationship between the solid lignin content versus the higher heating value. Almost a linear relationship could be found.

Figure 4-3 shows the percentage of total energy remaining in the solid residues, compared with the original starting material. At 150 °C and 2 hour treatment the energy content of the solid residues was 95% of the original wood. As the extraction temperature increased to 180 °C, 87% of the total energy was maintained in the residue.



When considering the use of the solid residues for energy content in a combustion process and the use of the extracted carbohydrates as feedstock for ethanol production, a careful analysis of the overall net benefit of the system versus extraction temperature and time needs to be evaluated.

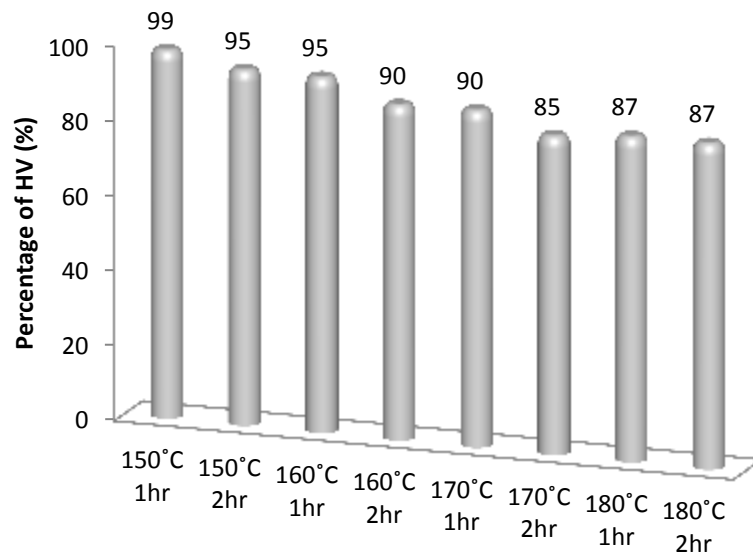


Figure 4- 3 Percentage of heating value recovered from original wood.

## 4.5 Summary

Several conditions were demonstrated to be reasonable for the value prior to combustion process. At 170 °C for 2 hours, a maximum of 13 grams of total monomer sugars were extracted out from 100 grams of starting softwood chips. After 1 hour extraction at 160 °C, a total of 11.41 g sugar was recovered from the filtrate, which accounted for about 91% (the highest) of the total solid recovered from the extracted solution. This data shows that the value prior to combustion process is quite complex. Optimization of the process requires consideration of many variables including yield of fermentable sugars, total energy retained in the residuals, and the effect of process conditions on equipment and operating activities. All of these considerations will impact the economics of such a process. Optimization of the process will also involve considering limitations such as raw material supply or in the demand for energy. Currently, these results in conjunction with parallel results for hardwoods (Pu, et al., 2011) are being used in an economic model to predict the profitability of such an operation.

## 4.6 Conclusions

By carrying out auto-hydrolysis of mix softwood chips from 150 °C to 180 °C, for 1 hour and 2 hours, hemicellulose was selectively extracted into the hydrolyzate with different sugar yields and byproduct, depending on the reaction condition applied. Higher temperature and longer residence times are favorable for maximizing the solid dissolved into the liquid phase. However, the total solid balance closure for both filtrate and residue was impaired by more volatiles that generated under harsher conditions. Acetic acid, furfural and HMF formed during the hot-water extraction and were found to steadily increase with increasing extraction temperature and reaction time. The higher byproduct generation led to a lower solid recovery yield in the filtrate. The pH value of the filtrate decreased as the temperature and reaction time increased. A linear correlation was found for pH as a function of temperature. The optimal sugar yield was found to be 170 °C for 2 hours, during which 13 grams of sugar was recovered from the extract out of 100 grams of oven-dried original wood material. Mannose had the highest yield for all extracted sugars. Mannose and galactose were primarily extracted in their polymeric form throughout all the conditions. The composition analysis of the solid residues verified that most of the hemicelluloses were effectively extracted into the liquid while the cellulose tended to remain in the residue. As the extraction

temperature increased, more material was dissolved, leaving higher lignin concentrations in the residues and thus higher heating values of the residues. The total energy that could be recovered in the residue ranged from 85% to 98% after extraction of the hemicelluloses, with lower total energy recovered with increasing temperature and time.

## 4.6 References

- Amidon T, Wood C, Shupe A, Wang Y, Graves M, Liu S (2008) Biorefinery: Conversion of woody biomass to chemicals, energy and materials. *Journal of Biobased Materials and Bioenergy* 2 (2):100-120
- Amidon T, Liu S (2009) Water-based woody biorefinery. *Biotechnology advances* 27 (5):542-550
- Andersson A, Persson T, Zacchi G, Stålbrand H, Jönsson A (2007) Comparison of diafiltration and size-exclusion chromatography to recover hemicelluloses from process water from thermomechanical pulping of spruce. *Applied Biochemistry and Biotechnology* 136 (140):971-983
- Bjerre AB, Soerensen E (1992) Thermal decomposition of dilute aqueous formic acid solutions. *Industrial & Engineering Chemistry Research* 31 (6):1574-1577
- Caparrós S, Díaz M, Ariza J, López F, Jiménez L (2008) New perspectives for *Paulownia fortunei* L. valorisation of the autohydrolysis and pulping processes. *Bioresource Technology* 99 (4):741-749
- Demirba A (2001) Relationships between lignin contents and heating values of biomass. *Energy conversion and management* 42 (2):183-188

- Demirba A (2002) Relationships between heating value and lignin, moisture, ash and extractive contents of biomass fuels. *Energy, Exploration & Exploitation* 20 (1):105-111
- FitzPatrick M, Champagne P, Cunningham M, Whitney R (2010) A biorefinery processing perspective: Treatment of lignocellulosic materials for the production of value-added products. *Bioresource Technology* 101 (23):8915-8922
- Galbe M, Zacchi G (2002) A review of the production of ethanol from softwood. *Applied microbiology and biotechnology* 59 (6):618-628
- Garrote G, Cruz JM, Domínguez H, Parajó JC (2003) Valorisation of waste fractions from autohydrolysis of selected lignocellulosic materials. *Journal of Chemical Technology and Biotechnology* 78 (4):392-398
- Garrote G, Dominguez H, Parajó JC (1999) Mild autohydrolysis: an environmentally friendly technology for xylooligosaccharide production from wood. *Journal of Chemical Technology and Biotechnology* 74 (11):1101-1109
- Garrote G, Domínguez H, Parajo JC (2001a) Kinetic modelling of corncob autohydrolysis. *Process Biochemistry* 36 (6):571-578

- Garrote G, Domínguez H, Parajó JC (2001b) Generation of xylose solutions from *Eucalyptus globulus* wood by autohydrolysis–posthydrolysis processes: posthydrolysis kinetics. *Bioresource Technology* 79 (2):155-164
- Garrote G, Parajó J (2002) Non-isothermal autohydrolysis of *Eucalyptus* wood. *Wood Science and Technology* 36 (2):111-123
- Gonzalez R, Daystar J, Jett M, Treasure T, Jameel H, Venditti R, Phillips R (2011) Economics of cellulosic ethanol production in a thermochemical pathway for softwood, hardwood, corn stover and switchgrass. *Fuel Processing Technology* 94 (2012):113-122
- Gonzalez R, Phillips R, Saloni D, Jameel H, Abt R, Pirraglia A, Wright J (2011) Biomass to energy in the Southern United States: Supply Chain and Delivered Cost. *BioResources* 6 (3):2954-2976
- Gonzalez R, Treasure T, Wright J, Saloni D, Phillips R, Abt R, Jameel H (2011) Exploring the potential of *Eucalyptus* for energy production in the Southern United States: Financial analysis of delivered biomass. Part I. *Biomass and Bioenergy* 35 (2):755-766
- Hess J, Wright C, Kenney K (2007) Cellulosic biomass feedstocks and logistics for ethanol production. *Biofuels, Bioproducts and biorefining* 1 (3):181-190

- Lavoie JM, Capek-Menard E, Gauvin H, Chornet E (2010) Production of pulp from *Salix viminalis* energy crops using the FIRSST process. *Bioresource Technology* 101 (13):4940-4946
- Leschinsky M, Sixta H, Patt R (2009) Detailed mass balances of the autohydrolysis of *Eucalyptus globulus* at 170 C. *BioResources* 4 (2):687-703
- Liu S, Amidon T, Francis R, Ramarao B, Lai Y, Scott G (2006) From forest biomass to chemicals and energy. Biorefinery initiative in New York State. *Industrial Biotechnology* 2 (2):113-120
- Ligero P, van der Kolk JC, de Vega A, van Dam JEG (2011) Production of xylo-oligosaccharides from *miscanthus x giganteus* by autohydrolysis. *BioResources* 6 (4)
- Li H, Saeed A, Jahan MS, Ni Y, van Heiningen A (2010) Hemicellulose removal from hardwood chips in the pre-hydrolysis step of the kraft-based dissolving pulp production process. *Journal of Wood Chemistry and Technology* 30 (1):48-60
- Li J, Henriksson G, Gellerstedt G (2005) Carbohydrate reactions during high-temperature steam treatment of aspen wood. *Applied biochemistry and biotechnology* 125 (3):175-188



- Lundqvist J, Jacobs A, Palm M, Zacchi G, Dahlman O, Stalbrand H (2003) Characterization of galactoglucomannan extracted from spruce (*Picea abies*) by heat-fractionation at different conditions. *Carbohydrate Polymers* 51 (2):203-211
- McCarty J, Falconer J, Madix RJ (1973) Decomposition of formic acid on Ni (110):: I. Flash decomposition from the clean surface and flash desorption of reaction products. *Journal of Catalysis* 30 (2):235-249
- Mills TY, Sandoval NR, Gill RT (2009) Cellulosic hydrolysate toxicity and tolerance mechanisms in *Escherichia coli*. *Biotechnology for biofuels* 2 (11)
- Persson T, Nordin A, Zacchi G, Jönsson A (2007) Economic evaluation of isolation of hemicelluloses from process streams from thermomechanical pulping of spruce. *Applied Biochemistry and Biotechnology* 136 (140):741-752
- Pettersen R (1991) Wood sugar analysis by anion chromatography. *Journal of Wood Chemistry and Technology* 11 (4):495-501
- Pu Y, Treasure T, Gonzalez R, Venditti R, Jameel H (2011) Autohydrolysis pretreatment of mixed hardwoods to extract value prior to combustion *BioResources* 6 (4)
- Ragauskas A, Williams C, Davison B, Britovsek G, Cairney J, Eckert C, Frederick W, Hallett J, Leak D, Liotta C (2006) The path forward for biofuels and biomaterials. *Science* 311 (5760):484

- Rughani J, McGinnis GD (1989) Combined rapid - steam hydrolysis and organosolv pretreatment of mixed southern hardwoods. *Biotechnology and bioengineering* 33 (6):681-686
- Salam A, Venditti R, Pawlak J, El-Tahlawy K (2011) Crosslinked hemicellulose citrate-chitosan aerogel foams. *Carbohydrate Polymers* 84 (4):1221-1229
- San Martin R, Perez C, Briones R (1995) Simultaneous production of ethanol and kraft pulp from pine (*Pinus radiata*) using steam explosion. *Bioresource Technology* 53 (3):217-223
- Stöcker M (2008) Biofuels and biomass-to-liquid fuels in the biorefinery: Catalytic conversion of lignocellulosic biomass using porous materials. *Angewandte Chemie International Edition* 47 (48):9200-9211
- Stoutenburg R, Perrotta J, Amidon T, Nakas J (2008) Ethanol Production from a Membrane Purified Hemicellulosic Hydrolysate Derived from Sugar Maple by *Pichia Stipitis* NRRL Y-7124. *BioResources* 3 (4):1349-1358
- Taherzadeh M, Karimi K (2008) Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: a review. *International journal of molecular sciences* 9 (9):1621-1651

- Thipse S, Sheng C, Booty M, Magee R, Bozzelli J (2002) Chemical makeup and physical characterization of a synthetic fuel and methods of heat content evaluation for studies on MSW incineration. *Fuel* 81 (2):211-217
- Tunc MS, Lawoko M, van Heiningen A (2010) Understanding the limitations of removal of hemicelluloses during autohydrolysis of a mixture of southern hardwoods. *BioResources* 5 (1):356-371
- Tunc MS, van Heiningen ARP (2008) Hemicellulose extraction of mixed southern hardwood with water at 150 C: Effect of time. *Industrial & Engineering Chemistry Research* 47 (18):7031-7037
- Vila C, Romero J, Francisco J, Garrote G, Parajó J (2011) Extracting value from Eucalyptus wood before kraft pulping: Effects of hemicelluloses solubilization on pulp properties. *Bioresource Technology*
- Westbye P, Köhnke T, Gatenholm P (2008) Fractionation and characterization of xylan rich extracts from birch. *Holzforschung* 62 (1):31-37
- Willför S, Sundberg A, Hemming J, Holmbom B (2005) Polysaccharides in some industrially important softwood species. *Wood Science and Technology* 39 (4):245-257

- Willför S, Sundberg K, Tenkanen M, Holmbom B (2008) Spruce-derived mannans-A potential raw material for hydrocolloids and novel advanced natural materials. *Carbohydrate Polymers* 72 (2):197-210
- White R (1987) Effect of lignin content and extractives on the higher heating value of wood. *Wood and fiber science* 19 (4):446-452
- Yu J, Savage PE (1998) Decomposition of formic acid under hydrothermal conditions. *Industrial & Engineering Chemistry Research* 37 (1):2-10
- Zhang J, Zhu Z, Wang X, Wang N, Wang W, Bao J (2010) Biotoxification of toxins generated from lignocellulose pretreatment using a newly isolated fungus, *Amorphotheca resinae* ZN 1, and the consequent ethanol fermentation. *Biotechnology for biofuels* 3:26-26

# **CHAPTER 5: Auto-hydrolysis and Acid-catalyzed Prehydrolysis of Mixed Hardwood to Extract Fermentable Sugars, and Their Effect on the Enzymatic Hydrolysis of the Solid Residues**

## **5.1 Abstract**

Pretreatment of biomass is one of most crucial steps in the process of lignocellulosic bioethanol production, since it helps open up the structure of the biomass matrix for easier approach of enzymes during enzymatic hydrolysis of the solids. A comparison study of auto-hydrolysis and acid-prehydrolysis of mixed hardwood chips was conducted to understand sugar yield differences in the liquid extract and the effect on the enzymatic hydrolysis of solid residues. Auto-hydrolysis was carried out at 160 °C and 180 °C, and the temperature of acid-prehydrolysis was set at 160 °C. Acetic acid and formic acid were selected for the acid-prehydrolysis, as they are recognized as the self-generated byproducts during auto-hydrolysis and have the catalytic ability of facilitating hydrolysis. Sugar measurement by using an ion chromatography (IC) system was performed to analyze both the prehydrolyzate and the enzymatic hydrolysis liquor; byproduct analysis was performed using a High Performance

Liquid Chromatography (HPLC) on the prehydrolyzate filtrate. Enzymatic hydrolysis was performed for all the solid residues from each pretreatment at the enzyme charges of 5, 10 and 15 FPU/gram of o.d. substrate. Before the enzymatic hydrolysis, all the pulps that generated from the solid residues were subjected to a mechanical refining process (P.F.I. Mill treatment) until a 6,000 revolution was achieved. As a comparison, enzymatic hydrolysis of pulps without the P.F.I Mill treatment was also carried out, but only with the 5 FPU enzyme charge. The introduction of acid into the pretreatment will increase the overall sugar yield and enhance the performance of enzymatic hydrolysis. However, increasing the acid addition from 2% to 6% did not show much improvement for sugar yield in the prehydrolyzate and from enzymatic hydrolysis of the residue. It was shown that acid-prehydrolysis at 160 °C with 6% formic acid charge has the highest sugar yield in the prehydrolyzate. Solid residues resulting from auto-hydrolysis at 180 °C showed 100% sugar conversion during the enzymatic hydrolysis with 10 and 15 FPU enzyme charge for 96 hours.

## **5.2 Introduction**

The urgency to discover alternative sources of sustainable and environmentally friendly energy has motivated cellulosic ethanol being received increasing attention from private and public research sectors. Bioconversion of lignocellulosic feedstock to bio-fuels has the potential of reducing greenhouse gasses (i.e. carbon dioxide) and providing more

employment in rural and industrial areas, compared with fossil based fuel products. Moreover, lignocellulosic biomass is known as the most abundant organic source on earth and is considered to be renewable and sustainable.

Main steps of producing bioethanol from the lignocellulosic biomass include pretreatment, enzymatic hydrolysis and fermentation. The eventual objective for the first two steps is to generate fermentable mono-saccharides by breaking down the polymeric structures of the carbohydrates in the biomass. Biomass pretreatment is a means to remove most of the hemicellulose and part of the cellulose from the woody matrix into the aqueous phase and to leave a comparatively open structure of the solid for further enzymatic hydrolysis. A lot of pretreatment approaches have been studied over a wide range of raw materials. Among all the pretreatment methods, auto-hydrolysis has gained a lot of interest due to several advantages: comparatively environmentally friendly since only water is used as the reaction media (Garrote, et al., 1999; Garrote, et al., 2001a; Garrote, et al., 2003); less corrosive process (Garrote, et al., 2001b); less undesirable sugar degradation relative to inorganic acid pretreatment; lower cost associated with operation because neutralization is unnecessary for this process (Carvalho, et al., 2004). During the process of auto-hydrolysis, acids are produced by the hydrolysis of hemicellulose and degradation of sugars (Amidon and Liu, 2009). Organic acids, for example, acetic acid formed from hydrolysis of acetyl groups in

hemicelluloses (Ligero, et al., 2011; Mill, et al., 2009; Zhang, et al., 2010), and formic acid generated from further degradation of sugar byproducts (i.e. HMF and furfural) (Mill, et al., 2009), as well as the dissolution of extractives in the biomass, lead to a decrease in liquor pH. Decreases in pH enhance the solubility of the hemicelluloses into the liquid phase, in turn, allows the recovery of carbohydrates in the forms of soluble mono-saccharides and oligosaccharides (Carvalho, et al., 2004). In order to assist the removal of hemicelluloses into the prehydrolyzate as well as enhance the accessibility of enzymes to the solid residues during the further enzymatic hydrolysis process, studies of introducing acids into the pretreatment have also been carried out. Both diluted acid and concentrated acid pretreatment have been conducted (Knappert, et al., 1980; Grethlein, et al., 1984; Grethlein, et al., 1991; Taherzadeh, et al., 1997; Fenske, et al., 1998; Nguyen, et al., 1999; Saha, et al., 2005). Compared with concentrated acid method, diluted acid pretreatment has the advantages of less inhibitors generation, less corrosive problem for reaction equipment and lower emphasis on acid recovery (Alvira, et al., 2010).

The objective of the present study is to compare the sugar yield in the prehydrolyzate from auto-hydrolysis and acid prehydrolysis of mixed hardwood chips and their effect on further enzymatic hydrolysis of the solid residues. Enzymatic hydrolysis of the prehydrolyzate is not in the scope of the present study; instead, an acid-hydrolysis treatment



of the prehydrolyzate was conducted to see how much fermentable sugars could be recovered from the liquid phase. One of the innovative aspects of this work is to use the P.F.I. Mill to treat the pulp that generated from the solid residues, to obtain a substrate that is believed to be more easily approachable by enzymes (Henriksson, et al., 2007). Comparison was carried out for enzymatic hydrolysis of substrates prepared with or without the P.F.I. Mill treatment. The acids employed in the acid prehydrolysis pretreatment were found in the prehydrolyzate from auto-hydrolysis: acetic acid and formic acid. As they are the acids self-generated during the auto-hydrolysis and have the function of self-catalyze the reaction process, it would be interesting to see how the presence of each acid at the beginning of the reaction will affect the sugar yield in the liquid as well as the enzymatic hydrolysis performance for the resulting residues.

## **5.3 Materials and Methods**

### **5.3.1 Feedstock**

Hardwood chips obtained from a local North Carolina pulp and paper mill, with dimensions of approximately 30 mm width, 30 mm length, and 3 mm thickness, were used as the starting material for hot-water extraction and acid-catalyzed prehydrolysis. This

feedstock is composed of several species including maple, gum and oak that naturally growing in the Southeastern U.S. These chips were stored in a cold room at 4°C and air dried for at least two days before use. Moisture content of the air-dried wood chips were measured by oven drying at 105°C overnight and calculated by the weight difference.

### **5.3.2 Hot-water Extraction and Acid-catalyzed Prehydrolysis**

Both hot-water extraction and acid-catalyzed prehydrolysis were carried out by a pulp digester (M/K System Inc., Danvers, MA). For each batch of cook, 600 grams of air-dried wood chips were used. The oven-dry weight of the chips that subjected to the treatment was determined based on triplicate moisture content measurements, as described above. Water to solid ratio was set at 4:1 for all the trials. Hot-water extractions were carried out at 160°C and 180°C and the temperature for all the acid-catalyzed prehydrolysis was held at 160°C. Two different acids: acetic acid and formic acid were added to the acid-catalyzed trials, respectively, to study their catalytic ability difference. Acetic acid and formic acid are generated from hydrolysis of the acetyl groups in hemicellulose and further degradation of sugar byproducts during the prehydrolysis. They are recognized as having the first and second highest concentrations in the prehydrolyzate (Mills, et al., 2010). That was the reason why the two organic acids were chose to investigate their catalytic performance during the

treatment. Two levels of acid addition were selected (2% and 6%), based on the o.d. weight of the starting wood chips. Prehydrolyzates of 50mL were collected from the bottom of the digester, at 0, 20, 40 and 60 min after the target temperature has been reached. A volumetric vessel submerged into iced water was employed during the sample collection procedure, for the purpose of quenching the flash came from the outlet.

After the extraction, filtrate was released from the bottom of the digester and collected after going through a water-cooling system. The remaining solid residues were washed under running tap water for at least 2 hours and subsequently soaked for 8 hours. The resulting residual chips were then centrifuged to achieve relatively uniform moisture content. Part of such obtained chips were subjected to moisture content measurement as described above; some were air-dried for at least 4 days prior to performing composition analysis, heating value measurement and also enzymatic hydrolysis. Solid content of the filtrate was only performed to the samples that collected at 60 min. Sugar measurement and byproduct analysis were carried out for all the filtrate samples. The wash water was not analyzed for sugars and other compositions.

### **5.3.3 Analysis of original wood and solid residues**

Both original wood chips and air-dried solid residues were ground to pass through a 40 mesh screen. Moisture content of as obtained wood powder was measured by the oven-dry method. Acid hydrolysis by 1.5 mL of 72% (w/w) sulfuric acid was performed to 0.1 grams of ground wood powder. After thoroughly stirring every 15 minutes at room temperature for 1.5 hours, the resulting slurry was carefully transferred to a serum bottle by washing with 56 mL DI water. The serum bottle was sealed and autoclaved for another 1.5 hours at 122°C. After that, the autoclaved hydrolysis solution was vacuum-filtered through a previously weighed filtering crucible and collected. This sample was subjected to sugar analysis and byproduct analysis. Deionized water was used to quantitatively transfer all remaining solids in the serum bottle into the filtering crucible. The crucible along with acid insoluble residue was oven dried to determine the acid insoluble lignin, which is also known as Klason lignin.

### 5.3.4 Sugar analysis of extracts

As mentioned above, the solid content measurement of filtrate was only carried out for the samples that collected at 60 minute after the target temperature has been reached. The measurement was achieved gravimetrically by oven drying at 105°C to a constant weight. 5 mL of sample was used for this method and triplicate measurements were carried out for each sample. Sugar monosaccharides of the extract were determined with an ion chromatography (IC) system (Dionex ICS-3000, Sunnyvale, CA) before and after acid hydrolysis of samples by using 3% sulfuric acid. The monomeric sugar content difference before and after the acid hydrolysis stands for the oligo- and polysaccharide content in the filtrate. The IC system was equipped with an auto sampler, a dual pump (model DP-1), an eluent generator (model EG-2), a guard column (carboPac PAI 2×50mm), an Ion-exchange column (carboPac PAI 2×250mm) and a pulsed amperometric detector using a gold electrode/ chromatography module (model DC-1). Degased Milli-Q water (0.22µm, Millipak express 20, Millipore) and 400 mN sodium hydroxide (Fisher Scientific, Fair Lawn, New Jersey) solution were used as the eluents at the flow rate of 0.3 mL/min. A 200 mN sodium hydroxide solution was added to post column to optimize detector sensitivity and baseline stability. Fucose was added to each sample as an internal standard. D-fucose, D-arabinose, D-rhamnose, D-galactose, D-glucose, D-xylose, and D-mannose were used as calibration

standards to make the sugar calibration curves. All the samples were diluted to proper times to bring the sugars concentration into the calibration ranges, and went through a 0.20  $\mu\text{m}$  nylon syringe filters (Millex-GN, Millipore Ltd., Ireland) before analysis.

### **5.3.5 Byproduct analysis of extracts**

Acetic acid, formic acid, furfural and hydroxymethyl furfural (HMF) were measured by a Dionex HPLC system (Dionex, Sunnyvale, CA), which including an ASI-100 automated sample injector, Solvent Rack SOR-100 module, P680 HPLC pump, and UVD170U multi wavelength ultraviolet detector. Compounds separation was achieved by using a 4.0 mm x 250 mm Acclaim® Organic Acid column (5 mm, Dionex, Sunnyvale, CA) coupled to an Acclaim Organic Acid-Guard column (5 mm, Dionex, Sunnyvale, CA). Non-linear gradient flow rate were employed by using 2.5 mmol L<sup>-1</sup> methanesulfonic acid (Sigma-Aldrich,  $\geq$  99.5%) and water/acetonitrile (Sigma-Aldrich, Chromasolv®, gradient grade for HPLC,  $\geq$  99.9%) (10:90, v/v) as the Mobile phase A and Mobile phase B solvents, respectively. Concentrations of formic acid and acetic acid of samples were measured at 210 nm and HMF and furfural at 277 nm. 4-tert-butylphenoxyacetic acid (Alfa Aesar, Ward Hill, MA) was dissolved into pure methanol and used as an internal standard (Chen et al. 2006; Lee et al. 2010). Standard curves were made for each byproduct by using a 7-point calibration. All the

samples were diluted properly to bring the concentration of byproduct into the calibration range, and then filtered through a nylon syringe filter before injection.

### **5.3.6 Higher heating value measurement**

A standard bomb calorimeter (1341 Oxygen Bomb Calorimeter, Parr Instrument Company, Moline, IL) was used to measure the higher heating value of both the original raw material and the solid residues. All the samples were first ground to pass a 40 mesh screen and then compressed into pellets by using a pellet press (Perkin Elmer 15.011, Britain), in order to achieve a complete but not vigorous combustion. The procedures of heat content measurement by using this standard bomb calorimeter were described in detail previously, Pu et al. (2011)

### **5.3.7 Enzymatic hydrolysis of residual solids and sugar analysis**

As mentioned in the previous section, some of the residual chips after washing, soaking and centrifuging, had been used to do the enzymatic hydrolysis to investigate how different temperatures, acids and acid addition levels affect the sugar conversion. Pulps were made by letting the chips go through a refiner twice, with the first time having a plate opening of 0.02 inched and the second time having a plate opening of 0.002 inches. Such

obtained pulps were centrifuged and their moisture contents were determined. Then, approximately 30 grams of o.d. pulps with the consistency of 10% were subsequently subjected to a P.F.I. Mill beating treatment to reach 6,000 revolutions. The resulting pulp was centrifuged and fluffed by a “fluffer”, followed by the consistency determination.

Enzymatic hydrolysis of as prepared substrates was carried out in 150 mL flasks by using enzyme Cellic C Tec2 (Novozymes, Franklinton, NC), with 100 mM acetate buffer used as the medium (pH=4.8). The activity of C Tec2 was measured to be 136 filter paper units per mL (FPU/mL) and the density was determined to be 1.238 g/mL. Three levels of enzyme dosage were applied: 5, 10 and 15 FPU per gram of o.d. substrate. 5 grams of o.d. substrate was used for all enzymatic hydrolysis trials and the consistency of solution was set at 5%. All the flasks were placed into an air incubator shaker (Series 25, New Brunswick Scientific CO., INC., Edison, New Jersey, U.S.A.) for up to 96 hours. The temperature of the incubator was set at 50°C and the rotating speed was 150 rpm. About 0.5 mL of liquor was withdrawn from each flask to a 2 mL polypropylene microcentrifuge tube, after the reaction had taken place for 8, 16, 24, 48 and 96 hrs. These centrifuge tubes were then immediately placed into boiled water for 3 minutes. After that, samples were centrifuged and the upper clear solution was filtered through a nylon syringe filter to be subjected to further sugar



analysis. The final solution, obtained after 96 hours of enzymatic hydrolysis, was filtered through a previously weighed filter paper. The filter paper along with the solid residue was placed into oven overnight to determine the weight loss of the substrate.

Sugar analysis was performed to all the samples that collected at different time point (as described above). Appropriate dilution of sample was made to fit the sugar calibration scale. Detailed sugar analysis method was discussed in the foregoing section.

## **5.4 Results and Discussion**

### **5.4.1 Solid content in residual chips and filtrate**

Table 5- 1 shows the solid content in the residual chips. All the extraction trials were performed by the same amount of air-dried chips (600 grams), so the total weight of oven-dried starting materials were 551.3 grams (moisture content of  $8.12 \pm 0.02\%$ ). From Table 5- 1, auto-hydrolysis at 180 °C resulted in the lowest total amount of o.d. residues (399.3 grams, corresponding to yield of 72.4%), which means that under this condition the highest amount of woody material has been removed from the original biomass. The highest solid yield in residues was obtained from auto-hydrolysis at 160 °C (about 85%). Compared with auto-

hydrolysis, acid-catalyzed prehydrolysis at the same temperature facilitated the solid removal. The addition of acetic acid decreased the residual solid yield up to about 4% (at the higher addition level), while formic acid adding caused the solid yield declined for 8% (at the 6% adding level). The reason for formic acid has a better catalytic ability in solid removal, relative to acetic acid, may rely on its stronger ability of dissociating hydrogen ion. Also, as more acid was introduced to the system, more solid was dissolved. However, the incremental solid removal due to the increasing of acid addition from 2% to 6% was not that significant (for acetic acid, about 1.7% more; for formic acid, about 2% more). It was also found that the more severe the condition, the higher moisture content of the solid residue. At 180 °C, the highest moisture content of 62.7% was obtained, followed by formic acid at 6% and 2% charging, acetic acid at 6% and 2% charging, and 160 °C without acid addition. This phenomenon implies that under a more severe condition, especially at higher temperature, the structure of the solid during the extraction process will be opened up more, resulting in a higher ability of absorbing and holding water of the residue.

Table 5- 1 Solid yield in the residual chips from different conditions. Range of duplicate measurements was reported.

Conditions	Acid added (%)	Temp. (°C)	Original Wood (od g)	Moisture (%)	Solid Residue <sup>d</sup> (od g)	Yield <sup>e</sup> (%)
Auto-H <sup>a</sup>	0	160	551.3±0.2	58.4±0.9	470.5	85.3
	0	180	551.3±0.2	62.7±0.8	399.3	72.4
AA <sup>b</sup>	2	160	551.3±0.2	59.5±1.5	456.0	82.7
	6	160	551.3±0.2	60.1±0.2	446.4	81.0
FA <sup>c</sup>	2	160	551.3±0.2	61.0±1.0	435.6	79.0
	6	160	551.3±0.2	61.2±0.4	424.8	77.1

<sup>a</sup> Auto-hydrolysis

<sup>b</sup> Acetic acid

<sup>c</sup> Formic acid

<sup>d</sup> Total oven dried solid in the residue, calculated by (solid content (w/w %) times total weight of wet residue)

<sup>e</sup> Weight percentage, calculated by (total oven dried solid in the residue / total original o.d. solid weight \* 100)

Table 5- 2 shows the solid content measurement from the liquid extract. From the results of solid yield in the residual chips, the opposite trend of solid yield in the extract can be forecasted. As Table 5- 2 shows, the highest solid content (almost 5%) of extract was observed for auto-hydrolysis at 180 °C. Auto-hydrolysis at 160 °C resulted in the lowest filtrate solid content (3.5%), corresponding to the highest solid yield in the solid residues. Also at 160 °C, as adding acid and increasing acid addition level, higher solid content in the filtrate was achieved. The introduction of formic acid contributed to a higher solid content in the filtrate, compared with acetic acid. The overall solid yield in the filtrated increased from 14.7% to up to 20.8%, based on oven-dried starting biomass, by either adding acid to the system or increasing the temperature by 20°C.

Table 5- 2 Solid yield in filtrate from different conditions. Range was reported for duplicate measurements.

Conditions	Acid added (%)	Temp. (°C)	Total Extract (g) <sup>a</sup>	Total Extract (mL) <sup>b</sup>	Solid Content (%)	Total Solids (od g) <sup>c</sup>	Yield (%) <sup>d</sup>
Auto-H	0	160	2285.5	2263.3	3.5±0.0	80.9	14.7
	0	180	2356.7	2296.2	4.9±0.0	114.8	20.8
AA	2	160	2300.0	2273.9	3.6±0.2	84.0	15.2
	6	160	2309.6	2270.2	3.9±0.0	91.2	16.5
FA	2	160	2320.4	2278.0	4.6±0.1	105.9	19.2
	6	160	2331.2	2278.7	4.7±0.1	109.2	19.8

<sup>a</sup> Calculated by subtracting total o.d. solids of the residue from total raw material (wood + water)

<sup>b</sup> Calculated from extract weight with known volume. Values used in the calculation of other compounds.

<sup>c</sup> Total solids in the extract, calculated by (extract solid content (w/w%) times total grams of extract)

<sup>d</sup> Weight percentage, calculated by (total o.d. solid in the extract / total o.d. original solid weight \*100)

A summary of solid content in both residual biomass and liquid filtrate, as well as the overall solid balance is illustrated in Table 5- 3. From Table 5- 3, desirable solid balance for all the conditions were obtained except for auto-hydrolysis at 180°C. A previous study by Pu, et al. (2011) showed that as temperature increases, worse solid balance was resulted. The explanation given was that, at higher temperature more volatile compounds will be generated, and while the solid content was measured under the oven condition these volatile compounds will evaporate, which will hurt the overall solid balance calculation. We can see from

Table 5- 3 that, by increasing temperature from 160 °C to 180 °C, the total solid balance decreased from 100 % to 93%. At the same temperature (160 °C), the addition of acid into to the system decreased the overall solid balance at a mild extent. No big difference was found for the total solid balance from switching the acids or increasing the acid addition level.

Table 5- 3 Solid content in the filtrate and solid residue after auto-hydrolysis or acid-catalyzed prehydrolysis. Results based on 100 grams of o.d. original wood

Conditions	Auto-H	Auto-H	AA 2%	AA 6%	FA 2%	FA 6%
Temperature (°C)	160	180	160	160	160	160
Solid in Filtrate (g)	14.7	20.8	15.2	16.5	19.2	19.8
Solid in Residue (g)	85.3	72.4	82.7	81.0	79.0	77.1
Total (g)	100.0	93.3	97.9	97.5	98.2	96.8

#### 5.4.2 Sugars in the extract

Table 5- 4 shows the sugar composition results from all the samples collected. All the results are presented in grams based on 100 grams of original materials. During the extraction (also known as pretreatment) process, water under high temperature and high pressure penetrates into the wood, causing partial hydrolysis of cellulose, dissolving part of the hemicelluloses, and removing a portion of lignin (Taherzadeh et al. 2008). The

hemicellulose is extracted from the wood chips in the form of either monomer sugars or liquid-soluble oligosaccharides with various degrees of polymerization. The oligosaccharides can be further hydrolyzed to monosaccharides by using acid or enzymes. In this study, 3% of sulfuric acid was used to hydrolyze all the oligomer sugars into monomer sugars. Monomer sugars are accounted as the effective fermentable sugars that being extracted from the biomass.

Arabinose was mostly extracted in the monomeric form under all the conditions (Table 5- 4). The majority of glucose, xylose and mannose were produced in the oligomer-sugar form, since the difference between their monomeric sugar amount and their total monosugars after breaking down all the oligo-sugars into monomers, are quite significant. At 160 °C with no acid added, the total amount of monomers that presented in the filtrate was only 0.84 grams, while after acid-hydrolysis of the filtrate the total sugar amount increased to 8.11 grams. Both acetic acid and formic acid addition had contributed to increase the total amount of sugars that generated in the extract. Formic acid enhanced the sugars production more than acetic acid did. Again, this may due to formic acid is stronger than acetic acid. At the retention time of 60 minutes, formic acid added at 6% level resulted in the highest overall sugars content in the filtrate, which is about 13.5 grams. The total sugars presented in the extract at 60 minutes for auto-hydrolysis at 180 °C were about 11.7 grams.

Generally, by gradually increasing the retention time from 0 minute to 60 minutes, the mono-sugars that generated in the filtrate were also increased, except for that auto-hydrolysis at 180 °C and formic acid addition of 6% at 160 °C arabinose was observed to begin to decrease in amount between 40 min and 60 min. By just looking at the total amount of sugars after the acid-hydrolysis, all the sugars except for mannose and glucose that produced during auto-hydrolysis at 180 °C were decreased in amount after 40 min. The total amount of glucose in the extract was decreased after 40 min for the formic acid addition at 2 and 6%, as well as acetic acid addition of 6%. However, we cannot address that sugar degradations were only occurred for those sugars that had decreased in their total amount. Rather, one should also combine the observation of how the oligo-sugars content change during the extraction and the analysis of overall byproducts to better understand the extent of sugar degradation.

Oligo-sugars were calculated by the difference between the content of total mono-sugars (after acid-hydrolysis treatment) and the mono-sugars in the filtrate. If plot the sum of all the sugars in their different forms (mono-sugars, oligo-sugars and total) respectively, we can get figures as shown in Figure 5- 1. Auto-hydrolysis at 160 °C, acetic acid addition of 2% and 6% (a, c, and d) showed continuously increasing in all the sugar forms. But the total oligo-sugars with acetic acid at 6% of addition (d) began to level off from 40 minutes. For

the conditions of formic acid adding, oligo-sugars were found to be decreased after 40 min for the 2% addition (e), and even earlier than 40 min for the 6% addition (f). The maximum amount of oligo-sugars for formic acid adding was around 4 grams. Most of the sugars in the filtrate of 160 °C auto-hydrolysis (a) were in the form of oligo-sugars. This can be judged by the close distance between the two lines that represent for the mono-sugars and the oligo-sugars, respectively. Even after 1 hour of auto-hydrolysis, the content of the oligo-sugars were still keep increasing. The highest oligo-sugar amount was more than 7 grams for this condition. Obviously, the addition of acid facilitated the hydrolysis of oligo-sugars into mono-sugars during the whole process. From the result of auto-hydrolysis at 180 °C (b), a decline in the amount of oligo-sugars was also observed. However, the amount of total oligo-sugars was found to be about 9.5 grams, which is higher than any of the other conditions. This means that by increasing the reaction temperature, not only the hydrolysis of oligo-sugars into mono-sugars will be accelerated; the process of oligo-sugars dissolving from the raw woody biomass into the liquid phase will also be speeded up at the mean while. Extraction at higher temperature is desirable for obtaining as much as sugars possible in the filtrate, in a timely manner, but can also lead to greater extent of sugar degradation. 180 °C also encountered with a total sugars decreasing after 40 min, which means that the speed of oligo-sugars transforming to mono-sugars is not as fast as the speed of mono-sugars degradation.



Table 5- 4 Sugar composition in the extract under each condition before (Mono) and after (Total) acid-hydrolysis by 3% H<sub>2</sub>SO<sub>4</sub> as grams of mono-sugar based on 100 grams of o.d. original wood.

Conditions		Auto-hydrolysis				Auto-hydrolysis				Acetic Acid 2%				Acetic Acid 6%				Formic Acid 2%				Formic Acid 6%			
Temp. (°C)		160				180				160				160				160				160			
Time (min)		0	20	40	60	0	20	40	60	0	20	40	60	0	20	40	60	0	20	40	60	0	20	40	60
Arabinan	Mono <sup>a</sup>	0.02	0.12	0.22	0.30	0.08	0.34	0.32	0.23	0.05	0.20	0.33	0.39	0.06	0.27	0.42	0.42	0.19	0.49	0.58	0.58	0.19	0.50	0.58	0.55
	Total <sup>b</sup>	0.06	0.30	0.44	0.49	0.24	0.36	0.29	0.21	0.09	0.29	0.40	0.42	0.11	0.33	0.44	0.43	0.21	0.43	0.51	0.50	0.17	0.44	0.47	0.46
Rhamnan	Mono	0.01	0.03	0.05	0.08	0.02	0.12	0.17	0.19	0.01	0.04	0.07	0.10	0.01	0.05	0.10	0.12	0.03	0.10	0.19	0.26	0.02	0.13	0.26	0.34
	Total	0.02	0.09	0.16	0.21	0.11	0.27	0.27	0.23	0.03	0.13	0.22	0.25	0.04	0.13	0.24	0.29	0.06	0.17	0.29	0.34	0.05	0.21	0.29	0.33
Galactan	Mono	0.00	0.02	0.05	0.08	0.02	0.14	0.24	0.31	0.01	0.04	0.09	0.14	0.01	0.06	0.13	0.18	0.03	0.13	0.25	0.36	0.03	0.22	0.41	0.55
	Total	0.04	0.16	0.31	0.44	0.14	0.44	0.52	0.50	0.03	0.20	0.35	0.45	0.05	0.23	0.41	0.51	0.09	0.32	0.50	0.57	0.08	0.37	0.54	0.60
Glucan	Mono	0.04	0.09	0.12	0.14	0.06	0.18	0.34	0.54	0.06	0.11	0.15	0.19	0.05	0.12	0.19	0.25	0.09	0.21	0.37	0.54	0.07	0.41	0.79	1.11
	Total	0.28	0.68	1.15	1.50	0.56	1.58	1.49	1.75	0.32	0.85	1.37	1.41	0.39	0.91	1.66	1.48	0.76	1.23	1.68	1.59	0.39	1.29	1.80	1.77
Xylan	Mono	0.01	0.02	0.09	0.22	0.02	0.74	2.26	3.64	0.01	0.06	0.22	0.49	0.01	0.11	0.43	0.83	0.04	0.47	1.53	2.97	0.05	1.42	3.98	6.37
	Total	0.02	0.56	2.50	4.97	1.10	7.22	9.00	7.80	0.06	1.32	3.48	5.69	0.10	1.52	4.32	6.56	0.27	3.18	6.61	8.47	0.26	4.30	7.58	9.28
Mannan	Mono	0.00	0.00	0.01	0.02	0.00	0.05	0.14	0.27	0.00	0.01	0.01	0.03	0.00	0.01	0.03	0.05	0.01	0.04	0.10	0.20	0.01	0.11	0.29	0.51
	Total	0.04	0.17	0.34	0.50	0.24	0.85	1.14	1.20	0.04	0.19	0.33	0.70	0.05	0.25	0.49	0.72	0.09	0.45	0.77	0.94	0.07	0.53	0.82	1.03
Sum <sup>c</sup>	Mono	0.08	0.28	0.55	0.84	0.20	1.58	3.48	5.18	0.13	0.46	0.87	1.33	0.14	0.62	1.30	1.85	0.37	1.44	3.02	4.91	0.37	2.78	6.31	9.43
	Total	0.47	1.96	4.90	8.11	2.39	10.71	12.72	11.68	0.57	2.98	6.15	8.92	0.74	3.38	7.55	9.99	1.49	5.78	10.36	12.41	1.02	7.13	11.51	13.47

Table 5- 4 Continued

<sup>a</sup> The amount of mono-saccharide formed in the extracts during the extraction process

<sup>b</sup> The total amount of mono-saccharide presented in the extracts after acid-hydrolysis by 3% H<sub>2</sub>SO<sub>4</sub>

<sup>c</sup> Sum of all the sugars listed above

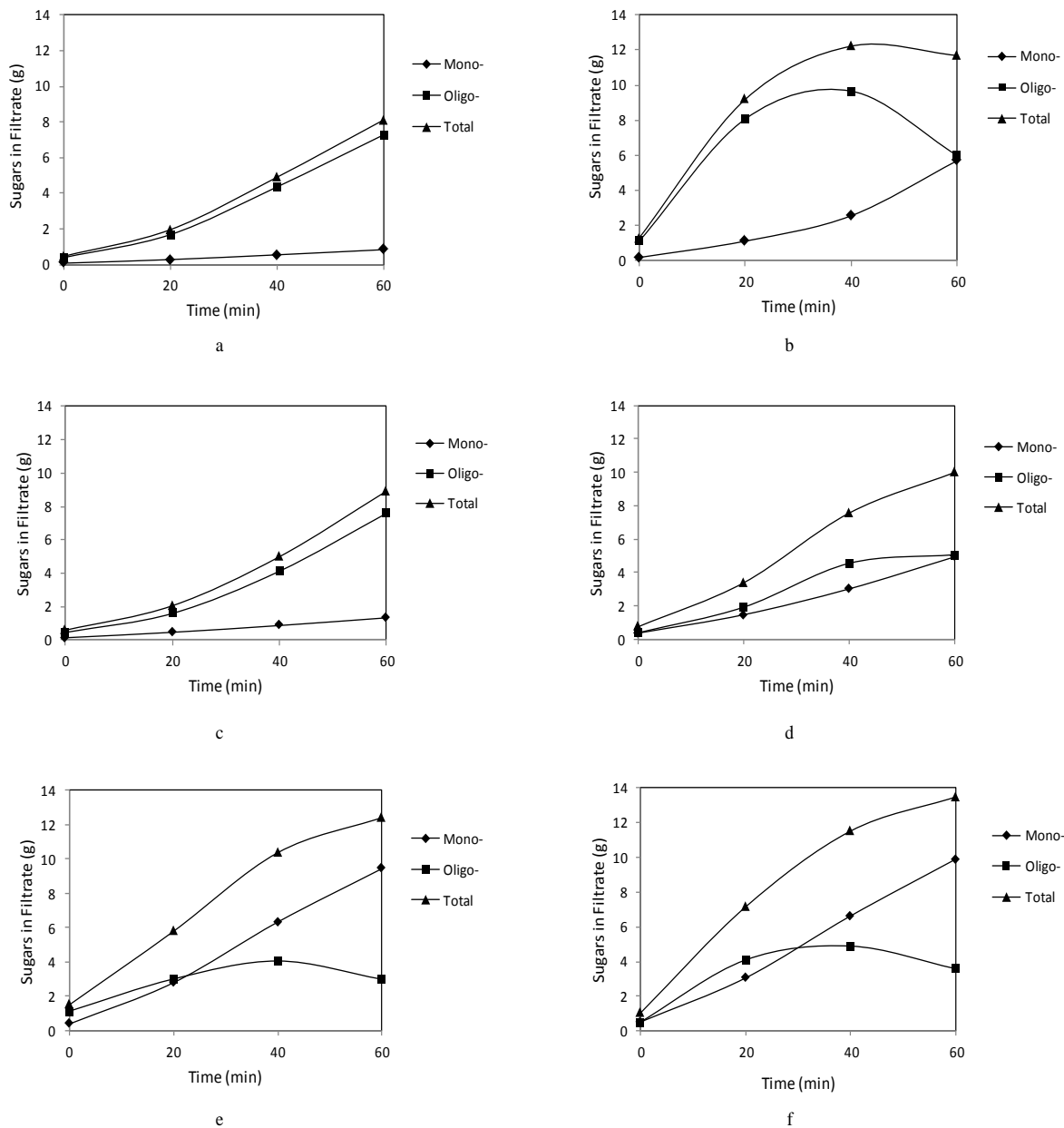


Figure 5- 1 The sum of all kinds of sugars that were present in the filtrate in the form of mono-sugars, oligo-sugars and total sugars (after breaking down oligo-sugars into mono-sugars), respectively, for each condition (a. Auto-hydrolysis at 160 °C; b. Auto-hydrolysis at 180 °C; c. 2% of acetic acid addition at 160 °C; d. 6% of acetic acid addition at 160 °C; e. 2% of formic acid addition at 160 °C; f. 6% of formic acid addition at 160 °C)

### 5.4.3 Sugars in the solid residues

The sugar composition of raw material and solid residues from each pretreatment condition are listed in Table 5-5.

Table 5- 5 Sugar composition of the raw material and of the solid residues from each condition as grams recovered from 100 grams of o.d. original material

Conditions Temperature (°C)	Raw material NA	Auto-H 160	Auto-H 180	AA 2% 160	AA 6% 160	FA 2% 160	FA 6% 160
Arabinan	0.6±0.1	0.1	0.0±0.0	0.1±0.1	0.1±0.0	0.1±0.0	0.1±0.0
Rhamnan	0.4±0.1	0.2	0.1±0.0	0.2±0.0	0.1±0.0	0.1±0.0	0.1±0.0
Galactan	0.6±0.0	0.1	0.1±0.0	0.2±0.0	0.1±0.0	0.1±0.0	0.1±0.0
Glucan	45.6±1.7	44.6	38.6±0.8	41.5±2.6	39.8±1.1	39.9±0.6	39.0±1.6
Xylan	16.3±0.1	6.2	3.4±0.2	6.7±1.5	7.1±0.0	5.6±0.2	4.7±0.1
Mannan	2.7±0.3	1.3	0.8±0.0	1.5±0.3	1.3±0.1	1.2±0.1	0.8±0.2
Lignin	26.3±0.8	25.6±2.5	26.0±0.4	25.3±0.4	24.9±0.8	25.7±1.7	25.9±1.6
Total Sugar	66.3	52.5	43.0	50.1	48.5	47.2	44.8
Sugar and Lignin	92.5	78.1	69.0	75.4	73.5	72.9	70.7

The total amount of sugars in the original wood was about 66 grams out of 100 grams of o.d. wood. During the pretreatment, sugars (most of the hemicellulose and part of the cellulose) are extracted from the raw material into the liquid phase, causing less sugars remaining in the solid part. We can see that, most of the cellulose (in the format of glucose)

was remained intact in the solid phase. Auto-hydrolysis at 160 °C only led to about 2% cellulose decreasing in the solid. As the severity of the pretreatment condition increasing, more cellulose was tending to be hydrolyzed and removed from the solid part. Most of the arabinose, rhamnose and galactose were removed from the starting material. However, a completed removal of all the sugars was difficult to achieve: even at 180 °C, there were still some of the sugars could be measured in the solid part.

#### **5.4.4 Byproduct analysis**

The process of sugar generation is coupled with sugar degradation. Acetic acid is generated from hydrolysis of the acetyl groups in the hemicellulose, and is normally observed at the highest concentration in the filtrate after the extraction process, compared with all the other byproducts (Mills, et al. 2009). Furfural and HMF had comparatively lower concentration in the filtrate and they are sugar degradation products from pentoses and hexoses, respectively. Formic acid is a byproduct from further degradation of HMF and furfural (Mill, et al. 2009) and constitutes the second highest byproduct concentration in the filtrate (Pu, et al. 2011). Table 5- 6 shows all the byproduct results from the samples collected during the extraction.

Table 5- 6 Byproducts identified in the filtrate by using HPLC (All results are in grams based on 100 grams of original o.d. wood. This data reflects both the additional acetic acid and formic acid that was produced during the pretreatment and the acetic acid and formic acid that was initially charged to the reactor.)

Conditions	Time (min)	Formic Acid	Acetic Acid	HMF	Furfural	Total
160°C Auto-H	0	0.3	0.3	0.0	0.2	0.8
	20	0.6	1.3	0.1	0.3	2.3
	40	0.8	2.3	0.1	0.4	3.6
	60	0.9	3.0	0.2	0.6	4.7
180°C Auto-H	0	0.6	0.7	0.1	0.3	1.6
	20	1.1	2.6	0.2	0.7	4.5
	40	1.6	4.8	0.3	1.4	8.0
	60	2.2	6.8	0.5	2.2	11.6
160°C AA2	0	0.3	1.8	0.0	0.2	4.3
	20	0.7	2.9	0.1	0.3	6.0
	40	0.9	3.6	0.1	0.5	7.1
	60	1.0	4.0	0.2	0.6	7.9
160°C AA6	0	0.3	1.9	0.0	0.2	8.4
	20	0.6	4.0	0.1	0.3	11.0
	40	1.0	5.5	0.2	0.5	13.1
	60	1.2	5.6	0.2	0.8	13.8
160°C FA2	0	0.6	0.5	0.0	0.2	3.3
	20	1.9	1.4	0.1	0.4	5.7
	40	2.2	2.4	0.1	0.6	7.2
	60	2.7	3.2	0.2	0.9	9.0
160°C FA6	0	0.9	0.7	0.0	0.2	7.8
	20	2.1	1.6	0.1	0.4	10.2
	40	3.3	3.4	0.2	0.8	13.7
	60	4.1	4.5	0.3	1.2	16.1

As the retention time increased from 0 min to 60 min, more and more byproducts were generated in the filtrate, Table 5- 6. In Table 5- 6, the amount of formic acid and acetic acid for the acid-catalyzed prehydrolysis have already included the acid amount that charged into the system. For example, with formic acid addition at 6%, the total amount of

byproducts that actually generated during the prehydrolysis at 60 min, should be calculated by 16.14 minus 6 grams (the amount of formic acid added to the system), which resulted in 10.14 grams of total byproducts. The highest total amount of byproducts obtained was from auto-hydrolysis at 180 °C (11.59 grams). The highest amount of acetic acid that generated (5.61 grams) was observed with acetic acid addition at 6% level. And the highest amount of formic acid that generated (4.14 grams) was obtained with 6% formic acid addition. Seems like that the acid that added to the system will facilitate the production of itself, to a greater extent; and also ease the generation of other byproducts, to a less extent. Remember discussed in the previous section, the total amount of sugars began to decrease after 40 minutes for the auto-hydrolysis at 180 °C. The non-ignorable amount of byproducts may explain how critically the sugar degradation will affect the overall sugars yield. In another sense, if a feasible and effective method can be found to recover the acids that generated in the filtrate during the acid-catalyzed prehydrolysis and recycle them back to the system, it would be encouraging and valuable to further study the economic implication and advantages behind this scheme of implementation.

#### 5.4.5 Heat content of residues

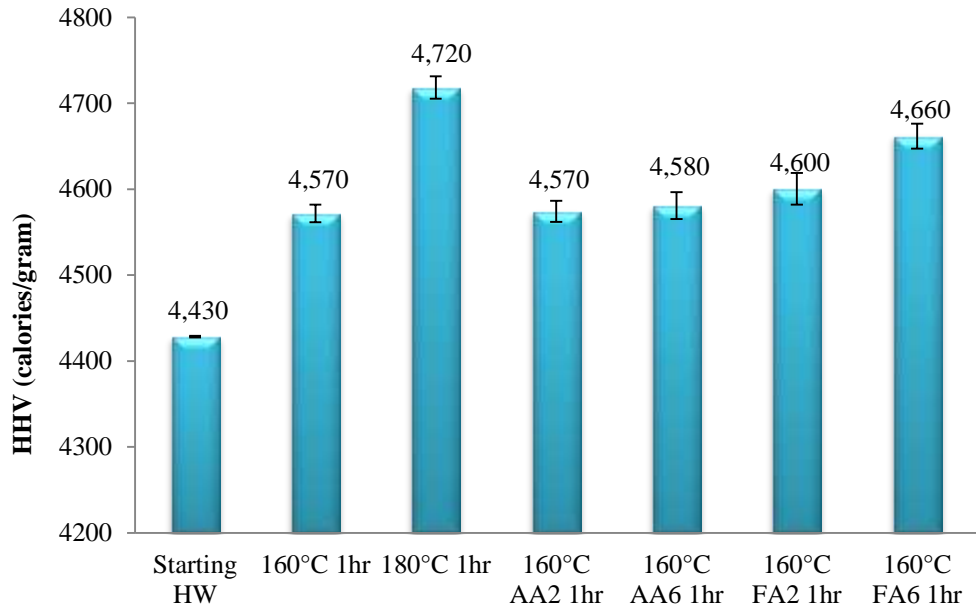
After the auto-hydrolysis or the acid-catalyzed prehydrolysis pretreatment, two ways can be utilized to recover the values of the resulting solid residues: enzymatic hydrolysis to break down the remaining cellulose and hemicellulose to mono-sugars for further fermentation, and, combustion of the solid residue to get the heating value recovered. In order to accomplish the enzymatic hydrolysis, multiple treatments of the solid residues are needed, primarily including pulp making and refining. We will talk about this in detail in the next section. Compared with enzymatic hydrolysis, direct combustion of the residual woody biomass generates heat and power for other utilizations, instead of consuming enormous amount of energy.

Figure 5- 2 shows the experimental measurements for the higher heating values (a) of the solid residues that generated from each condition, and the calculation results of the percentage of heating values (b) that recovered from the residues. From Figure 5- 2 (a), auto-hydrolysis at 180 °C generated residues with the highest heating value (4,718 calories per o.d. gram residue). At 160 °C, by adding acid to the system, by increasing the acid adding level and / or by switching acid from acetic acid to formic acid, the heating values of the residues increased. The highest higher heating value obtained for the 160 °C treatments was formic acid added at 6% (4,662 calories per o.d. gram of residue). During the pretreatment, hot

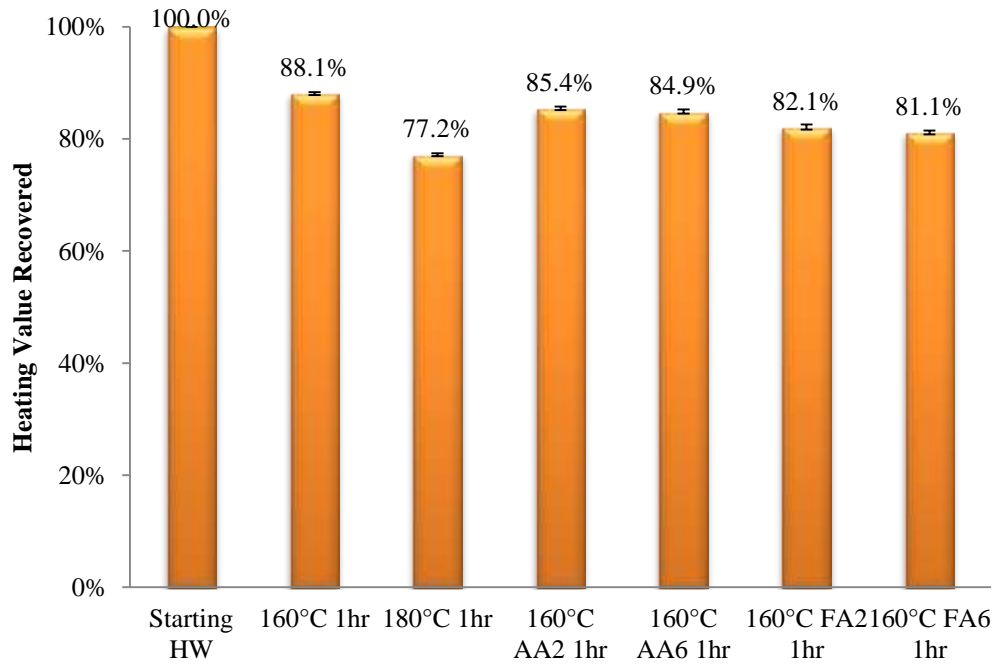


water penetrates into the biomass and cause partial dissolution of the materials (mainly hemicellulose), which results in a higher content of the lignin remaining in the residues. Lignin has a higher heating value compared with other compounds in the woody biomass. This is the main reason why after the pretreatment the solid residues will have a higher caloric value. Figure 5- 3 shows the lignin content in the original wood and that in the solid residues. All the results are based on the o.d. weight of solids.

Figure 5- 2 Higher heating value of the original woody biomass and solid residues (a) and total heating value recovered from the solid residues (b)



(a)



(b)

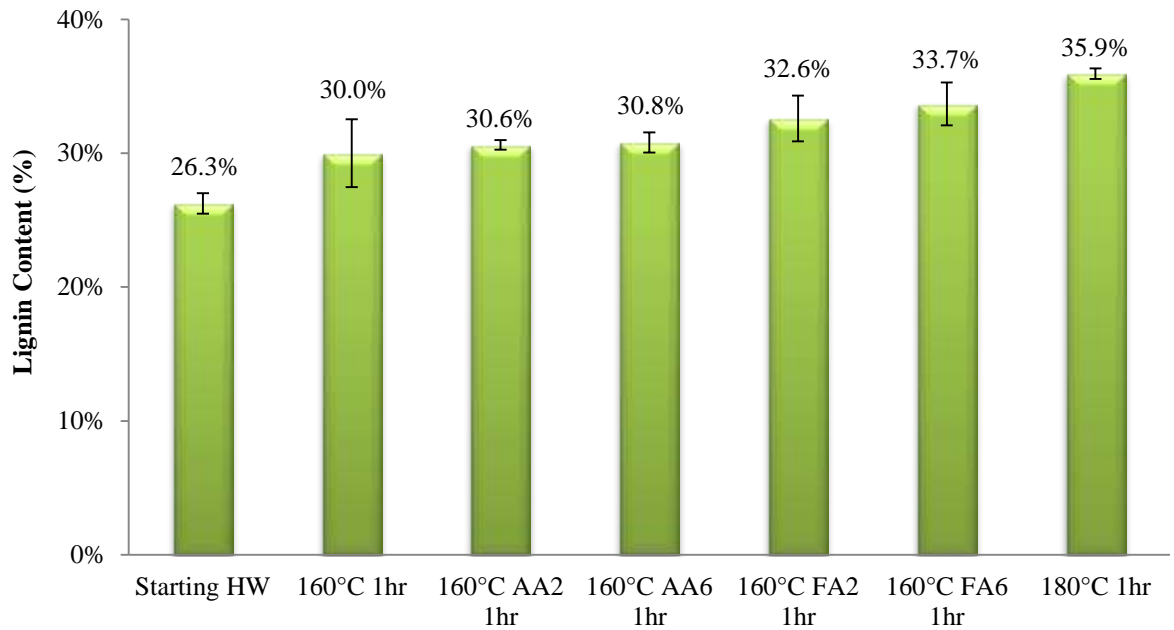


Figure 5- 3 Lignin content in the original material and solid residues (based on o.d. solids)

Figure 5- 3 shows the trend of the heating value of the solid (Figure 5- 2 (a)) to be the same as the trend of the lignin content in the solid. After auto-hydrolysis at 180 °C, the lignin content increased from 26.3% in the original wood to about 36% in the residue, both based on the weight of the solids. Figure 5- 4 shows there is almost a linear relationship can be observed for the heating value and lignin concentration of the solid residues. Figure 5- 2 (b) shows the percentage of heating value that can be recovered from the solid residues for each condition. Even though residues from the 180 °C treatment had the densest heating value, the total heating value that can be recovered for this condition was actually the lowest (less than 80%). The reason for this is simple: the total amount of residual chips from this condition

was the lowest, since more solids were already dissolved into the liquid phase during the pretreatment. Generally, as the severity of the condition increased (from no acid to acid addition, from lower acid addition level to higher acid addition level, from acetic acid addition to formic acid addition), the total amount of heating value that can be recovered will be decreased accordingly. When considering the use of the solid residues for energy content in a combustion process and the use of the extracted carbohydrates as feedstock for ethanol production, a careful analysis of the overall net benefit of the system versus extraction severity needs to be evaluated.

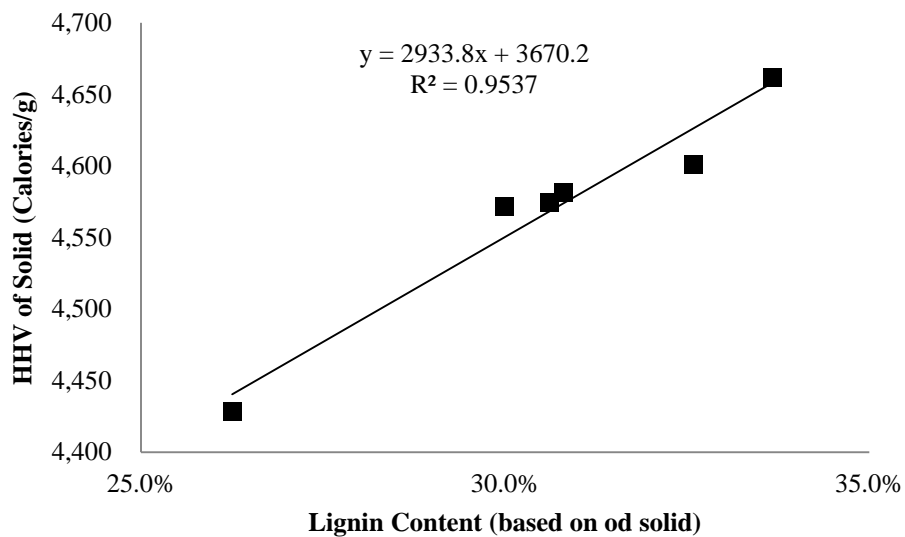
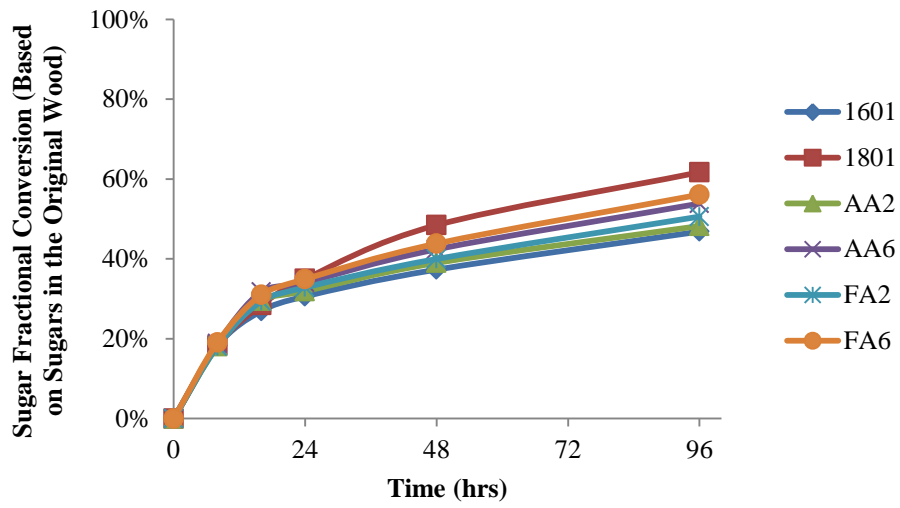


Figure 5- 4 The relationship between higher heating value and lignin content of the solid

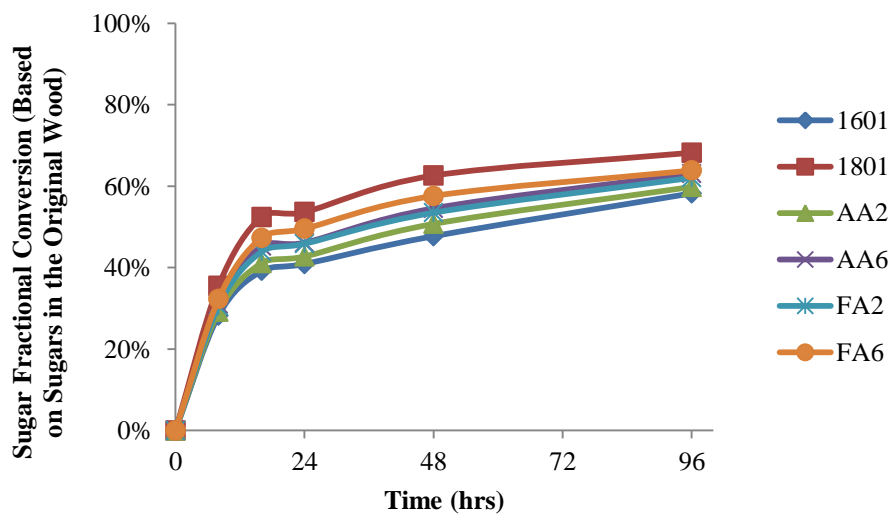
#### **5.4.6 Enzymatic hydrolysis**

Enzymatic hydrolysis was carried out to the solid residues from each pretreatment. As described in the experimental section, the merit of the present study was to use a P.F.I Mill to mechanically treat the pulp that made from the solid residues until a 6,000 revolution was reached. Figure 5- 5 shows the total sugar conversions (the percentage of total sugars that generated during the enzymatic hydrolysis based on the original total sugars that were present in the original wood) for each pretreatment condition at different time points (0, 8, 16, 24, 48 and 96 hours) by using enzymatic hydrolysis at three enzyme loading levels (5, 10 and 15 FPU/gram of o.d. substrate).

Figure 5- 5 Sugar fractional conversion (based on total sugars in the original wood) from enzymatic hydrolysis of solid residue (P.F.I treated) from each pretreatment condition at different enzyme loadings: (a) 5 FPU/gram of o.d. substrate, (b) 10 FPU/ gram of o.d. substrate, (c)15 FPU/ gram of o.d. substrate.

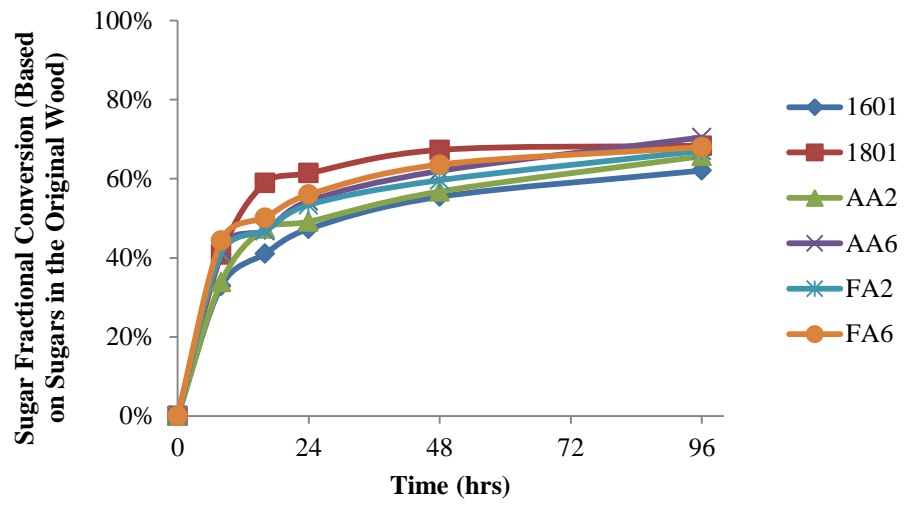


(a)



(b)

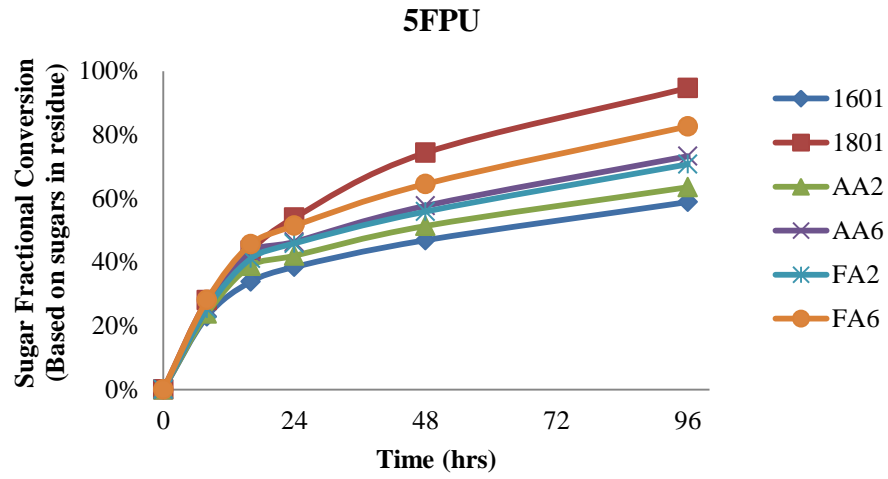




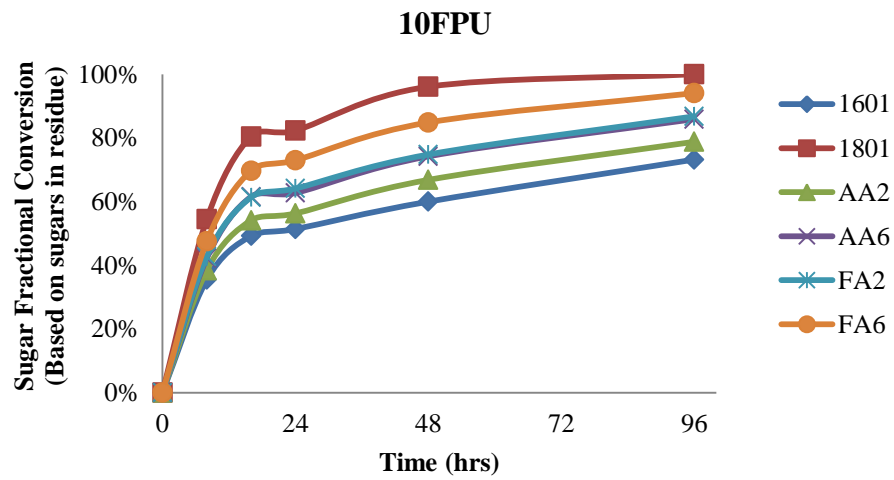
(c)

The sugars that can be detected in the enzymatic hydrolysis liquid were comprised of trace amount of rhamnose and galactose, a small amount of mannose and a majority of glucose and xylose. Figure 5- 5 shows that by increasing the enzyme charging level, the process of enzymatic hydrolysis has been speeded up, and the sugar fractional conversion was also increased at each time point. At the enzyme loading of 15 FPU, the sugar conversion reached a platform for the substrate from 180 °C auto-hydrolysis. Generally, the sugar fractional conversion during the process of enzymatic hydrolysis were found to be in a sequence of 180 °C auto-hydrolysis > 160 °C formic acid 6% > acetic acid 6% > formic acid 2% > acetic acid 2% > 160 °C auto-hydrolysis. The highest sugar conversion percentage (based on original total sugars) was found to be about 68%, after enzymatic hydrolysis of substrates from 180 °C auto-hydrolysis and 160 °C acid-prehydrolysis with 6% formic acid for 96 hours (with 15 FPU enzyme charge).

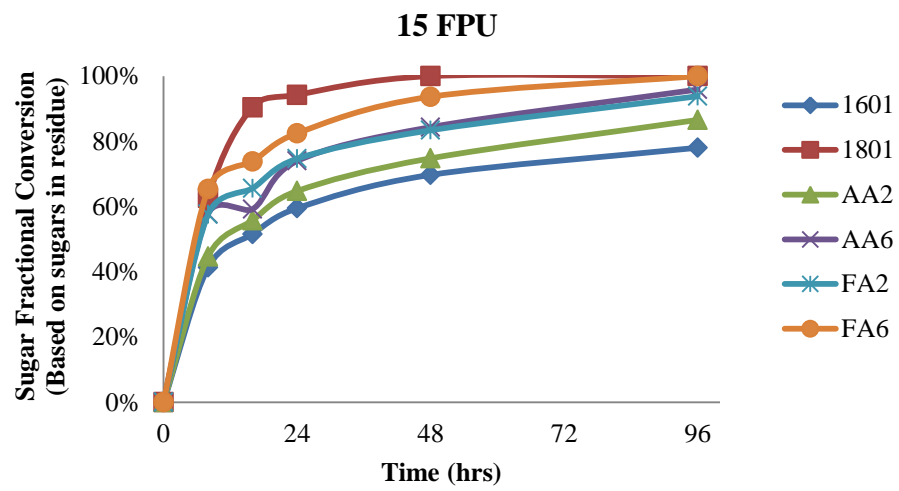
Figure 5- 6 Sugar fractional conversion (based on sugars in the residue) from enzymatic hydrolysis of solid residue (P.F.I treated) from each pretreatment condition at different enzyme loadings: (a) 5 FPU/gram of o.d. substrate, (b) 10 FPU/ gram of o.d. substrate, (c)15 FPU/ gram of o.d. substrate.



(a)



(b)



(c)

Figure 5- 6 shows the sugar fractional conversion after enzymatic hydrolysis based on the sugars (sugars in the residue) that entered the enzymatic hydrolysis system. Sugar conversion of 100% were achieved for substrate from 180 °C auto-hydrolysis after 96 hours at 10 FPU enzyme charge, and substrate from 160 °C acid-prehydrolysis with 6% formic acid after 96 hours at 15 FPU enzyme charge. Also, 100% sugar conversion was observed for substrate from 180 °C auto-hydrolysis after 48 hours at 15 FPU enzyme charge.

Table 5-7 listed all the sugar components fractional conversion during the enzymatic hydrolysis process under different conditions. Notice that auto-hydrolysis at 160 °C always had the highest xylose conversion due to higher content of xylose remained in the solid residue after the pretreatment. From Table 5- 5, glucose almost remained at the same level for all the conditions and had the highest content in the solid residues compared with any other sugar species. This is why in Table 5- 7, glucose always had the highest absolute fractional conversion rate relative to other sugars. Again, the severer the pretreatment condition, the higher the conversion for glucose. The fractional conversions for rhamnose and galactose were much lower than other sugars, since they were mostly removed from the biomass during the pretreatment processes.

Table 5- 7 Fractional conversion of each sugar component during enzymatic hydrolysis of solid residues from different conditions (based on 100 grams of original individual sugar in the wood)

FPU	Auto-H 160°C					Auto-H 180°C					AA 2% 160°C					AA 6% 160°C					FA 2% 160°C					FA 6% 160°C				
	8 hr	16 hr	24 hr	48 hr	96 hr	8 hr	16 hr	24 hr	48 hr	96 hr	8 hr	16 hr	24 hr	48 hr	96 hr	8 hr	16 hr	24 hr	48 hr	96 hr	8 hr	16 hr	24 hr	48 hr	96 hr	8 hr	16 hr	24 hr	48 hr	96 hr
<b>5 FPU</b>																														
<b>Rha</b>	1.1	1.2	8.4	8.5	10.6	0.6	0.5	6.5	6.6	7.3	0.9	8.6	7.9	8.2	10.0	0.8	8.6	7.7	7.7	9.9	0.8	7.8	7.3	7.6	8.3	0.8	7.4	6.9	7.0	7.6
<b>Gal</b>	1.7	2.3	2.3	2.6	2.9	1.2	1.1	1.1	0.7	2.3	1.5	2.0	1.5	2.3	2.9	1.4	2.0	2.1	1.9	3.1	1.3	1.8	1.3	1.5	2.3	1.3	1.5	1.1	1.5	2.1
<b>Glu</b>	17.3	27.0	31.1	39.2	50.0	23.6	37.0	37.2	63.7	81.0	18.8	31.9	35.2	43.8	54.8	20.7	36.0	39.2	49.6	63.5	21.5	35.5	40.0	49.3	62.2	24.0	39.5	44.8	56.5	72.3
<b>Xyl</b>	24.8	33.0	35.3	39.5	46.6	7.8	11.1	10.5	16.7	20.9	19.2	29.1	29.3	33.4	38.9	17.5	26.8	26.9	31.1	37.3	12.8	18.8	19.8	22.5	28.0	9.9	14.2	15.1	18.1	22.5
<b>Man</b>	3.4	1.6	6.7	9.2	16.4	1.6	1.9	3.0	5.5	11.3	3.3	4.0	6.2	9.2	15.0	3.2	3.8	5.9	8.6	15.1	2.4	2.4	4.4	6.1	14.2	1.5	1.8	2.9	5.4	10.8
<b>10 FPU</b>																														
<b>Rha</b>	1.3	9.0	8.7	9.4	10.9	0.6	7.3	6.9	6.8	8.6	0.9	9.2	7.8	8.6	10.5	0.7	8.2	7.7	8.4	9.9	0.8	7.8	7.3	8.4	9.3	0.6	7.8	6.7	7.8	9.1
<b>Gal</b>	2.9	4.3	4.2	4.6	5.4	2.2	3.0	2.9	3.2	3.5	2.8	4.0	3.7	4.4	5.0	3.0	4.0	3.6	4.2	5.0	2.7	3.5	3.3	3.5	4.5	2.4	3.2	3.1	3.3	3.7
<b>Glu</b>	30.1	41.7	44.1	52.2	63.9	46.9	69.1	71.2	82.7	89.7	33.0	46.9	49.3	58.6	68.9	36.7	53.8	55.1	65.5	75.3	37.8	54.6	57.3	66.6	76.8	41.6	61.3	64.6	74.7	82.2
<b>Xyl</b>	29.4	40.1	40.0	43.6	51.7	12.0	17.7	16.7	19.7	21.9	24.9	33.5	33.1	37.7	43.9	22.3	31.0	30.6	34.6	40.0	17.2	23.5	23.5	27.3	31.7	13.7	18.9	18.5	21.8	24.8
<b>Man</b>	1.8	7.0	10.0	17.2	28.0	1.3	4.7	3.8	10.0	16.5	3.6	7.0	9.3	18.8	29.8	2.8	5.8	8.9	14.8	26.4	3.6	5.6	7.5	14.1	23.6	3.1	5.2	5.5	11.0	19.4
<b>15 FPU</b>																														
<b>Rha</b>	1.3	8.8	8.6	9.7	11.3	0.4	7.0	6.5	6.6	8.4	0.9	8.5	7.9	8.7	11.3	0.8	8.3	7.5	8.4	10.7	0.7	7.7	7.2	12.8	9.8	0.6	7.6	7.0	7.7	8.8
<b>Gal</b>	4.8	6.0	6.2	6.8	8.0	3.6	4.6	4.4	4.9	5.2	4.4	5.5	5.8	6.4	7.3	5.0	5.1	5.6	6.0	7.2	4.6	4.6	5.0	5.3	6.1	4.5	4.9	4.6	5.3	5.8
<b>Glu</b>	35.7	45.4	52.3	61.5	68.9	53.9	78.0	81.5	89.0	89.7	39.5	55.3	57.6	66.4	76.4	51.2	56.9	65.9	74.8	84.3	51.6	58.9	67.2	79.4	83.6	57.8	65.2	73.1	82.5	88.5
<b>Xyl</b>	32.1	37.5	42.5	48.2	52.5	13.5	18.9	18.9	20.8	21.8	25.7	35.1	35.3	40.1	45.8	27.3	28.7	33.4	37.8	43.1	21.2	23.5	26.0	31.3	32.6	17.0	18.7	20.2	23.6	27.2
<b>Man</b>	5.1	5.5	12.4	20.4	31.4	3.3	5.9	8.2	13.1	21.6	3.6	9.1	12.0	19.7	33.6	4.8	6.1	10.6	19.3	33.4	5.0	6.6	9.2	18.0	26.4	4.4	6.4	8.0	15.6	28.5

A weight loss analysis was also performed to the solid residues after enzymatic hydrolysis for 96 hours, to verify the sugar yield and/or sugar conversion results.

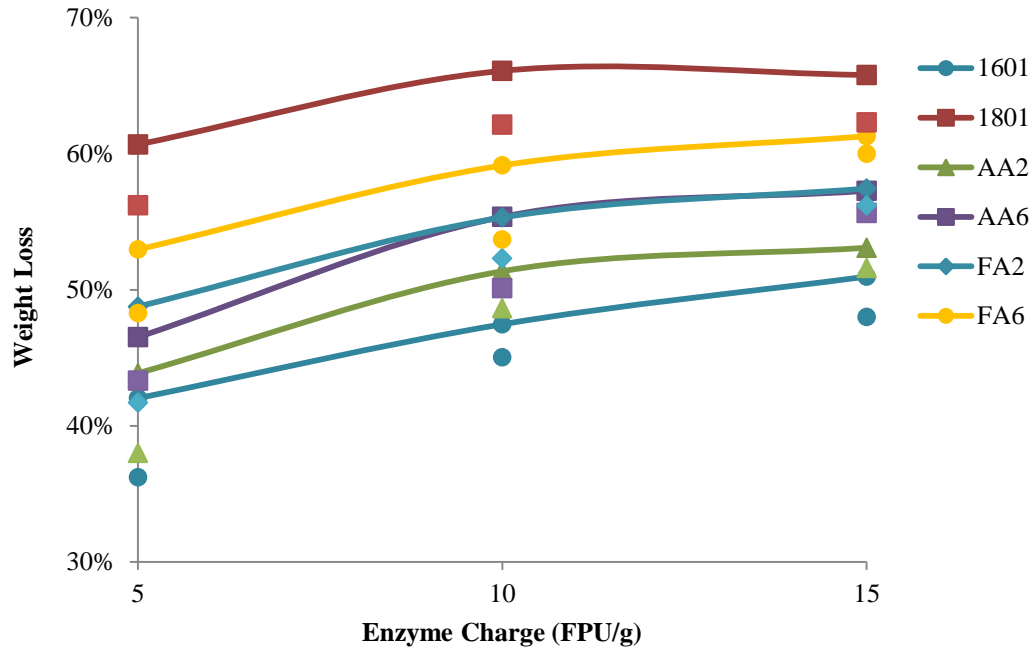


Figure 5- 7 Solid weight loss (lines) and sugar yield (dots) versus enzyme charge in FPU/g from the enzymatic hydrolysis of solid residues



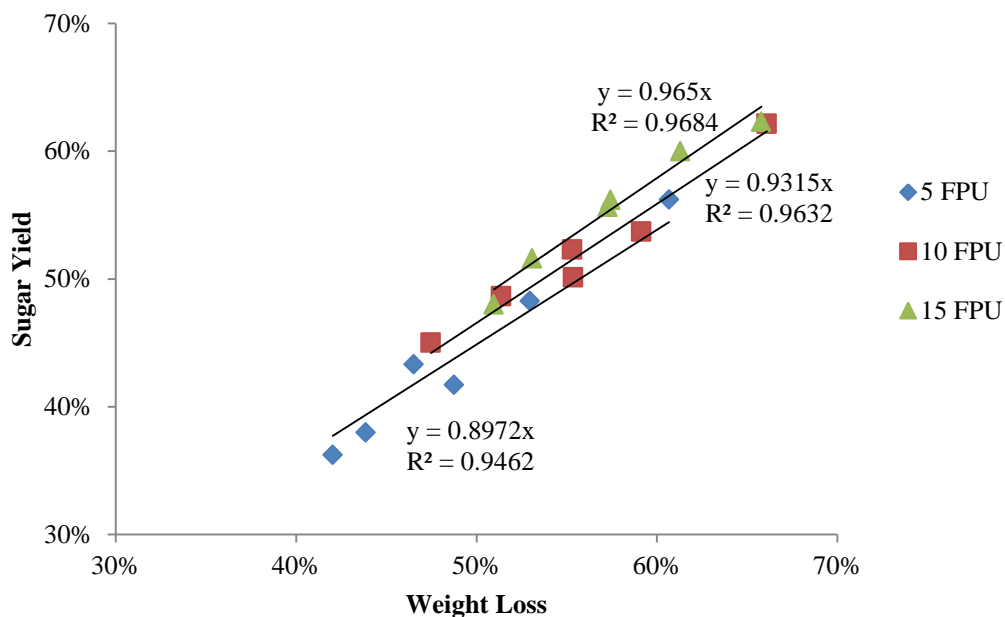


Figure 5- 8 Sugar yield vs. weight loss (all based on o.d. substrate) after enzymatic hydrolysis for 96 hours at different enzyme charge levels

The solid weight loss and sugar yield were calculated by the following equations:

$$\text{Solid weight loss} = \frac{(\text{gram original o.d. substrate} - \text{gram o.d. solid residue after enzymatic hydrolysis})}{\text{gram original o.d. substrate}}$$

$$\text{Sugar yield} = \frac{\text{gram sugar obtained during enzymatic hydrolysis}}{\text{gram original o.d. substrate}}$$

From Figure 5- 7, the sugar yield was always found to be lower than the weight loss from the enzymatic hydrolysis. The reason for this is most likely that, only the mono-sugars in the

enzymatic hydrolysis solution were quantified. However, there was still a small amount of oligo-sugars that were not completely hydrolyzed presenting in the solution. These oligo-sugars that did not account into the sugar yield can cause the differential between the solid weight lost and the sugar yield. We can also notice from Figure 5- 3 that, auto-hydrolysis at 180 °C resulted in a residue with a lignin content of almost 36%. This result confirmed that enzymatic hydrolysis of substrate from this condition, with 10 and/or 15 PFU enzymes loading, contributed to 100% sugar hydrolysis from the solid residue. Since the weight lost after enzymatic hydrolysis at 10 and/or 15 FPU for this condition was about 66%. Figure 5- 8 was plotted by o.d. substrate weight loss versus sugar yield (based on o.d. substrate). As enzyme load increased from 5 to 15 FPU, the slope of the linear line is gradually getting closer to 1. This indicates that higher enzyme charge level will facilitate the conversion of oligo-sugars to mono-sugars in the enzymatic liquor.

In order to investigate the effect of P.F.I. treatment of the substrate on the enzymatic hydrolysis, a parallel enzymatic hydrolysis of substrate without P.F.I treatment has also been carried out. Only 5 FPU enzyme loading was used for the substrate without P.F. I. treatment. Figure 5- 9 shows the sugar conversion percentage comparison between enzymatic hydrolysis of substrate with and without P.F.I treatment. The highest sugar conversion percentage (labeled numbers) was obtained from enzymatic hydrolysis of substrate with P.F.I treatment, for 96 hours.

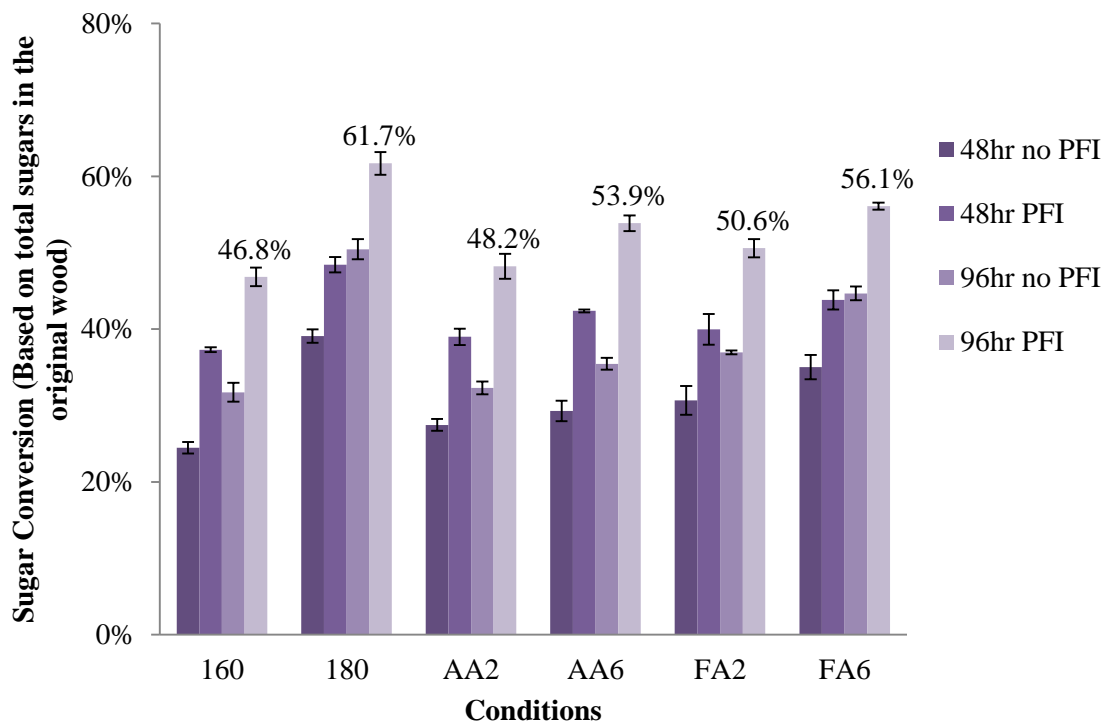


Figure 5- 9 Comparison of enzymatic hydrolysis of substrate with and without P.F.I. treatment (Sugar fractional conversion based on original total sugars in the wood; graph showing enzymatic hydrolysis with 5 FPU enzyme loading level for 48 hours and 96 hours).

It is shown that the difference between the enzymatic hydrolysis of the two kinds of substrates was quite obvious. By employing the P.F.I to the pulp that produced from the solid residue, the sugar conversion from enzymatic hydrolysis increased at least 10%. Without P.F.I treatment, sugar conversion for substrate from 180 °C auto-hydrolysis after enzymatic hydrolysis for 96 hours was about 50%, still the highest among all the other substrates from

other conditions. The same sugar conversion trend from substrate without P.F.I treatment as that of from P.F.I treated substrate can also be observed. Substrate generated from 180 °C auto-hydrolysis pretreatment always showed the best enzymatic hydrolysis performance, followed by formic acid 6%, acetic acid 6%, formic acid 2%, acetic acid 2% and auto-hydrolysis at 160 °C.

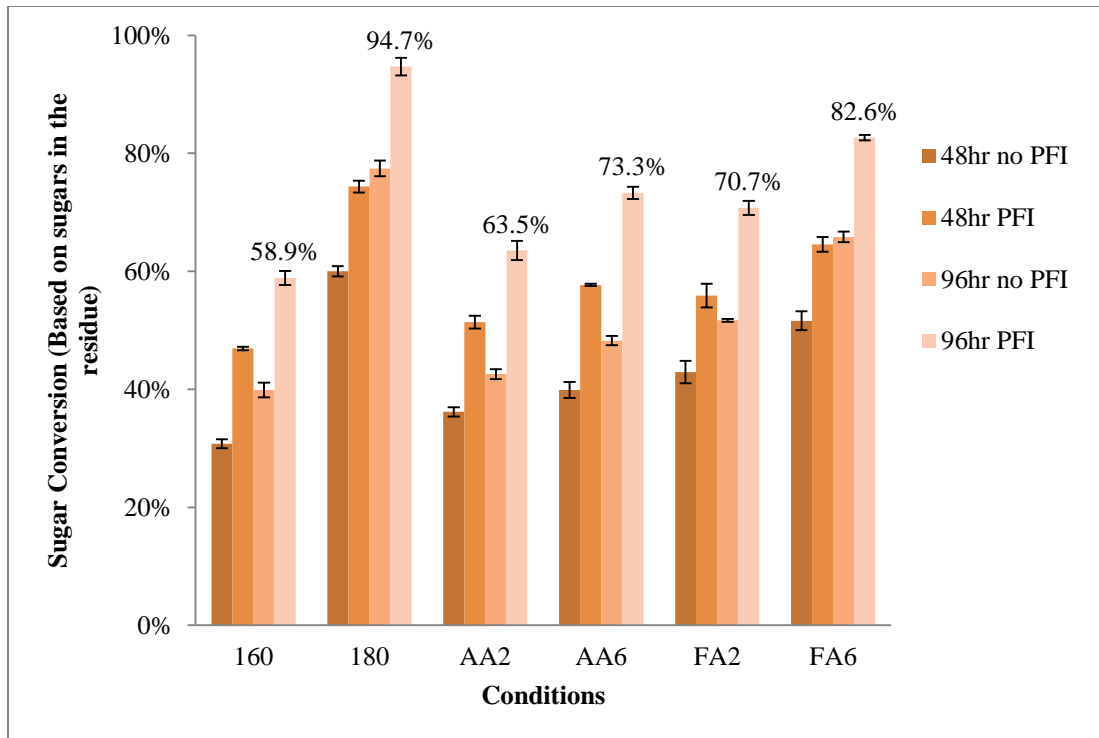


Figure 5- 10 Comparison of enzymatic hydrolysis of substrate with and without P.F.I. treatment (Sugar fractional conversion based on sugars in the residue; graph showing enzymatic hydrolysis with 5 FPU enzyme loading level for 48 hours and 96 hours).

Figure 5- 10 is similar to Figure 5- 9, but instead of showing sugar fractional conversion based on the original total sugars in the wood, it shows the sugar fractional conversion based on sugars that entered into the enzymatic hydrolysis system.

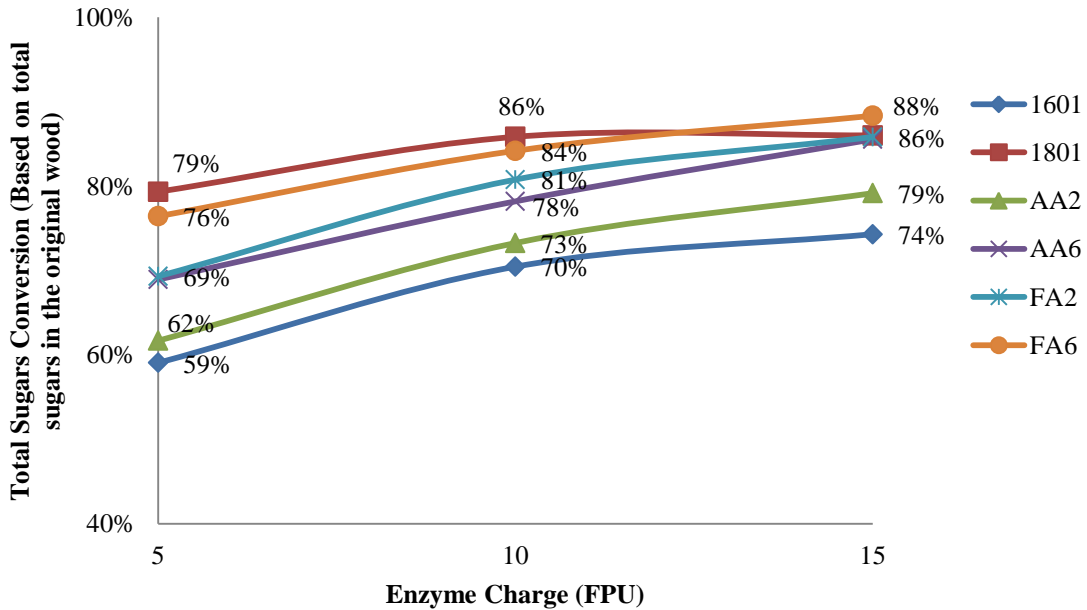


Figure 5- 11 Total sugars recovery (sugars from both prehydrolyzate and enzymatic hydrolysis) at different enzyme charge levels for each condition after 96 hours

Figure 5- 11 shows the overall sugar yield from both prehydrolyzate in the pretreatment processes and from enzymatic hydrolysis of the solid residues. From Figure 5- 11, the highest overall sugar yield (88%) was obtained by acid-prehydrolysis with 6% formic

acid at 160 °C, followed by auto-hydrolysis at 180 °C (86%), with 15 FPU enzyme charge level during the enzymatic hydrolysis process. Even with the lowest enzyme charge level (5 FPU), almost 80% overall sugar yield can be achieved by 180 °C auto-hydrolysis.

## 5.5 Conclusions

Pretreatments of mixed hardwood chips were carried out by either auto-hydrolysis or acid-prehydrolysis. Auto-hydrolysis at 180 °C showed the highest solid removal from the starting material, the highest total byproducts generation (acetic acid, formic acid, furfural and HMF), and the worst mass balance closure. The highest sugar yield (13.5% based on o.d. original material) in the prehydrolyzate was obtained by pretreatment using 6% formic acid at 160 °C. Sugar degradation was observed for auto-hydrolysis at 180 °C after 40 min of retention time, in terms of the total sugar yield. Formic acid showed better catalytic ability relative to acetic acid, with regard to the solid removal and the sugar yield in the extract. By introducing acid into the pretreatment process, the amount of byproducts generated into the liquid phase increased a lot. Increasing the acid content from 2% to 6% did not show significant improvement in either the sugar yield or solid removal. The performance of enzymatic hydrolysis of solid residues from each pretreatment can be summarized in the sequence of 180 °C auto-hydrolysis > 160 °C formic acid 6% > acetic acid 6% > formic acid

2% > acetic acid 2% > 160 °C auto-hydrolysis, based on the sugar conversion percentage results. The weight loss measurement of the solid residues after enzymatic hydrolysis confirmed the sugar conversion results from enzymatic hydrolysis, as well as indicated that there were still a small amount of oligo-sugars have not fully hydrolyzed by enzymes. The P.F.I. Mill treatment of the pulp from each pretreatment solid residue showed an enhancement of enzymatic hydrolysis performance (at least 10% sugar conversion increase). Both auto-hydrolysis at 180 °C and acid-prehydrolysis with 6% formic acid at 160 °C showed very high overall sugar yield (86% and 88%) after enzymatic hydrolysis for 96 hours (15 FPU). With the mildest enzyme charge (5 FPU), auto-hydrolysis at 180 °C still can achieve about 80% overall sugar yield after enzymatic hydrolysis for 96 hours.

## 5.6 References

- Amidon, T., Liu, S. (2009) Water-based woody biorefinery. *Biotechnology advances* 27 (5):542-550
- Alvira, P., Tomas-Pejo, E., Ballesteros, M., Negro, M.J. (2010) Pretreatment technologies for an efficient bioethanol production process based on enzymatic hydrolysis: A review. *Bioresource Technology* 101: 4851-4861
- Carvalho, F., Esteves, M.P., Parajo, J.C., Pereira, H., Girio, F.M. (2004) Production of oligosaccharides by autohydrolysis of brewery's spent grain. *Bioresource Technology* 91: 93-100
- Fenske, J., Hashimoto, A., Penner, M.H. (1998) Relative fermentability of lignocellulosic dilute-acid prehydrolysates application of a *Pichia stipitis*-based toxicity assay. *Applied Biochemistry and Biotechnology* 73: 145-157
- Garrote, G., Dominguez, H., Parajó, J.C. (1999) Mild autohydrolysis: an environmentally friendly technology for xylooligosaccharide production from wood. *Journal of Chemical Technology and Biotechnology* 74 (11):1101-1109
- Garrote, G., Domínguez, H., Parajó, J.C. (2001a) Kinetic modelling of corncob autohydrolysis. *Process Biochemistry* 36 (6):571-578



- Garrote, G., Domínguez, H., Parajó, J.C. (2001b) Generation of xylose solutions from Eucalyptus globulus wood by autohydrolysis–posthydrolysis processes: posthydrolysis kinetics. *Bioresource Technology* 79 (2):155-164
- Garrote, G., Cruz, J.M., Domínguez, H., Parajó, J.C. (2003) Valorisation of waste fractions from autohydrolysis of selected lignocellulosic materials. *Journal of Chemical Technology and Biotechnology* 78 (4):392-398
- Grethlein, H.E., Allen, D.C., Converse, A.O. (1984) A comparative study of enzymatic hydrolysis of acid-pretreated white pine and mixed hardwood. *Biotechnology and Bioengineering* 26: 1498-1505
- Grethlein, H.E. (1991) Common aspects of acid prehydrolysis and steam explosion for pretreating wood. *Bioresource Technology* 36: 77-82
- Henriksson, M, Berglund, L.A. (2007) Structure and properties of cellulose nanocomposite films containing melamine formaldehyde. *Journal of Applied Polymer Science* 106: 2817-2824
- Knappert, D., Grethlein, H., Converse, A. (1980) Partial acid hydrolysis of cellulosic materials as a pretreatment for enzymatic hydrolysis. *Biotechnology and Bioengineering* 22: 1449-1463

- Li, H., Saeed, A., Jahan, M.S., Ni, Y., Heiningen, A.V. (2010) Hemicellulose removal from hardwood chips in the pre-hydrolysis step of the kraft-based dissolving pulp production process. *Journal of Wood Chemistry and Technology* 30: 48-60
- Ligero, P., Kolk, van der J.C., Vega, de A., Dam, van J.E.G. (2011) Production of xlo-oligosaccharides from miscanthus x giganteus by autohydrolysis. *BioResources* 6 (4)
- Mills, T.Y., Sandoval, N.R., Gill, R.T. (2009) Cellulosic hydrolysate toxicity and tolerance mechanisms in *Escherichia coli*. *Biotechnology for biofuels* 2 (11)
- Nguyen, Q.A., Tucker, M.P., Keller, F.A., Beaty, D.A., Connors, K.M., Eddy, F.P. (1999) Dilute acid hydrolysis of softwoods. *Applied Biochemistry and Biotechnology*: 77-79, 133-142
- Saha, B.C., Iten, L.B., Cotta, M.A., Wu, Y.V. (2005) Dilute acid pretreatment, enzymatic saccharification and fermentation of wheat straw to ethanol. *Process Biochemistry* 40 (12):3690-3700
- Taherzadeh, M.J., Eklund, R., Gustafsson, L., Niklasson, C., Liden, G. (1997) Characterization and fermentation of dilute-acid hydrolyzates from wood. *Industrial and Engineering Chemistry Research* 36: 4659-4665

Zhang, J., Zhu, Z., Wang, X., Wang, N., Wang, W., Bao, J. (2010) Biodetoxification of toxins generated from lignocellulose pretreatment using a newly isolated fungus, *Amorphotheca resinae* ZN 1, and the consequent ethanol fermentation. *Biotechnology for biofuels* 3:26-26

## **CHAPTER 6: The Feasibility Analysis of Ethanol Production from Lignocellulosic Biomass before Energy Generation**

### **6.1 Abstract**

The present report was motivated by the so called “value prior combustion” (VPC) technology, by which ethanol and other value-added chemicals are produced from lignocellulosic biomass prior to combustion of these materials to generate electricity. The term “value” here was initially targeted at making extra profit by integrating an ethanol plant to an existing power generation facility. Base case was defined as the readily available energy facility. Hardwood mix and softwood mix were used as the two different kinds of feedstock. Raw materials were subjected to hot-water extraction under different temperatures (160, 170 and 180°C) to investigate the optimal economic investment in terms of variable conditions. Acid was also added to the pre-hydrolysis system to study the economic feasibility of increasing ethanol yield to a great extent, while taking the risk of improved revenue being written off by swelling capital investment and other costs. Feedstock input amount was set at 500,000 BDT per year for all the cases except in the increased-scale case

(about 700,000 BDT), in order to keep the power output almost the same as the base case while increasing the ethanol yield. All the simulations were constructed in Excel spreadsheets to establish mass and energy balances. Those simulations were based on the experimental data obtained in the laboratory scale, and economic analysis was carried out for each proposed case.

Economic feasibility was highly dependent on the chemical pricing, ethanol selling price, scale of the facility and separation strategies and/or technologies that involved in the process. The evaporation process before the acid-hydrolysis also shows significant influence on the feasibility result, as the amount of water removed directly affects the quantity of chemicals that will be consumed in the subsequent steps. The results of the present economic analysis will provide insights into the factors that will affect the profitability.

The analysis showed that hot-water extraction at 170 °C for 1 hour will provide a potential economic feasible scheme of ethanol production before combustion, only if, more cost-effective hydrolysis method or lower chemical pricing can be obtained. At the current stage of hydrolysis technology and pricing level, incremental internal rate of return (IRR) value cannot be obtained (normally a 12% incremental IRR should be targeted at to consider the project as profitable). The practicality of acid-catalyzed strategy is highly limited by

employing the acid separation and recycling facility and associated expensive chemicals, i.e., the ammonia. To increase the feedstock input amount to maintain the same power output level as in the base case will not help improve the overall process economics, even if taking advantage of economies-of-scale. The incremental IRRs for all the cases cannot be obtained, which means that all the scenarios discussed would not be successful investments compared with the base case. The highest NPV value, \$81,000,000, of all the cases considered will be softwood extraction for 1 hour at 170°C, with a discount rate of 12%, compared with the NPV value of base case, which is \$182,000,000.

## **6.2 Objective**

The objective of this study is to establish a technical economic evaluation of the VPC technology to evaluate whether integrating an ethanol production plant to an existing power generation plant will be feasible and profitable. Another economic study based on a greenfield power plant will be provided in Appendix I for comparison.

It is well known that lignocellulosic biomass is mainly composed of cellulose, hemicellulose and lignin. During the hot-water extraction process, some of the hemicelluloses and a small portion of the cellulose will be dissolved in the liquid phase. After

converting the oligomers to monomer sugars, ethanol can be produced through a fermentation process. The solid residue will be most of the celluloses and lignin, which can be further combusted to recover the heating value in the biomass. This is the essential idea of the VPC technology. Ethanol is a low-value product (Olsson, et al., 1996), therefore to consider adding an ethanol plant to an existing power plant needs rigorous process modeling and economic evaluations with regard to the profitability concerns.

Mass and energy balance of different proposed cases were created by using Excel spreadsheet with ready laboratory data and appropriate assumptions. Capital cost was estimated referring to the individual equipment cost in the Merrick & Company report (NREL, 1999), which is supported by the National Renewable Energy Laboratory (NREL). Other financial analysis including operating costs estimation and income statement. Sensitivity analysis was also carried out in this report.

### **6.3 Introduction**

Motivated by the urgency of looking for alternative sources of sustainable and environmentally friendly energy to solve the current social problems and concerns on fuels, liquid biofuels generated from renewable biomass has obtained increasing attention due to its attractive advantages (Table 6-1). Ethanol has been produced tremendously in Brazil as well as in the United State and some of the European countries (Hahn-Hagerdal, et al., 2006; Wyman, 1999).

Table 6- 1 Advantages of lignocellulose-based liquid biofuels (Hahn-Hagerdal, et al., 2006)

<ul style="list-style-type: none"> <li>• Biofuel sources are geographically more evenly distributed than the fossil fuels; thus, the sources of energy will, to a larger extent, be domestic and provide security of supply.</li> </ul>
<ul style="list-style-type: none"> <li>• Lignocellulosic raw materials minimize the potential conflict between land use for food (and feed) production and energy feedstock production. The raw material is less expensive than conventional agricultural feedstock and can be produced with lower input of fertilizers, pesticides, and energy.</li> </ul>
<ul style="list-style-type: none"> <li>• Biofuels from lignocellulose generate low net greenhouse gas emissions, reducing environmental impacts, particularly climate change.</li> </ul>
<ul style="list-style-type: none"> <li>• Biofuels might also provide employment in rural areas.</li> </ul>

Conversion of biomass to ethanol and energy is such a way to sustain our way of life since woody biomass can be replenished at a rate that is desirably consistent with our energy consuming pace (Ragauskas, et al., 2006). Unlike petroleum or fossil energy sources whose natural replenishment is in the time scale of 200 million years (which is regarded as nonrenewable), biomass can be recharged in the time scale ranging from 3 months to 80 years (Liu, et al., 2006). Moreover, lignocellulosic biomass is the most abundant organic source on the earth.

Lignocellulosic biomasses are basically composed of three components: cellulose, hemicelluloses and lignin (Hamelinck, et al., 2005). Cellulose is a linear homopolymer (one-dimensional polymer) with the structure of six-carbon glucose unit connected end to end. It provides the biomass with structure and strength. Hemicelluloses are heteropolymer built up with five- and six- carbon sugars, including glucose, mannose, arabinose, galactose, and xylose.



It is a two-dimensional polymer with lower molecular weight than cellulose, thus is easier to be broken down to sugars than cellulose is (Wyman, 1999). Lignin is an amorphous heteropolymer with three-dimensional structure mainly consists of phenylpropylene alcohol. It has a carbon to oxygen ratio nearly 1, thus is more energy dense substance with the highest heating value, compared with other components (Amidon, et al., 2008). Depending on its inertia and stability in the present of corrosive chemicals, lignin acts as a natural barrier to biological degradation to biomass.

The hot-water extraction process can partially extract hemicellulose oligomers (mainly xylo-oligomers with different degree of polymerization) from wood, with water as the medium under high temperature (Leschinsky, et al., 2009; Taherzadeh, et al., 2008). The extracted sugars can undergo fermentation to be converted to ethanol by microorganisms, thus hemicelluloses can be deemed as a potential renewable resource for bio-based fuels (Stoutenburg, et al., 2008; Hess, et al., 2007). Moreover, the heating value of the residues after hot-water extraction can be recovered by simply combustion or burning, as well as can be utilized in the paper production process.

In 2002, the total ethanol production in Brazil reached about 3000 million gallons, of which approximately 1300 million gallons were used as fuel (Gnansounou, et al., 2005). The same year, the United State had about 2100 million gallons of ethanol production (Gnansounou, et al., 2005). After 8 years, in 2010 (Table 6-2), the ethanol production in the U.S. was about 5 times higher than that in 2002.

Currently, about 80% of ethanol production in the world is obtained by fermentation of sugars, while the balance was synthesized from petroleum products, i.e. ethylene (Lin, et al., 2006). However, almost all of the ethanol produced to date was corn starch based (in U.S.A) and sucrose based (in Brazil), and was blended with gasoline with various proportions. Though some ethanol-from-cellulose plants were built during World War II to provide alternative fuels, not until April 2004 has the first demonstration lignocellulosic ethanol plant been put into operation in Canada (Lin, et al., 2006).

Table 6- 2 U.S. fuel ethanol production and imports (2000-2010) (Millions of U.S. liquid gallons) Source: (Gnansounou, et al., 2005)

<b>Year</b>	<b>Production</b>	<b>Imports</b>	<b>Demand</b>
2000	1,630	N/A	N/A
2001	1,770	N/A	N/A
2002	2,130	46	2,085
2003	2,800	61	2,900
2004	3,400	161	3,530
2005	3,904	135	4,049
2006	4,855	653	5,377
2007	6,500	450	6,847
2008	9,000	556	9,637
2009	10,600	190	10,940
2010	13,230	10	13,184

Note: Demand figures includes stocks change and small exports in 2005

Lignocellulosic biomass doesn't have the food competition issues compared with grains (Wyman, 1999). However, producing monomer sugars from lignocellulosic feedstock is much more difficult than from grains, due to its resistant to breakdown nature. Thus, several pretreatment technologies have been developed to make the lignocellulosic materials more accessible to chemicals and further treatments. During a common chemical pretreatment, acids, alkaline, ammonia or organic solvents are used to break down the cellulose and hemicellulose chains to achieve high yield of sugars. The problems involved with these methods include acid neutralization or recycle concerns, corrosion problems of the equipment and tremendous inhibitors generation during the process. Physical pretreatment utilizes steam explosion or liquid hot water for which no catalyst is required. These are the most prospective methods as no environmental concerns will be involved and the sugar recovery is high (Hamelinck, et al., 2005).

This study will be focused on hot-water extraction with only water as the extraction medium, as well as with acid addition to evaluate their individual economics.

## 6.4 Methods

### 6.4.1 Base Case

The base case was established by referring to an existing power generation plant. The annually feedstock input of the facility is about 500,000 BDT wood waste, with the power output of 70 MW (Figure 6-1). Generally, the feedstock will go through wood receiving and storage, wood preparation for burning, boiler to generate steam and finally to produce electricity.

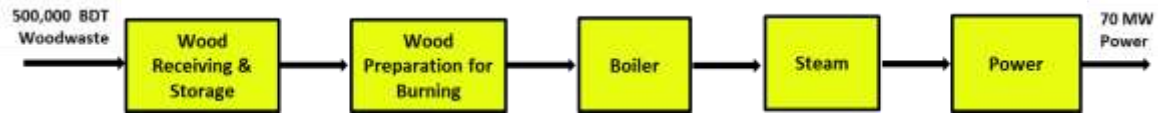


Figure 6- 1 Base case process flow graph

The main assumptions for the base case are summarized in Table 6-3.

Table 6- 3 Main assumptions for the base case

<b>Parameters</b>	<b>Value</b>	<b>Inflation</b>
<b>Wood waste cost per BDT (\$ )</b>	65	1%
<b>Boiler operation per year (hour)</b>	8400	-
<b>Power produced (MW)</b>	70	-
<b>Power selling price per MWh(\$)</b>	90	4%

#### **6.4.2 Proposed Cases and Process Design**

In order to study the feasibility of producing ethanol as a byproduct of the power plant, as well as to investigate how can the scale of plant, pretreatment technologies and reaction conditions affect the economics of the facility, three different scenarios were proposed against the base case:

- **Scenario I** - Integrate an ethanol plant to the existing power plant by employing the hot-water extraction of the feedstock for 1 hour under different temperatures (160, 170 and 180°C), followed by a sugar fermentation process to produce ethanol. The resulting solid residues are sent to the boiler to generate power. See Figure 6-2 for details:

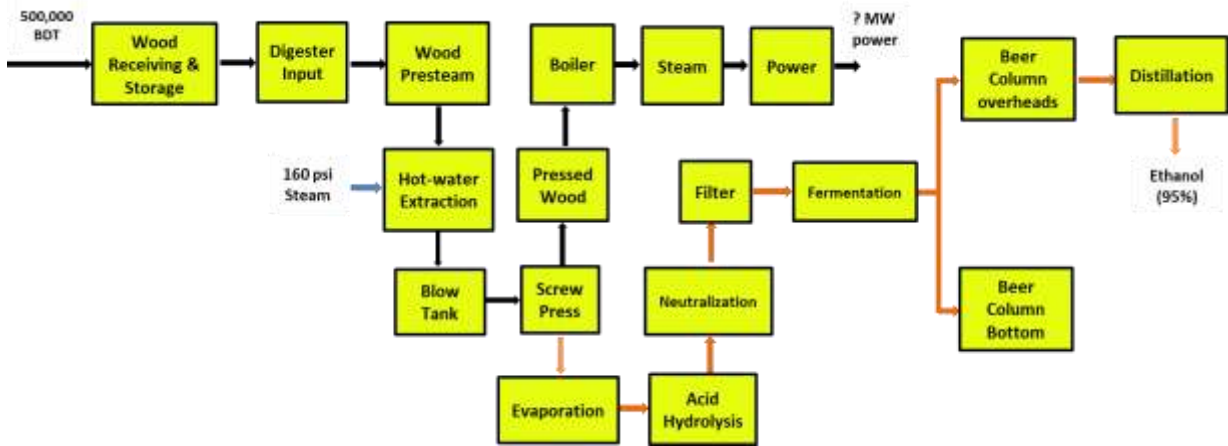


Figure 6- 2 Hot-water extraction for 1 hour flow sheet, no catalyst added

- **Scenario II** - Integrate an ethanol plant to the existing power plant by introducing formic acid as a catalyst to facilitate the prehydrolysis process under 160°C, and subsequent sugar fermentation process to produce ethanol. The resulting solid residues are sent to boiler to generate power (Figure 6-3);

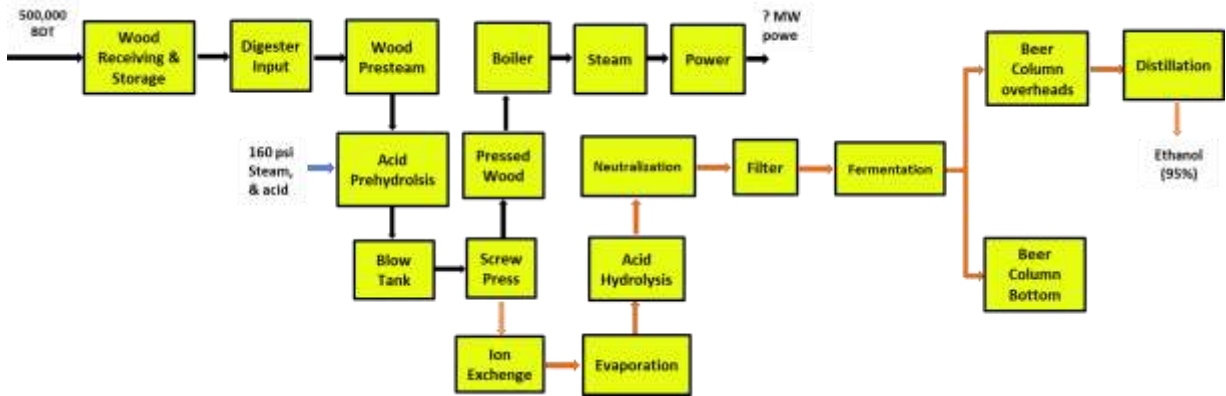


Figure 6- 3 Acid-catalyzed prehydrolysis under 160°C for 1 hour flow sheet

- Scenario III** - Integrate an ethanol plant to an existing power plant by increasing the feedstock input while using the same strategies and configuration as in Scenario I (Figure 6-2), in order to bring the power output to about the same level as that in the base case. 170°C was the only temperature utilized in this analysis. The resulting solid residues are sent to the boiler to generate power.

All of the three cases are carried out by both hardwood mix and softwood mix to study the influence of wood species on the economics. In our experimental studies, both formic acid and acetic acid were used to investigate their ability of catalyzing the hot-water extraction. The formic acid was eventually selected as it showed better catalyzing ability (see Section 5.4.2).

### 6.4.3 Feedstock

Feedstock species will have impact on the economic differential of all the cases. Table 6-4 shows the feedstock composition for hardwood mix and softwood mix as used in the economic process modeling. These data are obtained from the laboratory works.

Table 6- 4 Hardwood and softwood feedstock composition

<b>Component</b>	<b>% Dry Basis</b>	
	<b>Hardwood</b>	<b>Softwood</b>
<b>Cellulose</b>	46	46
<b>Mannans</b>	4	14
<b>Xylans</b>	19	7
<b>Lignin</b>	27	29
<b>Ash</b>	1	1
<b>Extractives</b>	3	3
<b>Total Solid</b>	100	100



The prices of feedstock will be highly dependent on the total input amount that will be sent to the process model. In the present analysis, the price of feedstock will be including both the value of the feedstock itself, and other transportation and handling fees (Gonzalez, et al., 2011). The price of both hardwood and softwood was assumed to be \$65 per bone dry ton (BDT) with a constant input of 500,000 BDT per year. This price is relative to the reported price by Gonzalez, 2011. However, it is believed that this price is a little bit overestimated by considering that the current existing power plant is using forest woody waste as the main raw material to generate power, but not fresh logs. A price of \$45 per BDT would be more reasonable; while we still took \$65 as the base price particularly considering that all the analysis was based on experimental results, which were obtained by using fresh wood chips as the starting material. On the other hand, it would be expected that lower ethanol yield will be as the consequence of using forest woody waste as the raw material to produce ethanol and power. Thus, a balance should be established between employing the lower price feedstock and decreasing the overall ethanol yield.

For the increasing scale of the facility, the feedstock price will be increased correspondingly according to how much more input will be added to the base line. This fact is based on the common knowledge that increasing material will add additional collection,

freight and handling fees to the cost. Table 6-5 indicates the price assumption behind the increasing scale case, in other word, to increase every 100,000 BDT feedstock annually will increase the feedstock price by \$1 per BDT.

Table 6- 5 Feedstock price assumption for the increasing scale case

Annual input (BDT)	Average Feedstock Price per BDT (\$)
<b>600,000</b>	66
<b>700,000</b>	67
<b>800,000</b>	68
<b>900,000</b>	69
<b>1,000,000</b>	70

#### **6.4.4 Hot-water Extraction**

Prior to the hot-water extraction, the feedstock will be preheated to 140 °F by recycled water from beer column bottoms and a following pre-steaming stage to remove some of the non-condensables (NREL, 1999) and allows heat to be loaded with low pressure steam that comes from the blow line after the extraction process. The hot-water extraction was achieved with or without chemical addition, depending on which scenario was applied. The extraction design inputs are summarized in Table 6-6.

Table 6- 6 Key design data for hot-water extraction reactor

<b>Design Inputs</b>	<b>Scenario I</b>	<b>Scenario II</b>	<b>Scenario III</b>
<b>Temperature</b>	160°C/ 170°C/ 180°C	160°C	170°C
<b>Solid to water ratio</b>	1:4	1:4	1:4
<b>Residence time</b>	1 hour	1 hour	1 hour
<b>Acid addition</b>	N/A	6% for HW, 2% for SW	N/A
<b>Byproducts</b>	Formic acid, acetic acid, furfural and HMF for all scenarios		
<b>Steam used</b>	160 psig steam, 358°F		
<b>Water used</b>	City process water, 65°F		

The acid added in the Scenario II will be formic acid, which was regarded as the most effective acid to enhance the overall sugar yields, according to our experimental results (see Section 5.4.2). During the acid-catalyzed prehydrolysis, formic acid generated internally will compensate for the acid needed for the cooking process; moreover, excess formic acid produced can also contribute to the revenue. Thus, if an efficient acid separation and recycling system can be established successfully, there will be no new formic acid added to the cooking step, but rather than continuously generated and recycled formic acid.

During the hot-water extraction process, about 50% of the hemicellulose and some of the cellulose (approximately 2%) will be dissolved in the liquid phase. The hemicellulose

dissolved will be presented in the forms of oligomers and monomers. Monomers are the simplest sugars that cannot be further broken down to smaller units, they are readily available fermentable sugars. Oligomers are sugar polymers that are composed of several mono-sugar units, and for the purpose of fermentation, oligomers should be converted to monomers by either chemical or biological method. This will be discussed more in detail in the acid-hydrolysis section. The main byproducts that will be generated in the sugar extraction process are acetic acid, furfural, formic acid and HMF. Acetic acid are formed from the acetate groups present in the hemicellulose polymer (NREL, 1999; Taherzadeh, et al., 2007).

Figure 6-4 shows the potential hydrolysis byproducts and their possible precursors.

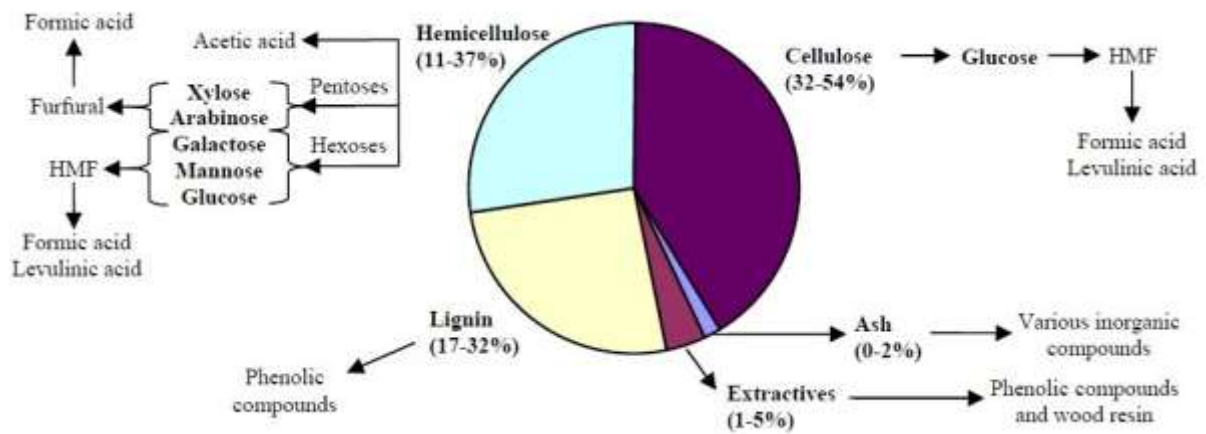


Figure 6- 4 Composition of lignocellulosic materials and their potential hydrolysis products (Taherzadeh, et al., 2007)

The sugars partitioning ratios (see equation below) into the liquid phase in each scenario are all different, depending on the reaction temperature, the extraction method and the feedstock species used. Table 6-7 and Table 6-8 summarize the sugar partitioning ratios (based on each sugar) and byproduct yields (based on o.d. starting materials) for all the scenarios. The lignin, ash and extractives partitioning ratios are set at 2%, 90% and 10% for all the cases (based on individual component).

$$\text{Partitioning Ratio} = \frac{\text{grams of material removed into the filtrate}}{\text{grams of original material}} \times 100\%$$

Table 6- 7 Sugar partitioning ratios and byproducts produced for all the scenarios (Hardwood)

Hardwood	Scenario I			Scenario II (Acid) 160°C	Scenario III (Increased Feedstock) 170°C
	160°C	170°C	180°C		
$\alpha$ - Cellulose	2%	2%	3%	6%	2%
Mannans	47%	50%	58%	100%	50%
Xylans	35%	50%	40%	50%	50%
Acetic Acid	1.1%	2.4%	4.0%	4.0%	2.4%
Furfural	0.1%	0.5%	1.3%	0.8%	0.5%
HMF	0.1%	0.1%	0.2%	0.2%	0.1%
Formic Acid	1.1%	1.6%	1.8%	6.0%	1.6%

Table 6- 8 Sugar partitioning ratios and byproducts produced for all the scenarios (Softwood)

Softwood	Scenario I			Scenario II (Acid) 160°C	Scenario III (Increased Feedstock) 170°C
	160°C	170°C	180°C		
$\alpha$ - Cellulose	2%	4%	5%	6%	4%
Mannans	35%	53%	56%	80%	53%
Xylans	40%	50%	50%	50%	50%
Acetic Acid	0.9%	1.4%	2.3%	2.1%	1.4%
Furfural	0.1%	0.2%	0.5%	0.4%	0.2%
HMF	0.1%	0.2%	0.4%	0.4%	0.2%
Formic Acid	1.7%	1.4%	1.5%	6.0%	1.4%

#### 6.4.5 Acid-hydrolysis and Evaporation

In order to convert all the oligomers to monomers, sulfuric acid was used in the acid-hydrolysis stage. It is assumed that all the oligomers can be successfully converted to monomers. The conditions for the acid-hydrolysis in this process modeling are: 4% sulfuric acid concentration, 122 °C, for 1 hour. The 160 psig fresh steam will be charged into this process to achieve the target temperature. Since sulfuric acid is a rather expensive chemical, the large amount of water present in the system from the previous stage could result in a huge amount of sulfuric acid consumption, in turn, will cause an unsuccessful investment. One

way to reduce the sulfuric acid consumption is to adding a multiple effect evaporation process before the acid-hydrolysis step in terms of removing most of the water. Evaporation will also bring great benefits to the final distillation process, as less energy would be spent in distillation to separate ethanol and water. Table 6-9 shows the general relation between the number of effects and the steam economy.

Table 6- 9 The number of effects vs. steam economy

No. of Effects	Steam Economy*
1	0.9
2	1.7
3	2.5
4	3.2
5	4.0
6	4.5

$$*\text{Steam Economy} = \frac{\text{lb of water evaporated}}{\text{lb of fresh steam}}$$

The multiple effects evaporator in the present analysis has 5 effects, thus, according to the table above, to remove a certain amount of water, one fourth of this amount of fresh steam will be consumed. The concentrated filtrate leaving the evaporation process will be 155 °F and is sent to the following acid-hydrolysis process. Analysis shows that, the evaporation process will save at least 50% of sulfuric acid that will be used in the acid-hydrolysis step, compared with no

evaporator implemented. Generally, the amount of water removed will be set at the 50% level, half of the water present in the filtrate after the screw press will be evaporated. It is not surprising that the percent of water that being removed has a big influence on the overall economics of the process. This is because the more water being removed, the less sulfuric acid will be employed in the later step, thus less cost will be involved. However, it doesn't mean that the more water removed the better, since the steam consumed in the evaporation step will decrease the power output in the end. Moreover, the more water being removed, the higher sugar concentration broth will be sent to the fermentation process. It is beyond the knowledge of the current report to answer how the sugar concentration will affect the fermentation performance. The highest water removal amount was set at the 80% level, which is believed to help improve the economics of the process model.

#### **6.4.6 Ion Exchange**

This process is exclusive to the Scenario II – Acid-catalyzed cooking process. The continuous ion exchange unit employed here is known as an ISEP (NREL, 1999), from Advanced Separation Technology, Inc. (AST), in Lakeland, Florida. Formic acid has even higher price than sulfuric acid. After the prehydrolysis process, significant amount of acetic acid and even more formic acid will be generated, due to the hasher conditions with the acid addition. In a



previous report (NREL, 1999), ion exchange technology was able to remove 100% of sulfuric acid and 88% of acetic acid in the filtrate. It is assumed in the present report that 88% of acetic acid and formic acid will be recovered from the filtrate and some of them will be recycled back to the cooking step as needed. The rest of the formic acid recovered will be sold. A weak base resin was used in this ion exchange method. Ammonia was used to regenerate resins at the level of 1.1 normal per normal of ions removed. Ion exchange will be performed after the screw press but before the evaporation of the prehydrolyzate.

#### **6.4.7 Neutralization**

In the case of acid-catalyzed process, after the ion exchange, evaporation and acid hydrolysis, filtrate is overlimed with calcium oxide to adjust the pH to a suitable level for the fermentation. During this process, calcium oxide will react with water first to form calcium hydroxide, then calcium hydroxide will react with the sulfuric acid present in the filtrate to form calcium sulfate (gypsum), which is a precipitate. Neutralization is also applied in other scenarios after the acid hydrolysis process. The gypsum formed in this process will be distributed among farmers around the facility as a fertilizer.

### 6.4.8 Fermentation

Sugar-rich broth obtained after the neutralization and the separation process will be fed into the fermentation process. During the fermentation, yeast was able to convert sugars to ethanol with carbon dioxide released as a byproduct. The conversion yields and stoichiometry of all the sugars are listed in Table 6-10.

Table 6- 10 Sugar conversion efficiency and stoichiometry in the fermentation process

Sugar	Efficiency	Stoichiometry
$\alpha$ - Cellulose	95%	51%
Mannans	95%	51%
Xylans	95%	51%

### 6.4.9 Distillation

Ethanol as produced via fermentation will have a concentration of 7% ~ 10%, depending on which scenario was used. The final target concentration of the ethanol is 95% in our cases. To accomplish this, a distillation process will be used to remove most of the

water. Two columns were used in the distillation: one to remove dissolved CO<sub>2</sub> and most of the water, another one to concentrate the ethanol to a near azeotropic composition (NREL, 1999).

The steam consumed in the distillation process was calculated based on Figure 6-5 below.

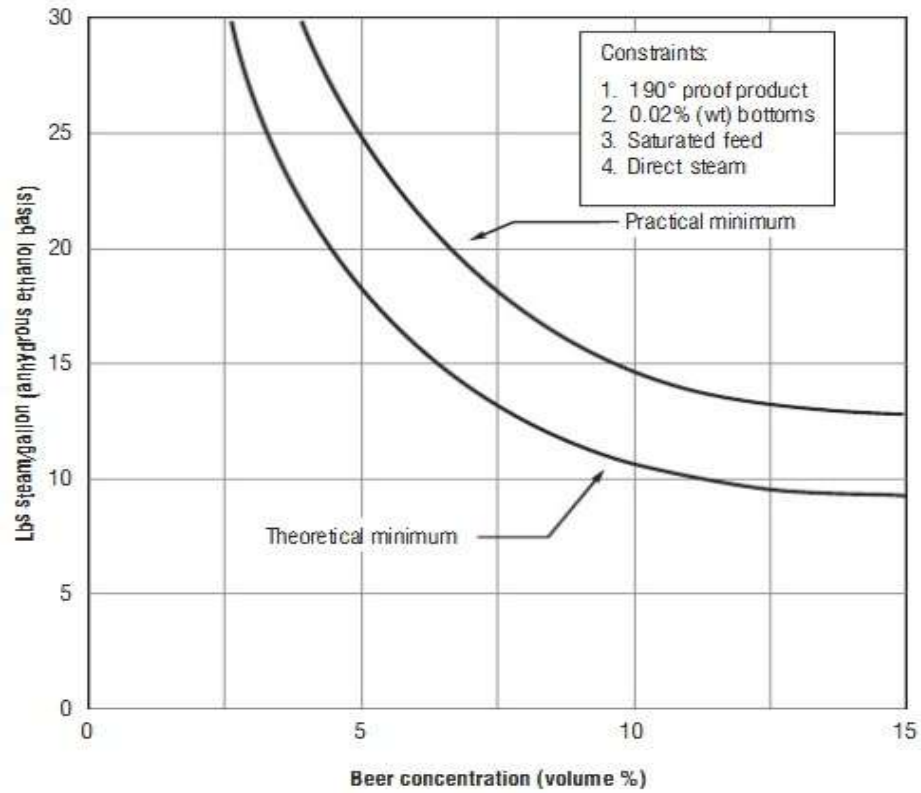


Figure 6- 5 Steam requirements ethanol stripper ( (Jacquies, et al., 2003)

## 6.5 Results and Discussion

### 6.5.1 CAPEX

Capital expenditures for all the scenarios are listed in Appendix II, III and IV. These data are based on the values provided by the Merrick & Company Report (NREL, 1999). We also followed a scaling equation (Robert Wooley, 1999) to adjust equipment costs for all the cases:

$$New\ Cost = Original\ Cost \times \left( \frac{New\ Size}{Original\ Size} \right)^{exp}$$

where *exp* is the scaling factor.

Since the price of all the equipment was based on the value of year 1997, the costs calculated by the above equation were then multiplied by a chemical engineering plant cost index (CEPCI) ratio, to adjust all the costs to 2013, which is the starting year of the process model. The CEPCI for 2013 is assumed to be the same as that is in 2010. Table 6-11 shows the examples of chemical engineering plant cost index value.

Table 6- 11 Chemical Engineering Plant Cost Index (2011)

Chemical Engineering Plant Cost Index (Source: Chemical Engineering Magazine)	
1997	386.5
1998	389.5
1999	390.6
2000	394.1
2001	394.3
2002	395.6
2003	402.0
2004	444.2
2005	468.2
2006	499.6
2007	525.4
2008	575.4
2009	521.9
2010	550.8

To summarize, the total capital expenditures for all the scenarios are showed in Figure 6-6, Figure 6-7 and Figure 6-8.

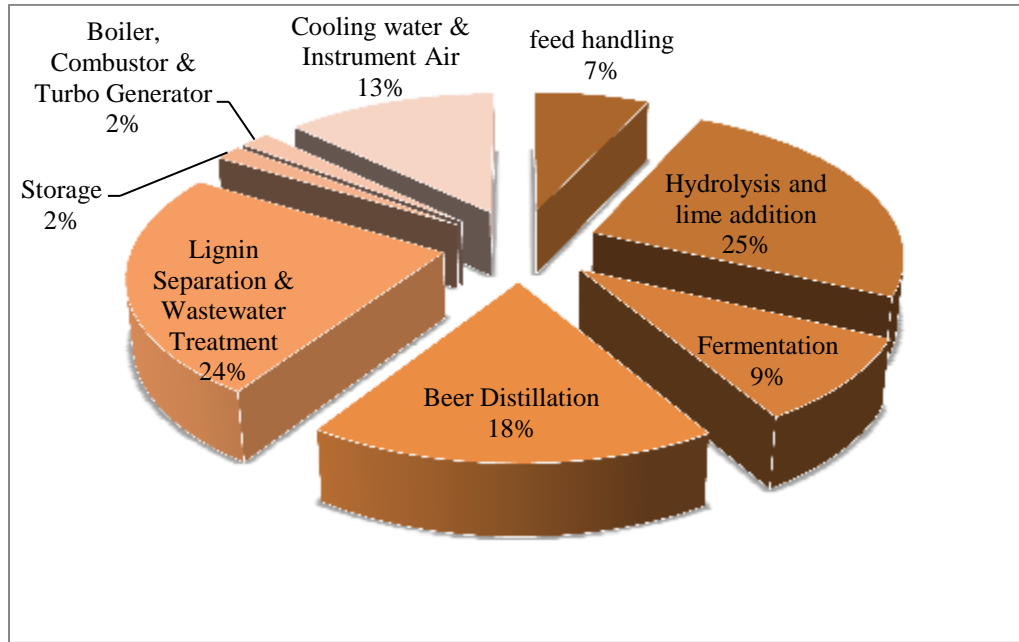


Figure 6- 6 Breakdown of installed equipment cost for Scenario I (Total CAPEX is \$80,000,000).

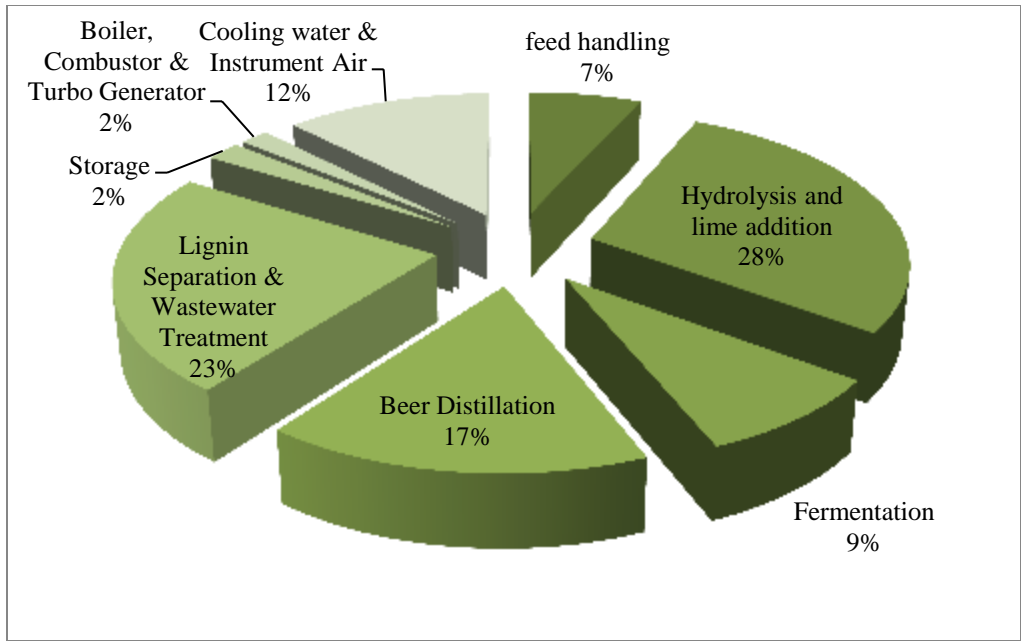


Figure 6- 7 Breakdown of installed equipment cost for Scenario II (Total CAPEX is \$84,000,000).

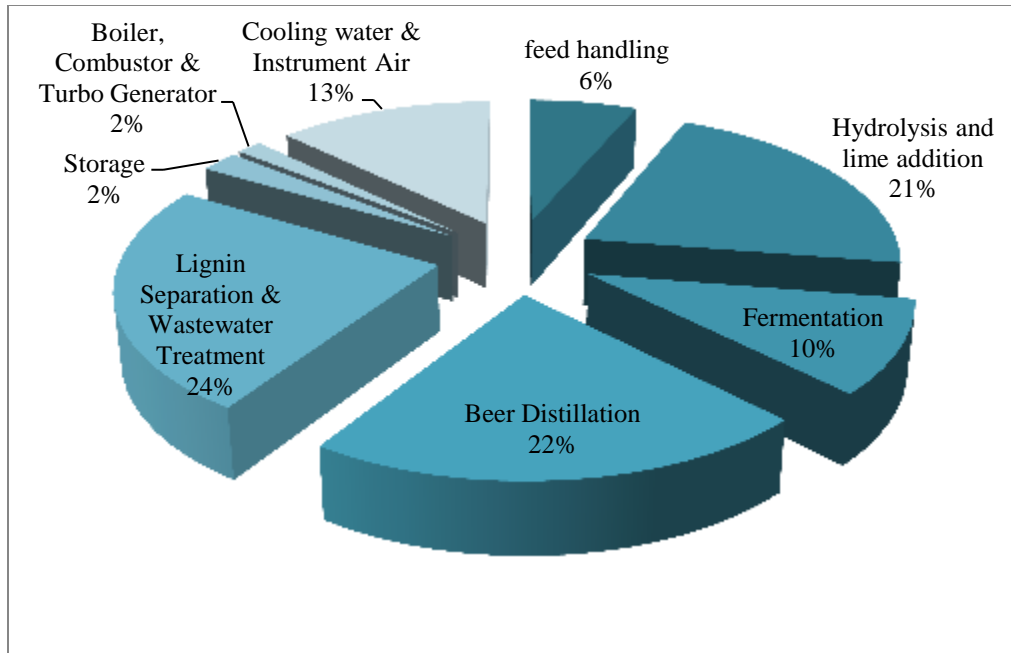


Figure 6- 8 Breakdown of installed equipment cost for Scenario III (Total CAPEX is \$102,000,000).

The total installed equipment costs for each case are \$80,000,000, \$84,000,000, and \$102,000,000, respectively.

### 6.5.2 General Assumptions

Assumptions that closely related to the economic analysis are listed in Table 6-12. All the chemical costs are escalating at 0.5% per year beginning in 2014, except that ethanol selling price is increasing at 3% per year. Power price is increasing at 4%, maintenance cost



and salaries are escalating at 2% per year, beginning in 2014. The ramp up schedule from 2013 for the first three years are 50%, 75%, 100%. The ethanol selling price was assumed based on a \$3 per gallon price. Figure 6-9 shows the historic ethanol and gasoline selling price from 1982 to 2010. The ethanol price enclosed in this graph already included the government subsidies, which is assumed to be \$1.01 per gallon in our cases. \$3 per gallon was finally selected as the ethanol selling price because currently there is a tremendous price increasing tendency for the gasoline price and \$3 per gallon is already competitive with the gasoline price.

Table 6- 12 Major assumptions used in the economic analysis

<b>Hours per year operation</b>	8400	<b>Power price per MWh</b>	\$90
<b>Start year</b>	2013	<b>Ethanol selling price per pound</b>	\$0.46
<b>Years of project life</b>	10	<b>Operating staff at \$45,000</b>	10
<b>Depreciation schedule</b>	7 year MACRS	<b>Supervisory staff at \$65,000</b>	2
<b>Terminal value, year 9 EBITDA X</b>	5	<b>Yeast cost, \$ per liter ethanol</b>	0.02
<b>Maintenance cost, % of initial CAPEX</b>	4	<b>Ammonia, \$ per Ton</b>	200
<b>CAPEX spending schedule</b>		<b>Sulfuric acid, \$ per Ton</b>	440
<b>% of spending in year -2</b>	20	<b>Lime, \$ per Ton</b>	200
<b>% of spending in year -1</b>	40	<b>% of Ethanol to yeast produce</b>	3
<b>% of spending in year 0</b>	40	<b>Wood waste cost, \$ per BDT</b>	65
<b>Overhead Cost, % of sales</b>	3		
<b>Startup cost in 2013</b>	\$ 1,000,000		
<b>Effective tax rate, %</b>	35		
<b>Discount rate of investment, %</b>	12		
<b>Asset value, % of previous year depreciation</b>	15		

### Ethanol and Unleaded Gasoline Rack Prices F.O.B. Omaha, Nebraska, 1982 - 2010

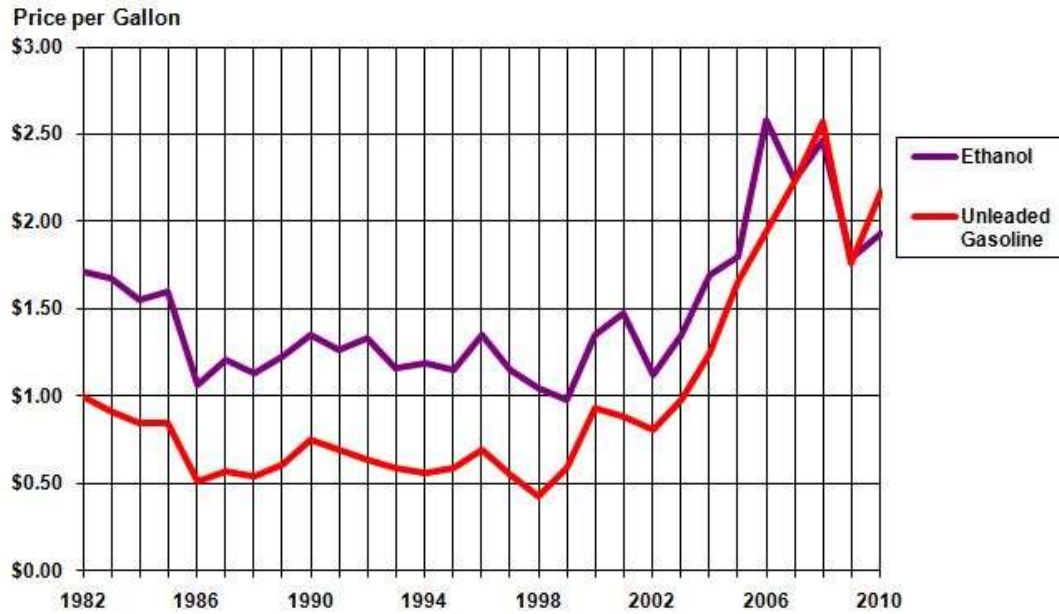


Figure 6- 9 Ethanol and unleaded gasoline rack prices. Source: (Official Nebraska Government Website, May 2011)

### 6.5.3 Financial Indicators

Net present value (NPV) and internal rate of return (IRR) are two important financial indicators for the economic evaluation. “In general, the IRR is the rate that causes the NPV of the project to be zero” (Ross, et al., 2010). Figure 6-10 illustrates the net present value (NPV) for all the scenarios for both softwood and hardwood, all at the discount rate of 12%. None of the scenarios creates a higher NPV compared with the base case, in turn; no

incremental IRR values were obtained for any case. The highest NPV value was obtained by the 1 hour extraction by hot water at 170°C for softwood, among all the scenarios except the base case. Generally, softwood shows better NPV results than hardwood under the same conditions, mainly due to the higher yield of sugars generated. It is also very easy to tell that, in terms of NPV value, the three scenarios have a sequence of scenario I > scenario II > scenario III. This implies us that all the actions that targeted at increasing the sugar yield, for example, to use acid catalyze the reaction and to increase the feedstock input, only produce opposite effect at the cost of remarkable capital cost and operation cost. From the incremental NPV graph (Figure 6-11), the same information as stated above can be obtained.

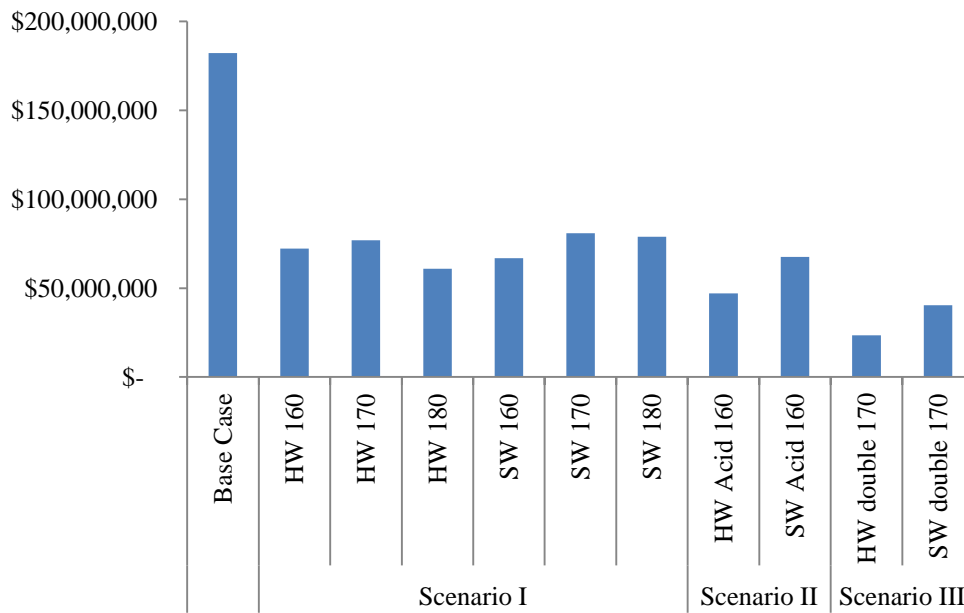


Figure 6- 10 NPV for all the scenarios (at the discount rate of 12%)

Figure 6 -12 shows the lowest ethanol yield and wholesale price in order to get a 12% IRR. Softwood in Scenario II (with acid addition) had the lowest ethanol selling price (\$5.9 per gallon) in order to achieve a 12% IRR. The corresponding ethanol yield in this case was around 13% (based on the original o.d. material), which is more than double of the ethanol yield before matching the IRR to 12%.

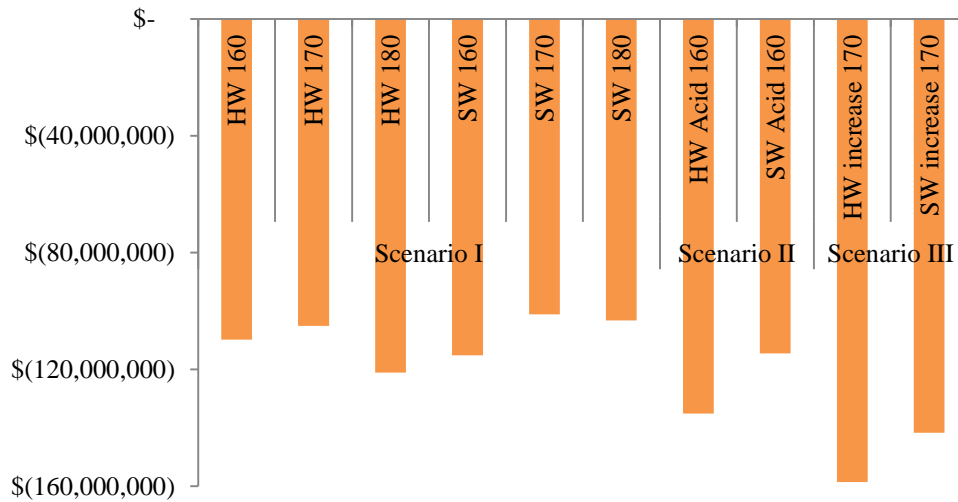


Figure 6- 11 Incremental NPV for all the cases (at the discount rate of 12%)

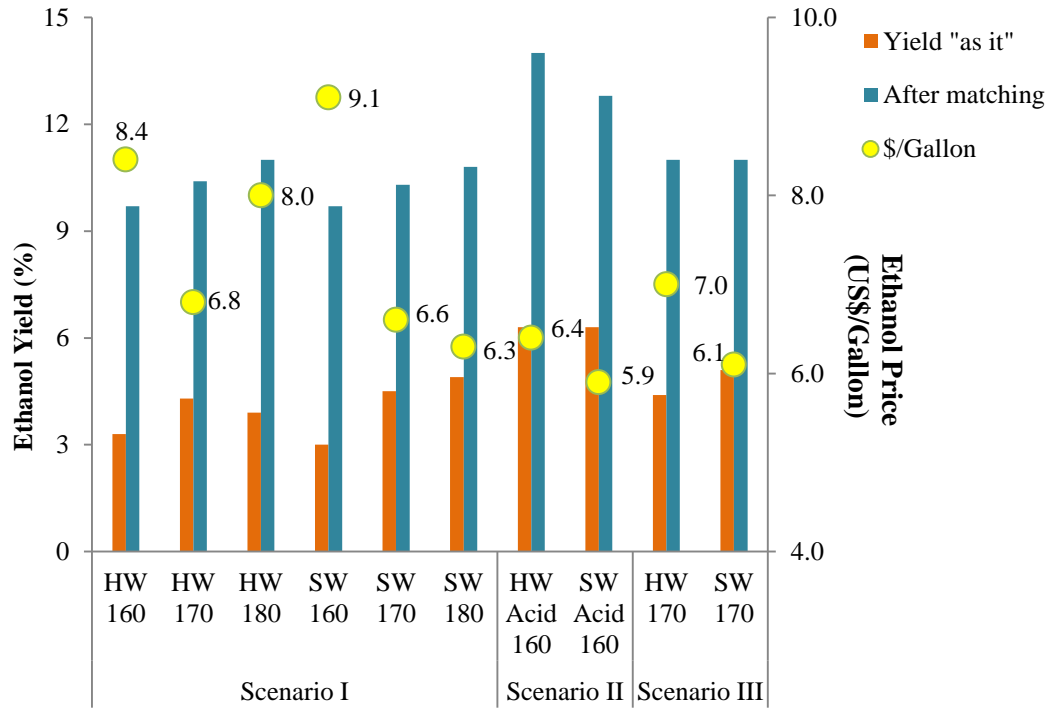


Figure 6- 12 Ethanol yield and wholesale price in order to achieve 12% IRR (Yield “as it” refers to the ethanol yield as simulated in our economic analysis; ethanol yield that “after matching” refers to the target ethanol yield in order to get a 12% IRR)

#### 6.5.4 Sensitivity Analysis

Sensitivity analysis was only performed to the scenario I 170°C, 1 hour for softwood to understand the impact of capital cost, ethanol selling price, power price, sulfuric price and ethanol yield on the economics of the project (Table 6-13). The analysis included +/-25% variations of the central assumptions. From the absolute value of percentage changes of the incremental NPV values shown in Table 6-13, we can conclude that the impacts of the economic parameters on the economics of the project have a sequence of:

Power price > Ethanol selling price > Ethanol yield > Capital cost > sulfuric acid price > Feedstock price

The changes in the feedstock price doesn't have any impact on the incremental NPV value, since the proposed case and the base case both use the same amount of feedstock in scenario I, changes will only be raised in the increased-scale case.

Even though all the scenarios are non-profitable, the results from the sensitivity analysis can provide us some ideas about which economic aspect has the most influence on the economics of scenario I and which has the least.

Table 6- 13 Sensitivity analysis with variation of +/-25% for CAPEX, ethanol selling price, power price, feedstock price, sulfuric acid price and ethanol yield (Scenario I 170°C, 1 hour for softwood)

	Capital cost			Ethanol selling price			Power price			Feedstock price			Sulfuric acid price			Ethanol Yield		
	Cost <sup>a</sup> (\$)	iNPV <sup>a</sup>	± <sup>f</sup> (%)	Price <sup>b</sup> (\$)	iNPV <sup>a</sup>	± (%)	Price <sup>c</sup> (\$)	iNPV <sup>a</sup>	± (%)	Price <sup>d</sup> (\$)	iNPV <sup>a</sup>	± (%)	Price <sup>e</sup> (\$)	iNPV <sup>a</sup>	± (%)	Yield (%)	iNPV <sup>a</sup>	± (%)
<b>+25%</b>	\$101	(\$116)	15%	\$0.57	(\$80)	-21%	\$113	(\$125)	23%	\$81	(\$101)	0%	\$550	(\$106)	5%	6%	(\$82)	19%
<b>0%</b>	\$81	(\$101)	0%	\$0.46	(\$101)	0%	\$90	(\$101)	0%	\$65	(\$101)	0%	\$440	(\$101)	0%	4%	(\$101)	0%
<b>-25%</b>	\$60	(\$86)	-15%	\$0.34	(\$122)	21%	\$68	(\$78)	-23%	\$49	(\$101)	0%	\$330	(\$96)	-5%	3%	(\$121)	-19%

<sup>a</sup>Money unit in million dollars

<sup>b</sup>Dollars per liter

<sup>c</sup>Dollars per MWh

<sup>d</sup>Dollars per BDT

<sup>e</sup>Dollars per Ton

<sup>f</sup>Percentage variation of incremental NPV with ±25% variation of parameters. Shows how sensitive the parameter is, in terms of affecting the incremental NPV.



## 6.6 Conclusions and Recommendations

With the completion of the economic analysis for the VPC technology, real incremental IRR cannot be found in any of the projects. Wood species did show difference in terms of economic performance of the project. In general, softwood shows better economic performance in the prehydrolysis process as a result of the higher sugar yield, which in turn, gives higher overall ethanol yield. As shown in the sensitivity analysis, ethanol yield is one of the most sensitive parameters that will affect the economics significantly.

Even though no incremental IRR value was achieved by the hot-water extraction technology under different temperatures, the NPV results still can indicate that the optimal temperature for both hardwood and softwood treatment is 170 °C.

The goal of the acid-catalyzed treatment was to increase the sugar yield significantly, in turn, to increase the revenue and thus the profitability. However, with the current stage of separation technology and the sky-striking price of related chemicals this will be very difficult to achieve.

Economic feasibility was highly dependent on the power selling price, ethanol selling price, and ethanol yield. It seems that the most prospective way to enhance the feasibility of the VPC technology is to find more cost effective separation method as well as advanced pretreatment to increase the sugar yield.

Finally, one should keep in mind that the current economic analysis was based on an existing power plant. From the investment point of view, another economic analysis on a greenfield ethanol plant can be carried out to compare with the VPC analysis to see if the latter one is a better investment when an ethanol plant is a necessity.

## 6.7 References

Chemical Engineering. - May 2011. - [www.che.com](http://www.che.com).

Amidon Thomas E. (2008) Biorefinery: Conversion of woody biomass to chemicals, energy and materials. *Journal of Biobased Materials and Bioenergy* 2: 100-120.

Ethanol and Unleaded Gasoline Average Rack Prices. Official Nebraska Government Website. May 20, 2011.

<http://www.neo.ne.gov/statshtml/66.html>.

Ethanol fuel in the United States. Wikipedia. May 12, 2011.

[http://en.wikipedia.org/wiki/Ethanol\\_fuel\\_in\\_the\\_United\\_States#cite\\_note-RFA1B-](http://en.wikipedia.org/wiki/Ethanol_fuel_in_the_United_States#cite_note-RFA1B-)

28

Gnansounou E., Dauriat A. and Wyman C.E. (2005) Refining sweet sorghum to ethanol and sugar: economic trade-offs in the context of North China. *Bioresource Tehcnology* 96.

Gonzalez Ronalds (2011) Economics of cellulosic ethanol production: green liquor pretreatment for softwood and hardwood, greenfield, and repurpose scenarios. *Bioresources*, 6(3).

- Hahn-Hagerdal B. (2006) Bio-ethanol- the fuel of tomorrow from the residues of today. Trends in Biotechnology, 24.
- Hamelinck Carlo N., Hooijdonk Geertje van and PC Faaij Andre (2005) Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle- and long-term. Biomass and Bioenergy, 28.
- Hess J. Richard, Wright Christopher T. and Kenney Kevin L. (2007) Cellulosic biomass feedstocks and logistics for ethanol production. John Wiley & Sons 1.
- Jacques KA, Lyons TP and Kelsall DR The alcohol textbook (2003). Vol. 4th Edition.
- Leschinsky Moritz, Sixta Herbert and Patt Rudolf (2009) Detailed mass balances of the autohydrolysis of eucalyptus globulus at 170 °C. Bioresources, 4(2).
- Lin Yan and Tanaka Shuzo (2006) Ethanol fermentation from biomass resources: current state and prospects. Appl Microbiol Biotechnol, 69.
- Liu Shijie (2006) From forest biomass to chemicals and energy. Industrial Biotechnology, 113-121.

NREL Softwood biomass to ethanol feasibility study (1999) Aurora : NREL.

Olsson Lisbeth and Hahn-Hagerdal Barbel (1996) Fermentation of lignocellulosic hydrolysates for ethanol production. *Enzyme and Microbial Technology*, 18.

Ragauskas Arthur J. (2006) The path forward for biofuels and biomaterials. *Science*, 484-489.

Robert Wooley Mark Ruth, David Glassner, and John Sheehan (1999) Process design and costing of bioethanol technology: a tool for determining the status and direction of research and development. *Biotechnology Progress*, 15: 794-803.

Ross Stephen A., Westerfield Randolph W. and Jaffe Jeffrey *Corporate Finance* (2010). McGraw-Hill/Irwin, Vol. 9th Edition.

Stoutenburg Rosanna M. (2008) Ethanol production from a membrane purified hemicellulosic hydrolysate derived from sugar maple by *pichia stipitis* NRRL Y-7124. *Bioresources*, 3(4).

Taherzadeh Mohammad J. and Karimi Keikhosro (2007) Acid-based hydrolysis processes for ethanol from lignocellulosic materials: a review. *Bioresources*, 2(3).

Taherzadeh Mohammad J. and Karimi Keikhosro (2008) Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: a review. *International Journal of Molecular Sciences*, 9.

Tyner Wallace E. (2007) BioEnergy-Fueling America through renewable resources. Purdue Extension, Purdue University, January:

<http://www.extension.purdue.edu/extmedia/ID/ID-342-W.pdf>.

Wooley Robert (1999) Process design and costing of bioethanol technology: a tool for determining the status and direction of research and development. *Biotechnology Progress*, 15: 794-803.

Wyman Charles E. (1999) Biomass ethanol: technical progress, opportunities, and commercial challenges. *Annu. Rev. Energy Environ.*, 24.

## CHAPTER 7: OVERALL CONCLUSIONS

Auto-hydrolysis of mixed hardwood chips and mixed softwood chips by using different conditions were carried out to study their performance of extracting hemicelluloses and how much heating value can be recovered after the extraction. These studies provided practical data for further economic analysis of combining bioethanol production from lignocellulosic materials with power generation, based on both greenfield and integration with an existing power plant. A further study of prehydrolysis by adding acid into the system was also employed, with the purpose of increasing the sugar yield. The effect of auto-hydrolysis and acid-catalyzed prehydrolysis on the performance of enzymatic hydrolysis of the solid residues after extraction was also studied. The overall conclusion of the study is summarized below.

The hot-water extraction of mixed hardwood was carried out from 150 °C to 180 °C, with 1 and 2 hours residence time. By examining the solid content in both the extraction liquid and solid residues, a significantly greater weight loss was found for the higher temperature and longer reaction time treatments, which correlated to a greater amount of volatile byproducts formed during the extraction process. Acetic acid, furfural, and HMF formed during the hot-water extraction and steadily increased with increasing extraction temperature and reaction

time. There were four “optimal” conditions found for sugar extraction from this mixed hardwood, in terms of different criteria: 180 °C, 1 hour had the highest mono-sugars (6.00 grams) in the filtrate without acid hydrolysis treatment; 160 °C, 2 hours had the highest sugar monomers after breaking down all the oligo-sugars to mono-sugars (9.96 grams); 170 °C, 2 hours resulted in the highest yield of sugar per unit of solid in the extract (68.6%); and 160 °C, 1 hour ended up with the highest sugar yield per unit of solid that supposed to be dissolved in the filtrate (44.7%). Xylose had the highest yield out of all extracted sugars. Xylose was primarily extracted in its oligomer-sugar form. The composition analysis of the solid residues verified that most of the hemicelluloses were effectively extracted into the liquid, while the cellulose remained in the residue. As the extraction temperature increased, more material was dissolved, leaving higher proportions of lignin in the residues and thus higher heating values of the residues. The total energy that could be recovered in the residue after the hot-water extraction was approximately 75% after extraction of the hemicelluloses.

By carrying out auto-hydrolysis of mixed softwood chips from 150 °C to 180 °C, for 1 hour and 2 hours, hemicellulose was selectively extracted into the hydrolyzate with different sugar yields and byproducts, depending on the reaction condition applied. Higher temperature and longer residence times were favorable for maximizing the solid dissolved into the liquid phase. However, the total solid balance closure for both filtrate and residue was impaired by more



volatiles that were generated under harsher conditions. Similar to the first study, byproducts generated during the hot-water extraction of mixed softwood chips were steadily increasing with increased extraction temperature and reaction time. The higher byproduct generation led to a lower solid recovery yield in the filtrate. The pH value of the filtrate decreased as the temperature and reaction time increased. It was very interesting that a linear correlation was found for pH as a function of temperature. The optimal sugar yield was determined to be 170 °C for 2 hours, during which 13 grams of sugar was recovered from the extract out of 100 grams of oven-dried original wood material. Mannose had the highest yield for all extracted sugars. Mannose and galactose were primarily extracted in their polymeric form throughout all the conditions. There was a similar trend determined for the heating value of the solid residues, that is, the more severe the extraction condition, the denser caloric value existed in the solid residue. The total energy that could be recovered in the residue ranged from 85% to 98% after extraction of the hemicelluloses, with lower total energy recovered with increasing temperature and time.

The comparison study of auto-hydrolysis and acid-prehydrolysis of mixed hardwood chips revealed that auto-hydrolysis at 180 °C showed the highest solid removal from the starting material, the highest total byproducts generation (acetic acid, formic acid, furfural and HMF), and the most undesirable mass balance closure. The highest sugar yield (13.5% based on o.d. original material) in the prehydrolyzate was obtained by pretreatment using 6% formic acid at

160°C. Sugar degradation was observed for auto-hydrolysis at 180 °C after 40 min of retention time, in terms of the total sugar yield. Formic acid showed better catalytic ability relative to acetic acid, with regard to the solid removal and the sugar yield in the extract. By introducing acid into the pretreatment process, the amount of byproducts generated into the liquid phase increased significantly. Increasing the acid content from 2% to 6% did not show significant improvement in either the sugar yield or solid removal. The performance of enzymatic hydrolysis of solid residues from each pretreatment can be summarized in the sequence of 180 °C auto-hydrolysis > 160 °C formic acid 6% > acetic acid 6% > formic acid 2% > acetic acid 2% > 160 °C auto-hydrolysis, based on the sugar conversion percentage results. The weight loss measurement of the solid residues after enzymatic hydrolysis confirmed the sugar conversion results from enzymatic hydrolysis, as well as indicated that there were still a small amount of oligo-sugars have not been fully hydrolyzed by enzymes. The mechanical (P.F.I. Mill) treatment of the pulp from each pretreatment solid residue showed an enhancement of enzymatic hydrolysis performance (at least 10% sugar conversion increase relative to no mechanical refining).

By carrying out technical economic evaluation of the VPC technology, it was determined that economic feasibility of this technology was highly dependent on the power selling price, ethanol selling price, and ethanol yield. Under the current technical state of

pretreatment and fermentation, the VPC technology is not economic feasible. It seems that the most prospective way to enhance the feasibility of the VPC technology is to find more cost effective separation method as well as advanced pretreatment to increase the sugar yield. Wood species did show difference in terms of economic performance of the project. In general, softwood shows better economic performance in the prehydrolysis process as a result of the higher sugar yield and more closed mass balance.

## **CHAPTER 8: RECOMMENDED FUTURE WORK**

Even though the economic analysis of integrating a bioethanol plant into a power plant based on the currently accomplished studies is discouraging, there are still a lot of work worth carrying out in order to fulfill the goal of employing sustainable cellulosic material as the raw material for biofuel production.

The study of auto-hydrolysis of mixed hardwood chips at 180 °C shows the maximum sugar yield in the extract occurs at the retention time of 40 min, after that, sugar degradation begins to be observed. It is recommended that to carry out auto-hydrolysis of either softwood or hardwood at 180 °C for only 40 min (or less) instead of 60 min, followed by the enzymatic hydrolysis of the solid residues. The enzymatic hydrolysis of solid residue from auto-hydrolysis of mixed hardwood chips at 180 °C for 1 hour showed the sugar conversion for the resulting residue was about 100%. The combined sugar yield from both the filtrate and the enzymatic hydrolysis was as high as about 90% in this case. It would be interesting to determine by reducing the pretreatment time from 60 min to 40 min, if the performance of the enzymatic hydrolysis of the resulting residue will be impaired.

So far, all the measurements of sugar yield in the filtrate were carried out by using diluted sulfuric acid to break down the oligo-saccharides into mono-saccharides. However, from the economic stand point of view, it is recommended to use enzymatic hydrolysis to carry out all the sugar conversion procedure to determine if the same yield will be obtained.

Moreover, in the practical industrial process, it would be unlikely to perform a thorough washing procedure for the solid residues to wash out all the byproducts that are generated in the pretreatment process. Thus, enzymatic hydrolysis of combined filtrate and solid residue is recommended to study the effect of the combination. It is possible that the overall sugar yield outcome would be impaired somehow, since it is well known that the presence of byproducts in the mixture potentially inhibits the performance of enzymes.

The acid-catalyzed prehydrolysis of mixed hardwood chips demonstrated that the introduction of acids into the pretreatment will improve the sugar yield in the filtrate and enhance the performance of the enzymatic hydrolysis of the resulting solid residues. It is recommended by the present author to carry out a pretreatment by combining the acid addition with the higher temperature (180 °C). It would be interesting to determine what the sugar yield and the enzymatic hydrolysis of the consequential solid residues turn out to be. It is anticipated by the present author that a large amount of byproducts will be generated during this high temperature and acid added pretreatment, which will constrain the performance of enzymatic hydrolysis if a combined solid and liquor is implemented.

Furthermore, if acid is introduced into the pretreatment system with the purpose of increasing the sugar yield and improve the accessibility of enzyme to the solid residue, it will be necessary to look for an efficient way to separate the acid as well as the newly generated acid from the entity of the system, thus, be able to achieve the circulation and reuse of the acids. Current candidates of the separation technology are ultra-filtration, ion exchange, distillation and liquid-liquid extraction.

As described in Chapter 5, all the enzymatic hydrolysis of solid residues were conducted at the consistency of 5%. It is recommended by the present author that to carry out a study of enzymatic hydrolysis with higher substrate consistency, in order to achieve higher concentration of fermentable sugars, and in turn, higher concentration of ethanol, with the purpose of saving energy consumption during the distillation process.

Economic analysis was only performed for bioethanol and power production based on the study of hot-water extraction of mixed hardwood and softwood, which only included the pretreatment of biomass and combustion of the solid residues. With the knowledge of acid-catalyzed prehydrolysis as well as the results of sugar yield from enzymatic hydrolysis of solid residues in the third study (Chapter 5), another economic analysis for an entirely different scheme of process should be performed enclosing both the pretreatment and the enzymatic hydrolysis. Different from the previously proposed process, which generates

both bioethanol and energy, the new process produces only bioethanol by converting the sugars in the liquid filtrate and in the solid residues into ethanol. Lignin that is recovered from the new process will also be converted to energy by combustion.

In the end, all the studies that have been conducted so far represented only the first two steps of the main bioethanol production process (pretreatment of the biomass and/or enzymatic hydrolysis of the solid residue). Fermentation of the sugars that are generated from the previous steps should also be conducted to understand the final yield of ethanol. Currently, the economic analysis of the fermentation process was mainly based on information from literatures as well as assumptions. A sound and convincing conclusion should only be made via rigorous experimental validation.

## **APPENDICES**



## **APENDIX I - CHAPTER 9: Co-Production of Electricity and Ethanol, Economics of Value Prior Combustion**

Paper accepted by Energy Conversion and Management in 2012. “Co-Production of Electricity and Ethanol, Economics of Value Prior Combustion”. Trevor Treasure, Ronalds Gonzalez, Richard Venditti, Yan Pu, Hasan Jameel, Steve Kelley and Jeff Prestemon

### **9.1 Abstract**

A techno-economic analysis of co-producing bioethanol and electricity from mixed southern hardwood and southern yellow pine is presented. Bioethanol is produced by extracting carbohydrates from wood via autohydrolysis, membrane separation of byproducts, enzymatic hydrolysis of extracted oligomers and fermentation to ethanol. The residual solids after autohydrolysis are pressed and burned in a power boiler to generate steam and electricity. A base case scenario of biomass combustion to produce electricity is used as a point of comparison for the co-production alternative cases. For the base case minimum electricity revenue of \$70-\$96/MWh must be realized to achieve a 6%-12% internal rate of return. In the alternative co-production cases the ethanol facility is treated as a separate

business entity that purchases power from the biomass power plant. A minimum ethanol revenue to achieve a 12% internal rate of return was estimated to be \$0.84-\$1.05/liter for hardwood and \$0.74-\$0.85/liter for softwood. Based on current market conditions and an assumed future ethanol selling price of \$0.65/liter the co-production of cellulosic bioethanol and power does not produce financeable returns.

## **9.2 Introduction**

The effective conversion of cellulosic biomass into different forms of energy has been the target for many researchers in the last decades [1-7]. Although several pathways have been developed (biomass to power, lignocellulosic biomass to ethanol, etc.) [1, 2, 5, 8-10], very few technologies meet the key requirements to become commercial: being profitable with current market conditions and environmentally friendly. The success of corn ethanol in the U.S. and sugar cane ethanol in Brazil has been widely discussed [1, 11-14]. Nevertheless, it is important to note that the economics of both processes benefit from the commercialization of byproducts, as well as a continued improvement in the efficiency of the conversion process (efficient conversion of the feedstock into ethanol and different

byproducts) [1, 10, 15]. Production of goods in addition to ethanol from lignocellulosic biomass may increase profitability and reduce investment risks which will attract investors. This paper presents the techno-economic analysis of co-producing cellulosic ethanol and electrical power. This process is accomplished via autohydrolysis and extraction of hemicelluloses (carbohydrate extraction for alcohol production) and burning the residues for power production; a process termed value prior combustion (VPC).

The hot-water extraction process, also known as autohydrolysis, can extract hemicellulose oligomers and monomers (mainly xylo-oligomers with different degrees of polymerization) from wood while leaving other components intact [16-20]. Temperature and reactor residence time are critical parameters to minimize sugar degradation and extraction yield. During hot-water extraction, acids are produced by the hydrolysis of hemicelluloses [18]. These acids, coupled with the dissolution of extractives in the biomass, cause the liquor pH to drop and effectively self-catalyze the hydrolysis process [21]. The sugar degradation products (furfural and hydroxymethylfurfural) are easily volatilized and may result in a loss of yield. The extracted xylose and other hemicellulose sugars can undergo fermentation to ethanol and can be considered a potential renewable resource for bio-based fuels [22, 23]. Although we have focused on fermentation of extracted sugars to produce ethanol,

hemicellulosic sugars can also be used to produce biodegradable plastics and chemicals that are currently derived from petroleum [18, 19, 24]. The residues after hot water extraction can be burned to produce steam and electricity or alternatively can be used as a raw material for wood and paper products.

The aim of this paper is to present the economics of co-producing power and cellulosic ethanol in an integrated process using southern mixed hardwood and southern yellow pine as feedstocks. The economics of standalone power production from biomass in a greenfield plant is explored first and represents a base case analysis. The following economic indicators were determined to gauge the economic performance of the base case and proposed cases: internal rate of return (IRR), net present value (NPV), payback period and minimum power selling price (to achieve a specific internal rate of return). After developing the base case, the proposed case involving biomass autohydrolysis and sugar extraction to produce ethanol while burning the residual solids, was developed and analyzed. The following discussion provides novel information needed to understand the tradeoff between producing power and ethanol in an integrated conversion process.

### **9.3 Materials and Methods**

In order to offer a guide for the information provided in this paper a brief description of each section is presented. The “Feedstock” section provides the chemical composition, moisture content and delivered cost of the raw materials. The “Basis for Evaluation” section establishes the framework for comparison across the paper; defining the base case (power production only) and alternative case (power and ethanol production). The “Proposed Pathway” section describes the integrated process for power and ethanol production in more detail by identifying the major unit operations as well as process conditions. The “Conversion Factors” section deals with wood component yields through autohydrolysis and defines the composition of both extraction liquor and solid residues. Process modeling framework, including software used, inputs, and constraints are presented in the “Process Simulation” section. Within the “Economics Analysis” section, the variables used for the estimation of the economic indicators and the methods to estimate cost drivers are presented.

### 9.3.1 Feedstock

Feedstocks used in this analysis are softwood (southern yellow pine) and hardwood (natural southern mixed hardwood); in the form of forest residues (also called hog fuel). The moisture content estimated for hog fuel was about 40% [25-27]. The average feedstock delivered cost was estimated at \$38.2 per dry short ton (\$42.1 per dry metric ton) for both softwood and hardwood. The estimation of the feedstock delivered cost was based on the cost per green ton [free on board (FOB)] and transportation cost (for an average transportation distance of 40 miles and transportation fee at \$0.13 per green ton per loaded mile) taken from the last eight quarterly publications of Timber Mart-South [28]. This average delivered cost was similar to the price paid for hog fuel in several locations in the Southern U.S. as of the third quarter of 2011 [27]. Though an average price of \$38.2 per dry short ton (BDT) was used, there is an expected distribution of feedstock cost following a Lognorm distribution (Figure 9-1). As Figure 9-1 illustrates, based on the sample data taken from Timber Mart-South, 90% of the values fall in a range between \$21 and \$67.3 per BDT. The distribution model fit was done using the distribution fit function of the @Risk software [29].

The chemical composition of the feedstock (softwood and hardwood) used for this study is a normalized version of compositional analysis data collected in the lab (Table 9-1).

The original compositional analysis was determined at the Department of Forest Biomaterials at North Carolina State University and is explored in greater detail by Pu et al. [21].

Proportional normalization of the feedstock composition was performed to satisfy mass balance constraints within the process model.

Table 9- 1 Chemical composition of softwood and hardwood feedstocks

Component	Hardwood (%)	Softwood (%)
Lignin	27%	29%
Glucan	46%	46%
Hexan	4%	14%
Xylan	19%	7%
Extractives	3%	3%
Ash	1%	1%

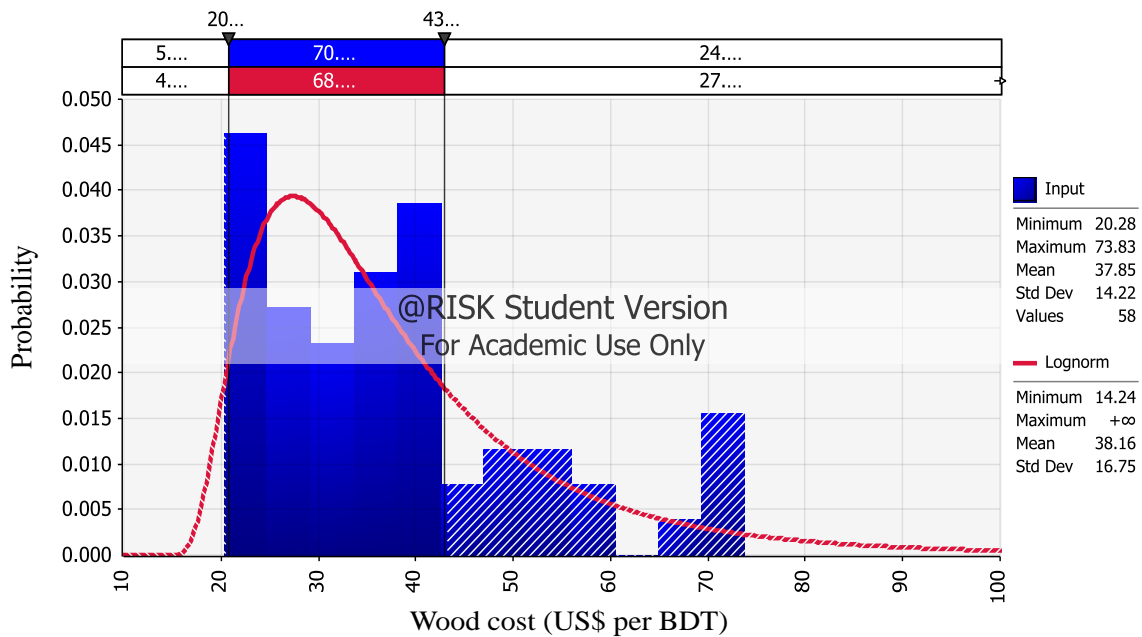


Figure 9- 1 Distribution of feedstock delivered cost in US\$ dollars per BDT, (1 dry metric ton = 1.1023 BDT).

### 9.3.2 Basis for Evaluation

As previously mentioned, this paper presents the economics of an integrated process producing power and ethanol. The economics of standalone power production from biomass is explored first. In an alternative case, power and ethanol are produced in the same facility. For the economic analysis, a greenfield concept was used. Further explanation for each case is presented next.



### **9.3.2.1 Base case**

Power production from biomass is evaluated in the base cases for softwood and hardwood, separately. The conversion process of a greenfield plant was simulated in WinGEMS [30] and the economics in an Excel spreadsheet. An annual input of 500,000 BDT (or 453,592 dry metric tons), is fed into the system to achieve a power production rate of ~72 MWh. The facility was assumed to operate for 350 days per year which results in ~605 GWh of power produced annually.

### **9.3.2.2 Alternative case**

In the alternative case, power and ethanol are co-produced in an integrated plant. The model was built in order to recalculate the amount of feedstock required to produce ~72 MWh. The amount of biomass coming to the facility will be higher than the Base Case because some of the material that was previously being burned to produce electricity is now being converted to ethanol. A total of six alternative cases were evaluated as outlined in Table 9-2. For all the cases, the model estimates the amount of feedstock required to produce 95% of the power capacity (~72 MWh), an additional production capacity of 5% has been assumed for capital investment (CAPEX) estimation. The same excess capacity and additional CAPEX requirement is also assumed in the base case.

Table 9- 2 Alternative cases in power and ethanol production.

Case	I	II	III	IV	V	VI
Feedstock	Hardwood	Hardwood	Hardwood	Softwood	Softwood	Softwood
Autohydrolysis Temperature ( °C)	160	170	180	160	170	180
Reaction time	1 hr	1 hr	1 hr	1 hr	1 hr	1 hr
Product	Power	Power	Power	Power	Power	Power
Co-product	Ethanol	Ethanol	Ethanol	Ethanol	Ethanol	Ethanol

### 9.3.3 Proposed pathway

The proposed pathway for integrated power and cellulosic ethanol production is illustrated in Figure 9-2. Lignocellulosic biomass is fed into the autohydrolysis reactor for 1 hour residence time at the specified temperature (Table 9-2). For all alternative cases, ~13% of the incoming feedstock is assumed to be under/above sized chips and generated saw dust that would not process well in the water hydrolysis reactor and is therefore sent directly to the combustor in the power plant. Thus, 87% of the total feedstock brought into the facility is fed to the water hydrolysis reactor for sugar extraction. After autohydrolysis the slurry is passed through a washing-screw press system to recover dissolved carbohydrates and reduce the moisture content of the solid residue to 40% before it is sent to the combustor for power

generation. In this unit operation it is assumed that 91% of the sugars are recovered in the filtrate for conditioning and fermentation to ethanol during washing and 9% of the dissolved carbohydrates are burned as opposed to being conditioned and fermented to produce ethanol. The filtrate, containing both monomeric and oligomeric carbohydrates as well as dissolved wood solids, is passed through a membrane system to remove undesired products generated during autohydrolysis such as furfural, hydroxymethylfurfural, acetic acid and formic acid. It was assumed that ~90% of the undesired byproducts are removed in the membrane system although laboratory studies have reported higher separation efficiencies [18]. Oligomeric sugars are then hydrolyzed using enzymes. The resulting filtrate (~16% sugar concentration, water removal by means of membrane filtration) is fermented and distilled to ethanol.

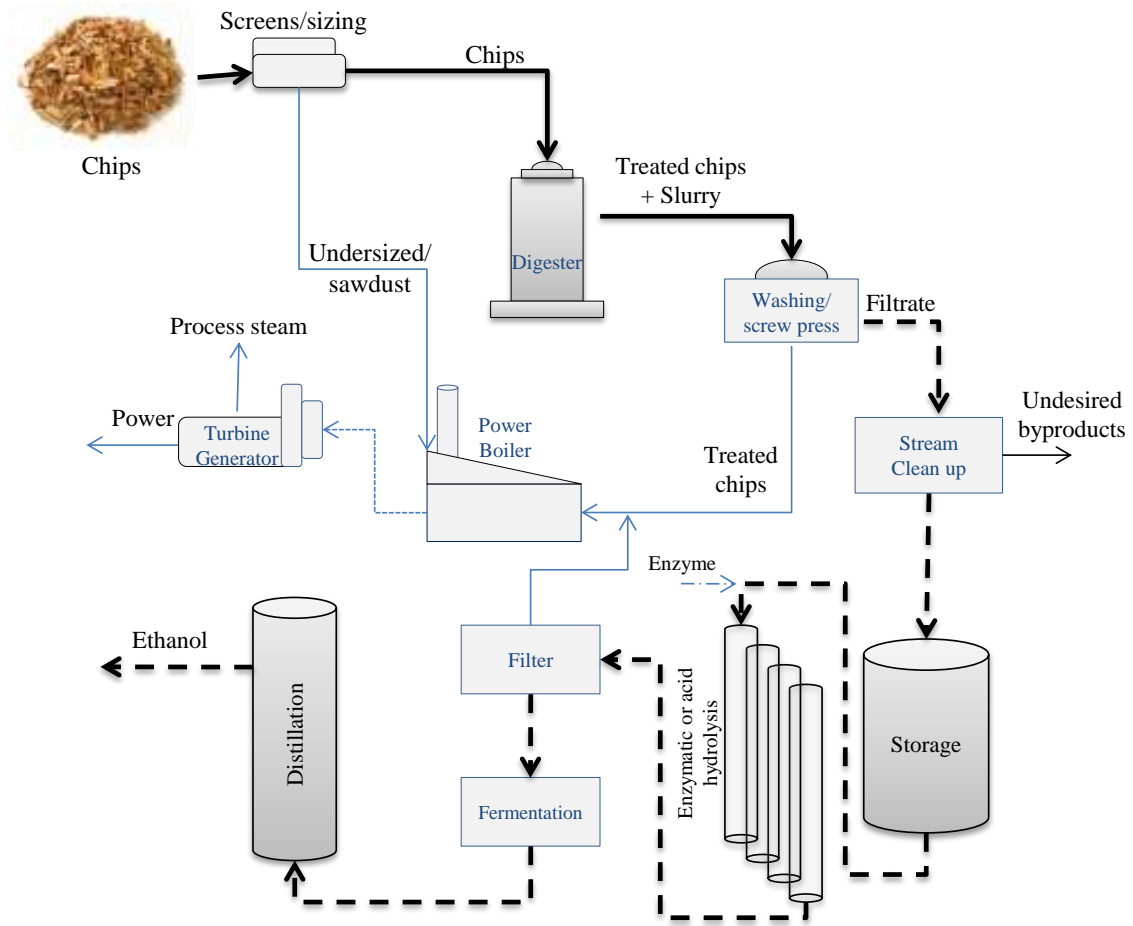


Figure 9- 2 Proposed integrated system for power and cellulosic ethanol production

### 9.3.4 Mass balance of extract and residues

After the autohydrolysis reactions take place, pentose and hexoses are partially extracted into the liquid phase. Degradation of sugars into non-desirable products also occurs

(furfural, hydroxymethylfurfural, acetic acid and formic acid). These products are not desirable because they constitute a yield loss and can inhibit downstream fermentation. As more degradation products are formed the material balance data collected in the lab becomes more open. Presumably this results from volatilization of degradation products. To account for this lack of material balance closure, a “Volatiles” component was incorporated into the dissolved solids stream structure of the process model. Dry matter loss to volatiles for hardwood is larger compared to softwood and increases as temperature increases; as the autohydrolysis temperature increases from 160°C to 180°C the amount of dry hardwood that degrades to a volatile component increases from 6.3% to 17.5% [21]. The complete mass balances for hardwood at 160°C, 170°C and 180°C are illustrated in Table 9-3. The mass balances below are reported on a 1,000 oven dry kg of raw material basis.

The amount of material extracted from hardwood, at all temperatures, was more than softwood. The amount of material degraded to unspecified volatiles is lower for softwood compared to hardwood; as the autohydrolysis temperature for softwood increases from 160°C to 180°C the amount of material converted to volatiles increases from 0% to 5.0% [21]. The complete mass balances for softwood at 160°C, 170°C and 180°C are illustrated in Table 9-4. Again the mass balances have been recreated with an initial starting material of 1,000 kg for illustration purposes.

Table 9- 3 Extract and residues mass balance for hardwood after autohydrolysis

Mass Balance Hardwood			Temperature 160 C		Temperature 170 C		Temperature 180 C	
Starting material 1000 kg (O.D.)								
			Solids		Solids		Solids	
Componet	%	Kg	Componet	Kg	Componet	Kg	Componet	Kg
Lignin	27%	270.0	Lignin	264.6	Lignin	264.6	Lignin	264.6
Glucan	46%	460.0	Glucan	448.9	Glucan	449.0	Glucan	358.4
Hexan	4%	40.0	Hexan	0.0	Hexan	0.0	Hexan	0.0
Xylan	19%	190.0	Xylan	86.8	Xylan	24.2	Xylan	0.0
Extractives	3%	30.0	Extractives	0.0	Extractives	0.0	Extractives	0.0
Ash	1%	10.0	Ash	1.0	Ash	1.0	Ash	1.0
Total		1000.0	Sub total	801.3	Sub total	738.7	Sub total	624.0
			Dissolved solids		Dissolved solids		Dissolved solids	
			Component	Kg	Component	Kg	Component	Kg
			Lignin	5.4	Lignin	5.4	Lignin	5.4
			Glucan	1.9	Glucan	4.3	Glucan	6.8
			Hexan	6.1	Hexan	10.0	Hexan	9.0
			Xylan	3.7	Xylan	19.0	Xylan	29.2
			Extractives	3.0	Extractives	3.0	Extractives	3.0
			Ash	9.0	Ash	9.0	Ash	9.0
			Oligomers	82.6	Oligomers	90.5	Oligomers	65.6
			Acetic Acid	11.0	Acetic Acid	24.0	Acetic Acid	40.0
			Furfural	1.0	Furfural	5.0	Furfural	13.0
			HMF	1.0	HMF	1.0	HMF	2.0
			Formic Acid	11.0	Formic Acid	16.0	Formic Acid	18.0
			Volatiles	63.0	Volatiles	74.0	Volatiles	175.0
			Sub total	198.7	Sub total	261.3	Sub total	376.0
			<b>Total material</b>	<b>1,000.0</b>	<b>Total material</b>	<b>1,000.0</b>	<b>Total material</b>	<b>1,000.0</b>

Table 9- 4 Extract and residues yield for softwood after autohydrolysis (change name dissolve)

Mass Balance Softwood			Temperature 160 C		Temperature 170 C		Temperature 180 C	
Starting material 1000 kg (O.D.)			Solids		Solids		Solids	
Componet	%	Kg	Componet	Kg	Componet	Kg	Componet	Kg
Lignin	29%	290.0	Lignin	284.2	Lignin	284.2	Lignin	284.2
Glucan	46%	460.0	Glucan	448.7	Glucan	440.3	Glucan	434.1
Hexan	14%	140.0	Hexan	68.0	Hexan	39.8	Hexan	11.1
Xylan	7%	70.0	Xylan	40.0	Xylan	23.9	Xylan	16.8
Extractives	3%	30.0	Extractives	27.0	Extractives	7.0	Extractives	0.0
Ash	1%	10.0	Ash	1.0	Ash	1.0	Ash	1.0
Total		1000.0	Sub total	868.9	Sub total	796.2	Sub total	747.2
			Dissolved solids		Dissolved solids		Dissolved solids	
			Component	Kg	Component	Kg	Component	Kg
			Lignin	5.8	Lignin	5.8	Lignin	5.8
			Glucan	1.9	Glucan	9.8	Glucan	19.2
			Hexan	13.6	Hexan	20.1	Hexan	25.2
			Xylan	4.6	Xylan	17.0	Xylan	20.7
			Extractives	3.0	Extractives	3.0	Extractives	3.0
			Ash	9.0	Ash	9.0	Ash	9.0
			Oligomers	66.6	Oligomers	87.7	Oligomers	72.9
			Acetic Acid	8.6	Acetic Acid	14.0	Acetic Acid	23.0
			Furfural	0.9	Furfural	2.0	Furfural	5.0
			HMF	0.9	HMF	1.5	HMF	4.0
			Formic Acid	16.2	Formic Acid	14.0	Formic Acid	15.0
			Volatiles		Volatiles	20.0	Volatiles	50.0
			Sub total	131.1	Sub total	203.8	Sub total	252.8
			<b>Total material</b>	<b>1,000.0</b>	<b>Total material</b>	<b>1,000.0</b>	<b>Total material</b>	<b>1,000.0</b>

### **9.3.5 Process Simulation**

A complete steady-state mass and energy balance process model for the integrated power plant and biorefinery facility was produced using WinGEMS V.5.3 [30]. This process simulation software was originally developed for use in the pulp and paper industry and therefore has specialty blocks and unit operations (solid/liquid handling washing and separation) particularly useful for application in pulp and paper and biorefinery facilities. The simulation results were exported to a Microsoft Excel spreadsheet where it could be referenced for the economic evaluations. Two main simulation models were built: i) the base case where only power was produced and ii) an integrated process where power and alcohol are coproduced and the steam and electrical demands of the alcohol production facility are met by the power plant. Heating value of the feedstock both for the base case and alternative cases was estimated based on its composition (cellulose, hemicellulose, lignin, extractives and ash) following the methodology proposed by Jimenez and Gonzalez (1991) [31].



### **9.3.5.1 Capital investment power plant**

Capital investment for biomass power plants vary greatly depending on the power production capacity and process technology. Capital investment was estimated based on reported values found in the literature (based on dollar per kilowatt), with figures ranging from \$1,500/kw (year 2007) [32], \$3,235/kw (year 2007) [33], \$2,500/kw (year 2009) [34]. Capital investment (CAPEX) for this project was estimated based on a production capacity of 72 MWh (plus an additional 5% for CAPEX estimation). We assumed a CAPEX value of \$2,800 (as 2011) per kW of electricity. The CAPEX was escalated to year 2012, using the civil works construction cost index system of the U.S. Army Corps of Engineers [35]. Total CAPEX (including 2% of indirect costs and 2% of contingency, as well as land) was estimated at \$241.7 million. The value of the land alone was estimated at \$1.1 million. A sensitivity analysis to this estimation is presented in the Results and Discussion.

### **9.3.5.2 Capital investment biorefinery**

Capital investment for the biorefinery plant includes: land purchase, land preparation, raw water treatment, waste water treatment, water hydrolysis extraction, enzymatic hydrolysis, membrane clean up, fermentation, beer column, rectification column, dehydration,

and product storage and shipment) was estimated. This yielded a \$48.9 million investment (as 2012) for an ethanol production capacity of 7 million gallons (26.5 million liters), including 2% of indirect costs and 2% of contingency. The CAPEX of the biorefinery is recalculated for each feedstock and autohydrolysis treatment temperature, so it sizes the CAPEX of the biorefinery depending on the total ethanol output. The estimated CAPEX for the biorefinery complex producing 7 million gallons of ethanol per year (26.5 million liters per year) is presented in Table 9-5. CAPEX for the biorefinery was built based on previous techno-economic reports and by consulting experts [8, 36-38].

Table 9- 5 Capital investment for an ethanol biorefinery producing 7 million gallons per year (Softwood 170 °C). Source: [8, 36-38]

Area	Greenfield (US\$)
Land purchase	36,953
Land preparation	1,011,525
Raw water treatment	433,417
Waste water treatment	650,126
Hydrolysis	18,584,406
Enzymatic hydrolysis	11,533,420
Membrane clean up	3,921,363
Fermentation	5,630,195
Beer column	1,278,155
Rectification column	1,186,793
Dehydration	1,165,117
Product storage and shipment	1,658,609
<b>Total</b>	<b>47,090,080</b>

### 9.3.6 Economic Analysis

The major cost drivers and assumptions are listed for the economic analysis of the base and alternative case in Table 9-6 and Table 9-7.

Table 9- 6 Power plant assumption

Description	Value
Feedstock supply, BDT/year	500,000
Startup Year	2013
Terminal Year	2027
% of CAPEX spending in Year -2	30%
% of CAPEX spending in Year -1	50%
% of Spending in Year 0	20%
% of Nominal Capacity, Project Year 1	80%
% of Nominal Capacity, Project Year 2	90%
Working Capital Per Cent of Direct Cost	10%
Years Depreciation Schedule	10
Tax Rate, with Tax Loss Carryforward	35%
Discount Rate	6%
Terminal Value, Year 15 EBITDA Multiple	7
Hours per Year	8,400
Biomass Cost, \$ per dry Ton	38.2
Moisture Content %	40%
Hourly and Administrative Staff (Non-Maintenance)	16
Salaried Staff	4
Maintenance Expense,including Labor, % of Replacem	1.0%
Capital Reinvestment, % of Replacement Asset Value	0.5%
Other Fixed Costs, % of Sales	1.0%
Sales and Other Overhead, % of Sales	1.0%

For all cases, the evaluation horizon has been set for 15 years. A terminal value in year 15 of seven times year 15 EBITDA (Earnings Before Interest, Taxes, Depreciation and amortization) was assumed. The discount rate used for the biomass to electricity production case (Table 9-7) was 6%; this was based on the value of the weight average capital costs (WACC) for electric utility companies in the east coast of the U.S. [39] and the market return of “risk free” portfolios (based on the return of U.S. treasury bills) [40]. In the case of ethanol production, a discount rate of 12% has been assumed for this project because this is a technology yet to be demonstrated on commercial scale and this discount rate is consistent with other studies [1, 2, 41, 42]. All costs have been scaled up to year 2012. The analysis has been set to estimate the minimum power or ethanol selling price to achieve a specific rate of return (or discount rate) rather than assuming a price for ethanol (or power). A discussion of how these minimum selling prices compare to current prices found in the market is presented in section 3.9 of this manuscript.

Table 9- 7 Biorefinery assumptions

Description	Value	S	Description	Value	S
Excess wood	Backcalculated		Biomass Cost, \$ per dry Ton	38.2	E
Startup Year	2013	A	Moisture Content, % of Green Ton	40%	E
Terminal Year	2027	A	Enzyme Cost, \$ per Gallon Ethanol	0.20	A
% of Spending in Year -2	30%	E	Yeast Cost, \$ per Gallon Ethanol	0.07	1
% of Spending in Year -1	50%	E	Hourly and Administrative Staff (Non-Maintenance)	21	E
% of Spending in Year 0	20%	E	Salaried Staff	4	E
% of Nominal Capacity, Project Year 1	80%	E	Maintenance Expense,including Labor, % of replacement asset value	1.0%	E
% of Nominal Capacity, Project Year 2	90%	E	Capital Reinvestment, % of Replacement Asset Value	0.5%	E
Excess Material Use in Project Year 1	30%	E	Other Fixed Costs, % of Sales	1.0%	E
Working Capital Per Cent of Direct Cost	10%	E	Sales and Other Overhead, % of Sales	1.0%	E
Years Depreciation Schedule	10	E	Hydrolysis residence time	1h	2
Tax Rate, with Tax Loss Carryforward	35%	E	Sugar loss during washing/screw press	9.1%	E
Discount Rate	12%	A	Filter efficiency	90%	A
Terminal Value, Year 15 EBITDA Multiple	7	A	Fermentation efficiency C5	85%	A
Hours per Year	8,400	A	Fermentation efficiency C6	95%	A

S= Source; A= Assumption; E= Expert consultation [37, 38]; 1= [1] ; 2= [21]

## 9.4 Results and Discussions

In order to understand the tradeoff between producing power and cellulosic ethanol in an integrated process, it is important to review some aspects of stand-alone biomass power production costs, profitability as well as effect of feedstock and moisture content.

### **9.4.1 Power production**

Power production varies depending on the chemical composition and moisture content of the feedstock. In our process simulation, the same annual input of hardwood or softwood at the same moisture content produced slightly different amounts of electricity. An annual supply of 500,000 BDT of softwood produced ~ 73.3 MWh, while the same quantity of hardwood produced ~72.8 MWh, with an efficiency of 22.83% and 22.75% respectively. These values are consistent with other published values [32, 43, 44].

### **9.4.2 Power production costs**

Power production cost using an annual input of 500,000 BDT of softwood (40% moisture content) is presented in Figure 9- 3 (bars show absolute values while pie chart shows percentage values). Major cost drivers are biomass and depreciation (\$34.3 and \$42.2 per MWh) adding up to ~ 88% of total costs. A similar cost structure was observed for hardwood (not shown here). The relative importance of feedstock cost in the total power production cost is one of the major limitations to increase the size of biomass power plants. Higher tonnage input of biomass would require longer feedstock hauling distances and

increased delivered costs. One major handicap of biomass power compared to coal power is the cost of delivered raw material. Coal can be delivered at a cost relatively insensitive to the quantity demanded while biomass becomes increasingly more expensive as more biomass at a single location is demanded.

#### **9.4.3 Minimum selling revenue**

The minimum selling revenue analysis estimates the required minimum whole sale price of electricity to achieve a specific internal rate of return. The minimum revenue of electricity in order to achieve an internal rate of return of 6%, 8%, 10% and 12%, using softwood or hardwood are shown in Figure 9-4. In general, minimum revenue values are lower in softwood because softwood has a slightly higher heating value resulting in more power production per unit biomass. Minimum revenue for softwood ranges from \$70 per MWh (at 6% IRR) to \$95 per MWh (at 12% IRR), while minimum electricity revenue for hardwood ranges from \$71 per MWh (at 6% IRR) to \$96 per MWh (at 12% IRR).

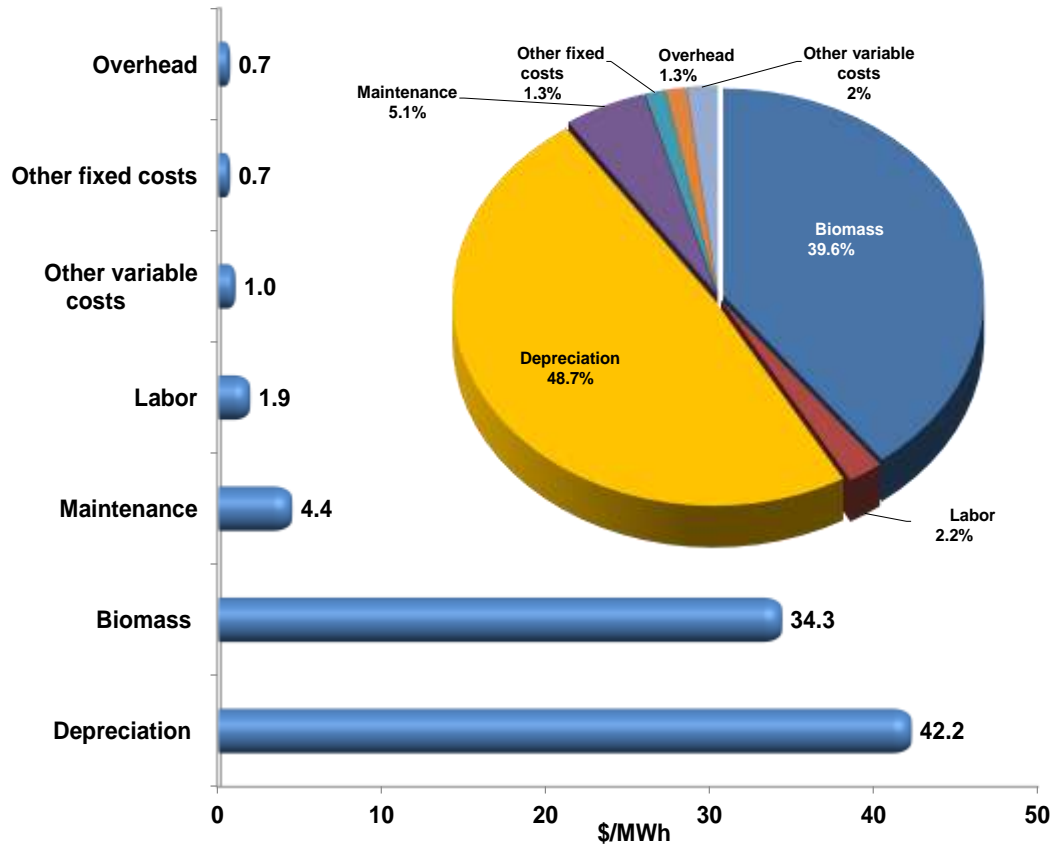


Figure 9- 3 Power production cost using softwood as feedstock

#### 9.4.4 Moisture content effect on power production and minimum wholesale price

One of the major factors influencing biomass to power production efficiency is the moisture content of the feedstock. It is expected that feedstock with lower moisture content



will produce higher energy output compared to feedstock with higher moisture content. Figure 9-5 shows the effect of moisture content on electricity production and minimum electricity revenue (using hardwood as feedstock) to achieve a specific rate of return of 6% and 12%. For this sensitivity analysis a range of 20% to 55% moisture content is presented. As moisture content increases, electricity production (MWh) decreases. Feedstock at 20% moisture content would produce ~79 MWh, while the outcome for feedstock at 55% moisture would be 66.6 MWh. When moisture content is lower and electricity production is higher (20% moisture content), then minimum electricity wholesale revenue is \$65 and \$88 per MWh to achieve 6% and 8% IRR respectively. When moisture content increases by 35%, the minimum whole sale electricity revenue rises to \$78 per MWh (6% IRR).

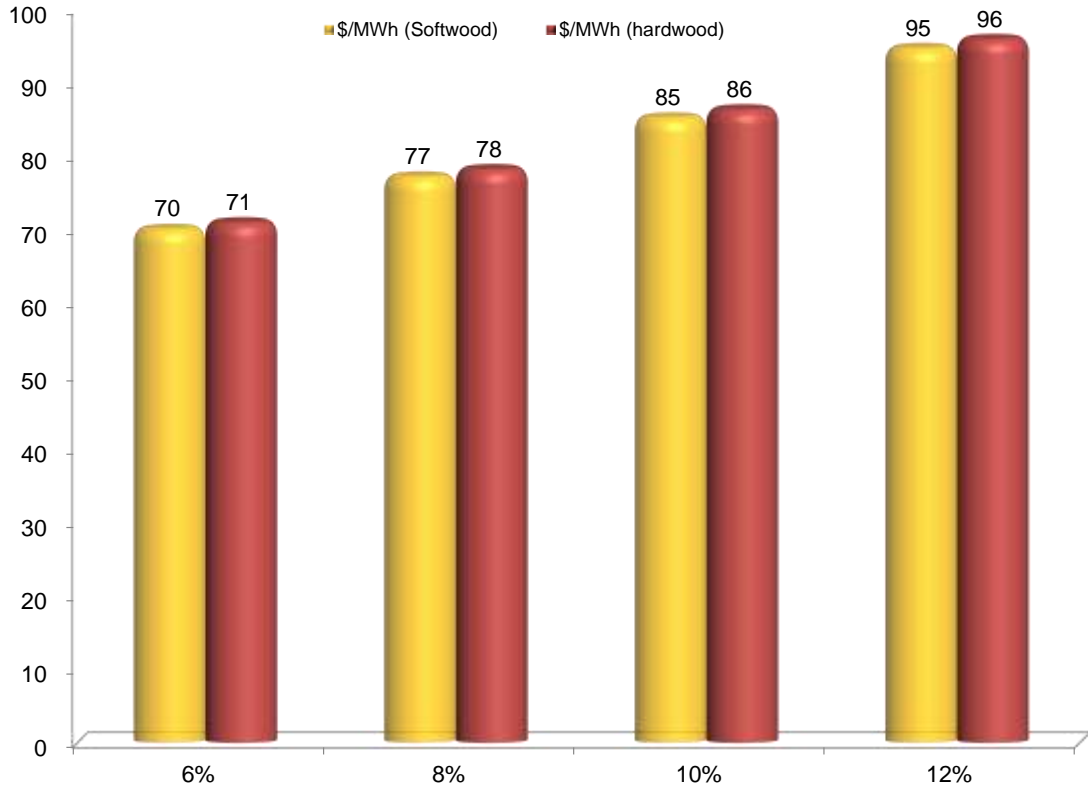


Figure 9- 4 Minimum revenue per MWh of electricity at different values of internal rate of return (IRR)

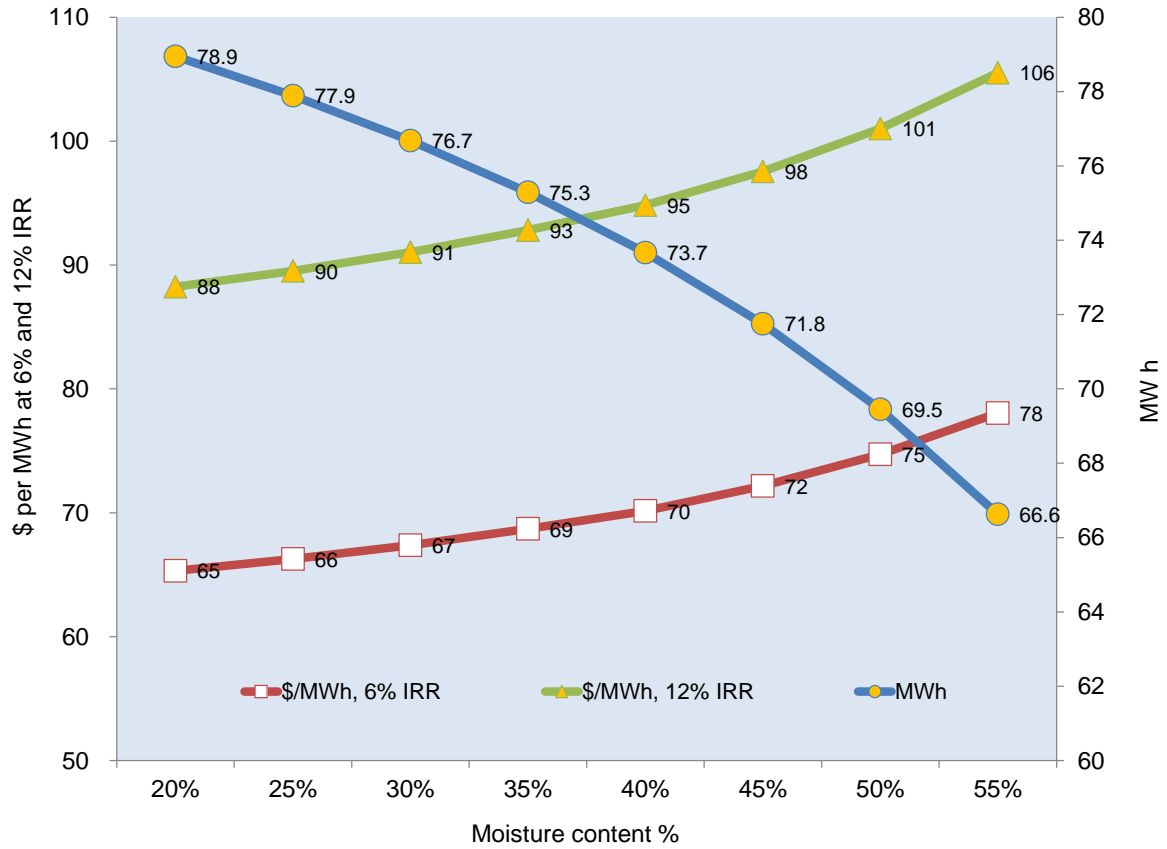


Figure 9- 5 Effect of moisture content on electricity production for 500,000 BDT and minimum revenue (to achieve 6% and 12% IRR).

#### **9.4.5 Ethanol production cost**

Ethanol production costs, minimum ethanol revenue and other economic indicators are analyzed for each of the alternative cases (as listed in Table 9-2). The ethanol production costs for softwood at 170° C are shown in Figure 9-6. The method for distributing production cost for ethanol, specifically for feedstock and energy, is as follows: the model estimated the amount of feedstock required to produce ~72 MWh, all additional wood (additional wood to the base case input of 500,000 BDT per year) was charged to the cost center of ethanol feedstock. Energy cost was estimated from the energy used (by the biorefinery facility), and it was considered as a cost to the biorefinery assuming a cost rate of \$64 per MWh. In other words, the electrical demand of the ethanol production equipment is satisfied by the electricity produced by the biomass power facility and sold at whole sale price. In Figure 9-6 it can be observed that feedstock (35% of production costs), depreciation (26%) and energy (14%) are the major cost drivers accounting for ~75% of total production costs.

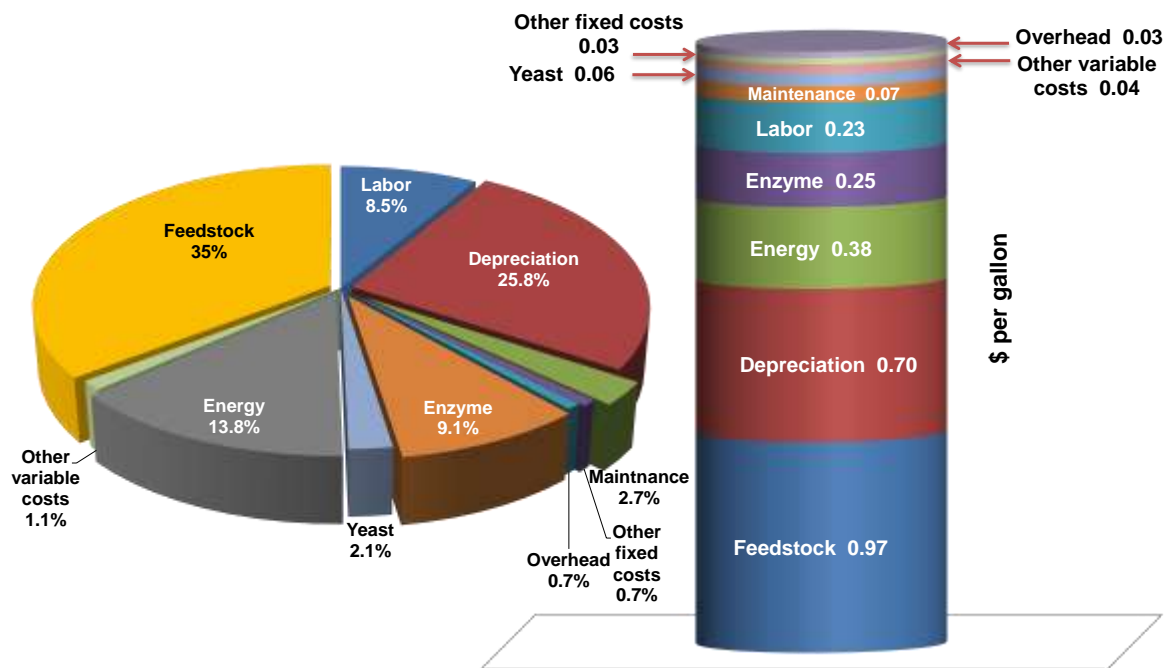


Figure 9- 6 Percentage of ethanol production costs (Softwood 170°C), 1 gallon = 3.785 liters.

The main findings of the economic analysis focus on the interaction between the different extraction conditions, feedstocks and the economic indicators for ethanol production. Figure 9-7 shows additional wood input, ethanol production and total wood sent to the water hydrolysis reactor for sugar extraction (87% of total wood input). The highest ethanol production scenario is observed for softwood at 170 °C (26.6 million liters per year).

Both softwood and hardwood presented the highest ethanol output at 170 °C. Lower additional wood input was found in softwood because the amount of material extracted to produce ethanol is lower at a given temperature compared to hardwood. For the two feedstocks, the additional wood input increases at higher temperature (more material extracted during autohydrolysis) [21]. However, higher extraction rates do not necessarily translate into greater ethanol production because of yield loss to sugar degradation products at higher temperatures. With additional wood input ranging from 118 thousand BDT per year (softwood 160 °C) to 249 thousand BDT per year (Hardwood 180 °C).

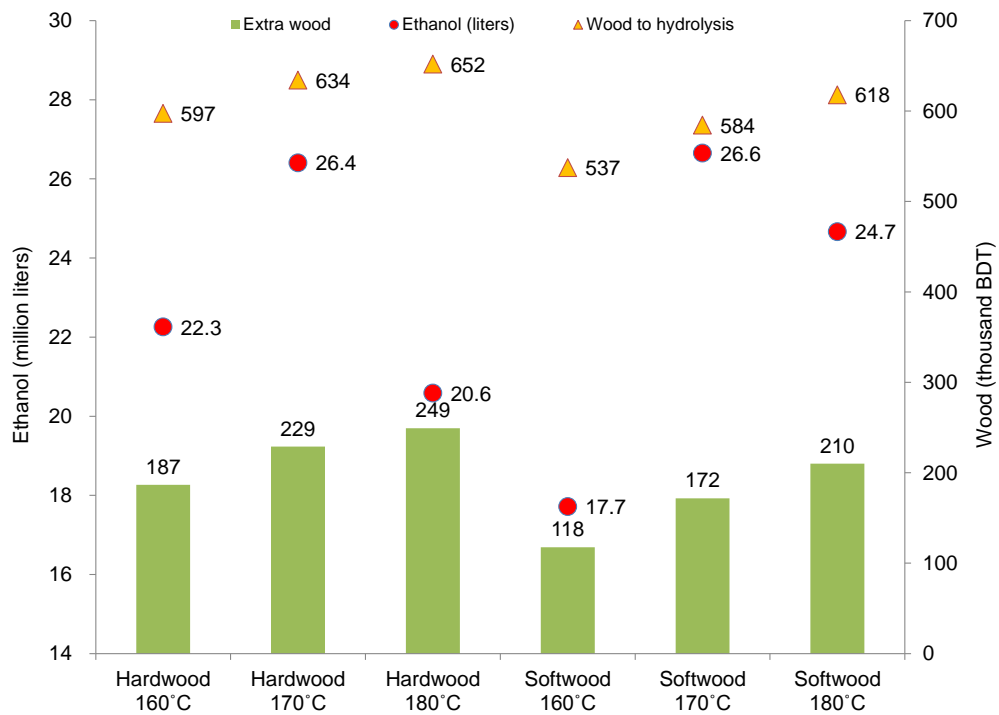


Figure 9- 7 Ethanol production, wood to hydrolysis, excess of wood purchased and total wood input for each autohydrolysis condition

### 9.4.6 Minimum ethanol revenue, cash cost and production cost

Figure 9-8 shows production costs, cash cost and minimum ethanol revenue (estimated to achieve 12% IRR). The lowest production costs, cash costs and minimum ethanol revenue are observed at 170°C for both feedstocks and conditions considered. Overall lower values are observed for softwood, explained by the less sugar degradation to unwanted components, producing more ethanol output and requiring less additional wood input. Minimum ethanol revenue (MER) ranged from ~ \$0.74-1.05 per liter of ethanol (FOB) at plant for the cases considered.

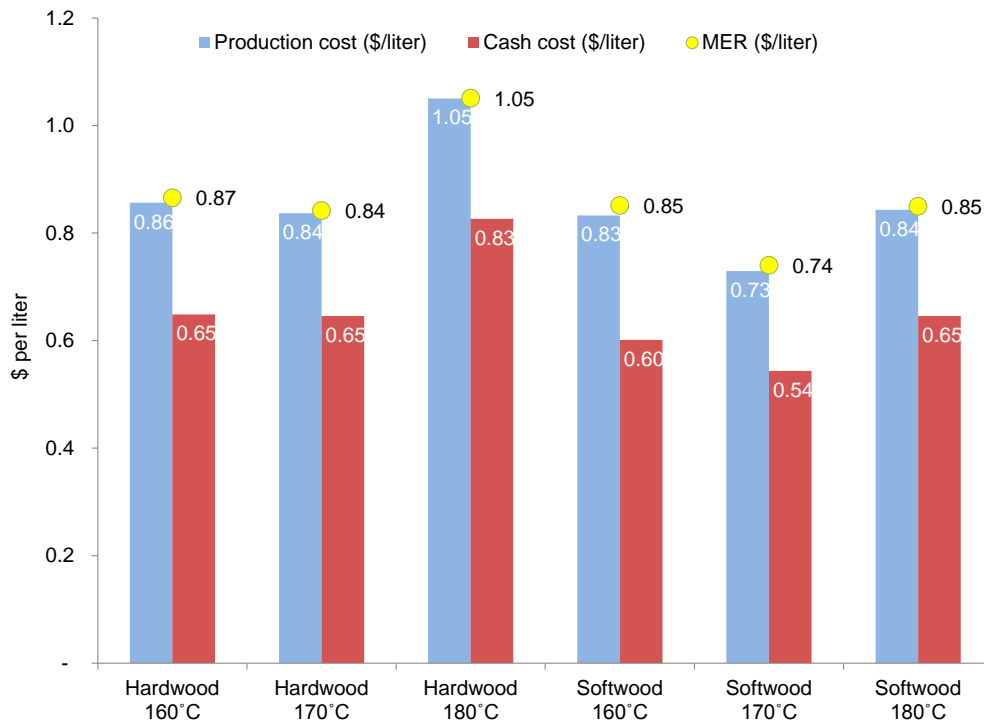


Figure 9- 8 Minimum ethanol revenue (12% IRR), cash cost and production cost for each autohydrolysis condition

#### **9.4.7 Return on investment and payback**

Returns on investment, payback and minimum ethanol revenue were estimated for all cases. Return on investment (ROI) is a popular financial indicator calculated as the ratio between the after tax income with respect to the assets used to generate such revenue in the project. Across the fifteen year evaluation horizon, both feedstocks at 170°C present the higher ROI. Lower ROI was observed for both feedstocks at the highest temperature (180°C). Payback is the time required to offset the initial investments. In other words, it is the time required such that accumulated free cash flow at historical values becomes positive. As expected the lower payback periods are observed in those conditions with lower production costs, cash costs and minimum ethanol revenues, with payback around 9 years (softwood 170°C followed by hardwood 170 °C).

#### **9.4.8 By-products**

As discussed previously, degradation of sugars occurs at elevated temperatures in the presence of acid leading to the formation of byproducts of which furfural; hydroxymethylfurfural, acetic acid and formic acid are the most abundant. Table 9-8 illustrates the amount of these four components recovered after separation from the



hydrolyzate stream (using membranes). More byproducts are produced from hardwoods at a given temperature and more byproducts from a given feedstock as autohydrolysis temperatures increase. No revenue has been considered from these byproducts but they could be purified with additional equipment and sold.

Table 9- 8 Formation of acetic acid, formic acid, furfural and hydroxymethylfurfural for each autohydrolysis condition

Byproducts (ton/year)	Harwdwood 160 C°	Harwdwood 170 C°	Harwdwood 180 C°	Softwood 160 C°	Softwood 170 C°	Softwood 180 C°
Acetic acid	4,486	10,399	17,827	3,132	5,585	9,708
Formic acid	5,098	7,880	9,117	6,723	6,347	7,196
Furfural	463	2,461	6,585	395	906	2,397
Hydroxymethylfurfural	463	492	1,012	395	682	1,918

#### 9.4.9 Sensitivity analysis

A sensitivity analysis describes how the system variables can impact the economic forecast of a project. An analysis of this kind also helps to guide future development to mitigate risk. The response variable chosen to understand sensitivity impact was the minimum ethanol revenue (estimated to achieve a 12% IRR). The sensitivity analysis was built with variation of  $\pm 25\%$  of the central values for CAPEX, ethanol yield, biomass cost and enzyme cost (Figure 9-9).

Yield is the most sensitive variable, followed by biomass cost and CAPEX. In the most favorable case, a 25% increase in yield may drop minimum ethanol revenue to \$0.64 per liter. Reducing feedstock cost and enzyme cost individually by 25% can decrease the minimum ethanol revenue to ~\$0.67 per liter of ethanol.

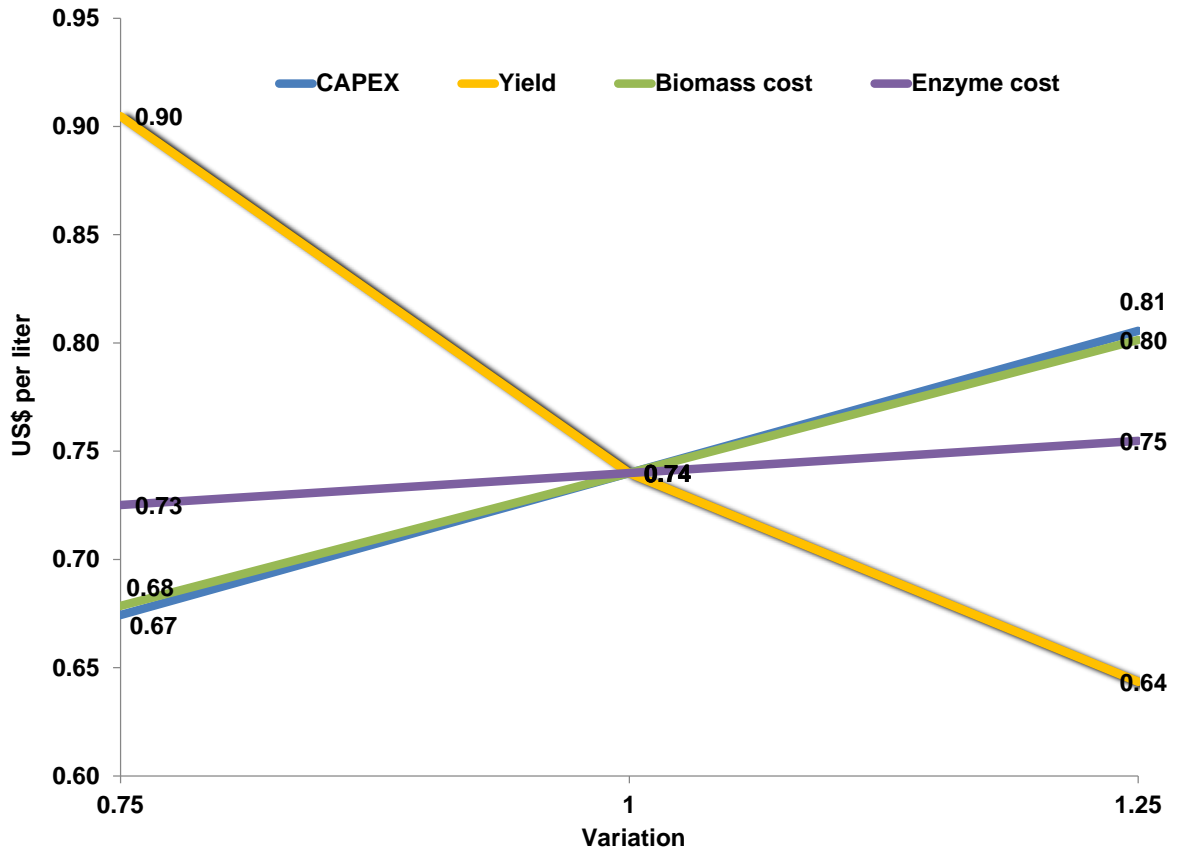


Figure 9- 9 Sensitivity of minimum ethanol revenue (12% IRR) with variation of +/-25% for CAPEX, yield, biomass cost and enzyme cost (Case: Softwood 170°C).

The distribution of ethanol market price in the period between January 2002 and July 2011 is shown in Figure 9-10. The distribution indicates that approximately 20% of the ethanol selling prices fall in the range of \$0.64-\$0.95 per liter. Figure 9-10 illustrates the historic distribution of ethanol rack selling price while Figure 9-11 presents the historic selling price for ethanol and regular gasoline in Omaha, Nebraska, U.S.[45]. Although the selling price for ethanol has increased drastically over the past decade, a reasonable estimate of future ethanol selling price is likely around \$0.60-\$0.70/liter. If a future ethanol selling price of \$0.65/liter is assumed, the technology here outlined to produce bioethanol via autohydrolysis of wood would need to increase the yield of the process by 25% (Figure 9-9) in order to satisfy the risk requirement of 12% IRR. This technology is relatively insensitive to enzyme cost but a reduction of CAPEX and biomass costs are other areas in addition to yield that have potential to improve the financial prospects of a VPC project. Note that the calculated minimum ethanol revenue calculations ranged from \$0.74 to \$1.05 per liter of ethanol for the six cases, indicating that it is not economically feasible under current ethanol prices to pursue VPC.

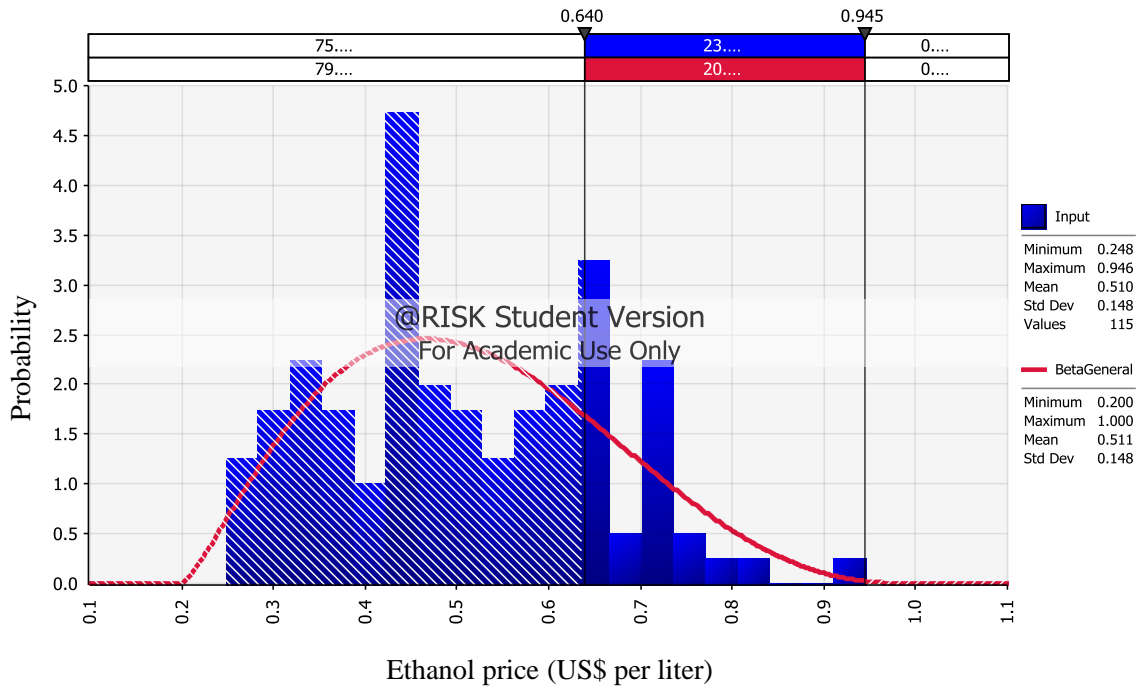


Figure 9- 10 Ethanol price FOB Omaha (Nebraska, U.S.) in the period Jan 2002 – Jul 2011

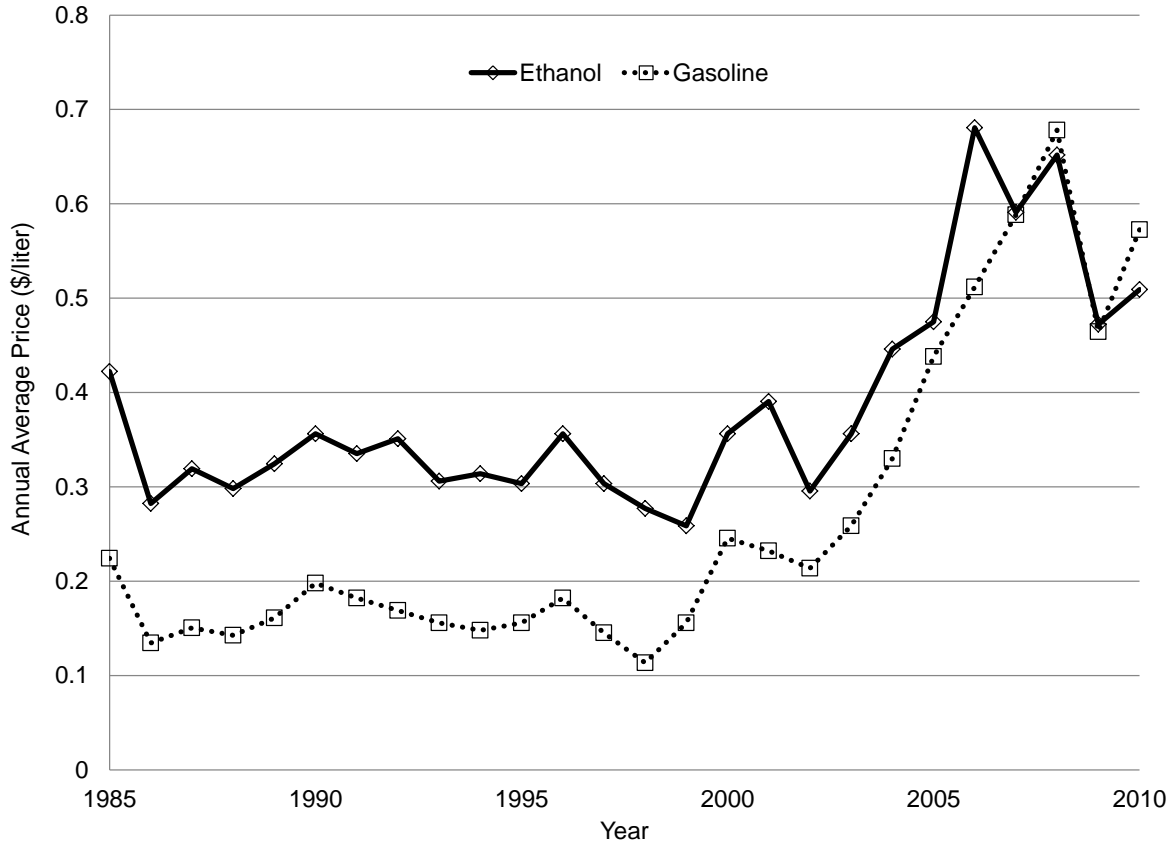


Figure 9- 11 Historic ethanol and regular gasoline price FOB Omaha, Nebraska, U.S.

In order to provide a measure of the probability of failing or success, the probability distribution of the NPV is presented as a function of all operational data and the probability distribution of enzyme cost, feedstock cost, CAPEX and yield. All distributions were fit using @Risk software [29] . The probability distribution of enzyme cost (\$ per liter), CAPEX

and ethanol output (in liters) were modeled following a rectangular distribution based on the assumption of  $\pm 25\%$  with respect to the central assumption listed in the methodology section. These potential sources of variations affect the distribution of the NPV values of the project (Figure 9- 12); the simulation was made with 500 iterations using the simulation modulus of @Risk. For this evaluation, instead of evaluating the minimum revenue per liter of ethanol, a whole selling price of \$0.65 per liter of ethanol is used along with a discount rate of 12%. From the distribution of the NPV listed in Figure 9- 12, now it is possible to assign a percentage of failure or success for the project. It can be observed that only 33% of the distribution of the NPV is above zero, which means that there is probability of 33% to achieve an internal rate of return equal or higher than 12%.

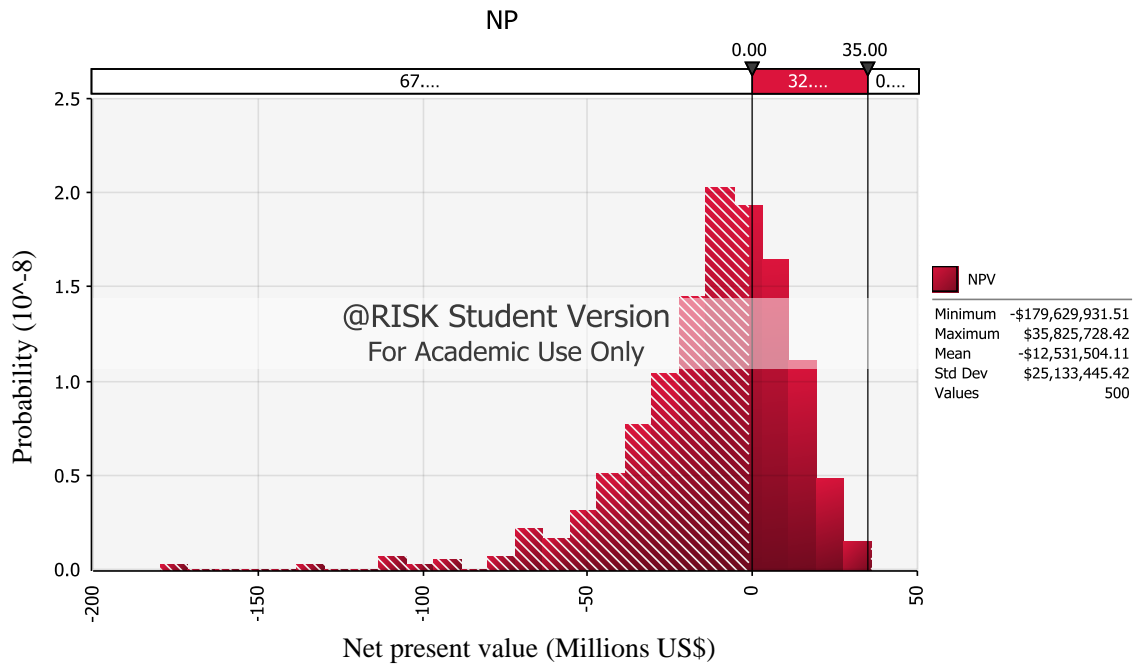


Figure 9- 12 Probability distribution of the NPV value of the project (discount rate 12%).

## 9.5 Conclusions

The concept of VPC (value prior combustion) is technically feasible but the minimum ethanol revenues required to produce a 12% internal rate of return are high enough to discourage investors. Under the current assumptions and scenarios evaluated, the lowest minimum ethanol revenue to achieve a 12% IRR (\$0.74/liter) occurs for softwood at an extraction temperature of 170°C. This revenue requirement is higher than our assumed future ethanol selling price of \$0.65/liter. The base case analysis showed that electrical power from biomass must sell for \$70-\$96/MWh to achieve internal rates of return 6%-12%. The financial performance of this autohydrolysis technology appears to be most sensitive to yield followed by CAPEX and biomass cost. Biomass cost, much like ethanol selling price, is subject to rules of the open market. Therefore, it is suggested that focus be placed on improving yield and reducing CAPEX before this technology can be applied commercially.



## 9.6 References

- [1] R. Gonzalez, T. Treasure, R. Phillips, H. Jameel, D. Saloni. Economics of cellulosic ethanol production: Green liquor pretreatment for softwood and hardwood, greenfield and repurpose scenarios. *BioResources*. 6 (2011) 2551-67.
- [2] R. Gonzalez, T. Treasure, R. Phillips, H. Jameel, D. Saloni, R. Abt, et al. Converting Eucalyptus biomass into ethanol: Financial and sensitivity analysis in a co-current dilute acid process. Part II. *Biomass and Bioenergy*. 35 (2011) 767-72.
- [3] N. Mosier, R. Hendrickson, R. Dreschel, B. Dien, R. Bothast, G. Welch, et al. Principles and Economics of Pretreating Cellulose in Water for Ethanol Production. American Chemical Society National Meeting American Chemical Society. Paper2003.
- [4] N. Mosier, C. Wyman, B. Dale, R. Elander, Y. Lee, M. Holtzapple, et al. Features of promising technologies for pretreatment of lignocellulosic biomass. *Bioresource technology*. 96 (2005) 673-86.
- [5] C. Wyman. Cellulosic ethanol: A unique sustainable liquid transportation fuel. *Material Research Society*. 33. (2008).
- [6] C. Wyman, B. Dale, R. Elander, M. Holtzapple, M. Ladisch, Y. Lee. Coordinated development of leading biomass pretreatment technologies. *Bioresource Technology*. 96 (2005) 1959-66.

- [7] C.E. Wyman. Biomass ethanol: technical progress, opportunities, and commercial challenges. *Annual Review of Energy and the Environment*. 24 (1999) 189-226.
- [8] A. Aden, M. Ruth, K. Ibsen, J. Jechura, K. Neeves, J. Sheehan, et al. Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis and enzymatic hydrolysis for corn stover. NREL. (2002).
- [9] R. Gonzalez, R. Phillips, D. Saloni, H. Jameel, R. Abt, A. Pirraglia, et al. Biomass to energy in the Southern United States: Supply Chain and Delivered Cost. *BioResources*. 6 (2011) 2954-76.
- [10] X. Wu, J. McLaren, R. Madl, D. Wang. Biofuels from Lignocellulosic Biomass. *Sustainable Biotechnology*. (2010) 19-41.
- [11] J. Goldemberg. Ethanol for a sustainable energy future. *Science*. 315 (2007) 808.
- [12] J. Goldemberg, S. Coelho, P. Nastari, O. Lucon. Ethanol learning curve--the Brazilian experience. *Biomass and Bioenergy*. 26 (2004) 301-4.
- [13] D. Pimentel, T.W. Patzek. Ethanol production: energy and economic issues related to US and Brazilian sugarcane. *Biofuels, Solar and Wind as Renewable Energy Systems*. (2008) 357-71.
- [14] P. Gallagher, G. Schamel, H. Shapouri, H. Brubaker. The international competitiveness of the US corn ethanol industry: A comparison with sugar ethanol processing in Brazil. *Agribusiness*. 22 (2006) 109-34.

- [15] RFA. Ethanol, DDGS exports surge. Retrived 10/06/2010. Available from <http://www.ethanolrfa.org/news/entry/ethanol-ddgs-exports-surge/>. 2010.
- [16] M. Leschinsky, H. Sixta, R. Patt. Detailed mass balances of the autohydrolysis of *Eucalyptus globulus* at 170 C. *BioResources*. 4 (2009) 687-703.
- [17] M. Taherzadeh, K. Karimi. Pretreatment of lignocellulosic wastes to improve ethanol and biogas production: a review. *International journal of molecular sciences*. 9 (2008) 1621-51.
- [18] T. Amidon, S. Liu. Water-based woody biorefinery. *Biotechnology advances*. 27 (2009) 542-50.
- [19] T. Amidon, C. Wood, A. Shupe, Y. Wang, M. Graves, S. Liu. Biorefinery: Conversion of woody biomass to chemicals, energy and materials. *Journal of Biobased Materials and Bioenergy*. 2 (2008) 100-20.
- [20] R. White. Effect of lignin content and extractives on the higher heating value of wood. *Wood and fiber science*. 19 (1987) 446-52.
- [21] Y. Pu, T. Treasure, R. Gonzalez, R. Venditti, H. Jameel. Autohydrolysis pretreatment of mixed hardwoods to extract value prior to combustion *BioResources*. 6 (2011).
- [22] J. Hess, C. Wright, K. Kenney. Cellulosic biomass feedstocks and logistics for ethanol production. *Biofuels, Bioproducts and biorefining*. 1 (2007) 181-90.

- [23] R. Stoutenburg, J. Perrotta, T. Amidon, J. Nakas. Ethanol Production from a Membrane Purified Hemicellulosic Hydrolysate Derived from Sugar Maple by *Pichia Stipitis* NRRL Y-7124. *BioResources*. 3 (2008) 1349-58.
- [24] A. Salam, R. Venditti, J. Pawlak, K. El-Tahlawy. Crosslinked hemicellulose citrate-chitosan aerogel foams. *Carbohydrate Polymers*. 84 (2011) 1221-9.
- [25] B. Stanton, J. Eaton, J. Johnson, D. Rice, B. Schuette, B. Moser. Hybrid poplar in the Pacific Northwest: the effects of market-driven management. *Journal of Forestry*. 100 (2002) 28-33.
- [26] J.H. Turnbull. Use of biomass in electric power generation: the California experience. *Biomass and Bioenergy*. 4 (1993) 75-84.
- [27] Confidential. Power production in Southern U.S. Personal information. Southern U.S., 2011.
- [28] TMS. Timber Mart-South Market News Quarterly The Journal of South Timber Market News. 1st Quarter 2011 (2011).
- [29] Palisade. Risk analysis software. @Risk. Palisade Corporation. (2011).
- [30] Metso. Engineering simulation software. WinGEMS 5.3. Palisade Corporation. (2011).
- [31] L. Jimenez, F. Gonzalez. Study of the physical and chemical properties of lignocellulosic residues with a view to the production of fuels. *Fuel*. 70 (1991) 947-50.

- [32] IEA. Biomass for Power Generation and CHP. Retrived 05/26/2011. Available from <http://www.iea.org/techno/essentials3.pdf>. 2007.
- [33] EPRI. Program on Technology Innovation: Integrated Generation Technology Options. Retrived 05/24/2011. Available from [http://www.energync.net/wdocs/2009 Prism MERGE Gen Options Report.pdf](http://www.energync.net/wdocs/2009_Prism_MERGE_Gen_Options_Report.pdf). 2008.
- [34] AOPC. Waste to Energy Initiative. Retrived 5/25/2011. Available from <http://www.slideshare.net/tblconference/renewable-energy-biomass-power-plant-project>. 2009.
- [35] USACE. Civil Works Construction Cost Index System. US Army Corps of Engineers. EM 1110-2-1304. (2000).
- [36] D. Humbird, R. Davis, L. Tao, C. Kinchin, D. Hsu, A. Aden, et al. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol. NREL. NREL/TP-5100-47764. (2011).
- [37] R. Phillips. Kraft pulp mill CAPEX. Confidential2010.
- [38] R. Phillips. Lignin filter. Factored vendor quote. Confidential2010.
- [39] A. Damodaran. Cost of Capital by Sector. Retrived 5/20/2011. Available from [http://pages.stern.nyu.edu/~adamodar/New\\_Home\\_Page/datafile/wacc.htm](http://pages.stern.nyu.edu/~adamodar/New_Home_Page/datafile/wacc.htm). 2011.

- [40] USFRS. Selected interest rates. United States Federal Reserve System. Retrived 5/20/2011. Available from <http://www.federalreserve.gov/releases/H15/update/>. 2011.
- [41] A. Aden, M. Ruth, K. Ibsen, J. Jechura, K. Neeves, J. Sheehan, et al. Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis and enzymatic hydrolysis for corn stover. NREL. NREL/TP-510-3243. (2002).
- [42] W. Frederick, S. Lien, C. Courchene, N. DeMartini, A. Ragauskas, K. Iisa. Co-production of ethanol and cellulose fiber from Southern Pine: A technical and economic assessment. *Biomass and Bioenergy*. 32 (2008) 1293-302.
- [43] NREL. Lessons Learned from Existing Biomass Power Plant. National Renewable Energy Lab. NREL/SR-570-26946. (2000).
- [44] DOE. ABC's of Biopower. Retrived 6/25/2011. Available from [http://www1.eere.energy.gov/biomass/abcs\\_biopower.html](http://www1.eere.energy.gov/biomass/abcs_biopower.html). 2011.
- [45] NEO. Ethanol and unleaded gasoline average rack prices. Official Nebraska Government Website. Retrived 9/26/2011. Available from <http://www.neo.ne.gov/statshtml/66.html>. 2011.

## APENDIX II: Individual Equipment Cost Summary (Scenario I)

Section	Equip. No.	Description	Quantity(Req. & Spares)	1997 Unit cost	Install. Factor	Total cost	1997 Unit Install.	1997 Total Install.	Scaling Factor	Size Ratio	Total cost after scale	Total cost for 2013
A100 Wood chip feed handling	C-101	Chip conveyor to storage	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	C-102	Chip stackers	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	C-103	Reclaim conveyor	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	C-104	Conveyor to screening	1	\$ 240,713	1.75	\$ 240,713	\$ 180,535	\$ 421,248	0.3	1.62	\$ 486,847	\$ 701,235
	C-105	Conveyor to chip silo	1	\$ 209,315	1.75	\$ 209,315	\$ 156,986	\$ 366,301	0.3	1.62	\$ 423,344	\$ 609,768
	C-106	Chip conveyor to process	1	\$ 209,315	1.75	\$ 209,315	\$ 156,986	\$ 366,301	0.3	1.62	\$ 423,344	\$ 609,768
	C-107	Lignin conveyor to BF conveyor	1	\$ 250,000	1.75	\$ 250,000	\$ 187,500	\$ 437,500	0.3	1.62	\$ 505,630	\$ 728,290
	M-101	Truck scale	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	M-102	Truck dumper	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	M-103	Chip receiving hopper	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	M-104	Bulldozer	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	M-105	Tramp iron magnet	1	\$ 8,000	1.75	\$ 8,000	\$ 6,000	\$ 14,000	0	1.62	\$ 14,000	\$ 20,165
	M-106	Air density separation system	1	\$ 86,306	1.75	\$ 86,306	\$ 64,730	\$ 151,036	0.5	1.62	\$ 192,237	\$ 276,891
	M-107	Chip slicer	1	\$ 136,915	1.75	\$ 136,915	\$ 102,686	\$ 239,601	0.6	1.62	\$ 320,035	\$ 460,967
	M-108	Chip silo	1	\$ 383,363	1.75	\$ 383,363	\$ 287,522	\$ 670,885	0.6	1.62	\$ 896,102	\$ 1,290,711
	M-109	Vibrating silo discharger	1	\$ 78,493	1.75	\$ 78,493	\$ 58,870	\$ 137,363	0.3	1.62	\$ 158,754	\$ 228,663
	M-110	Silo discharge feeder	1	\$ 31,397	1.75	\$ 31,397	\$ 23,548	\$ 54,945	0.3	1.62	\$ 63,501	\$ 91,464
	M-111	Belt scale	1	\$ 5,233	1.75	\$ 5,233	\$ 3,925	\$ 9,158	0.3	1.62	\$ 10,584	\$ 15,245
	S-101	Disc scalping screen	1	\$ 26,164	1.75	\$ 26,164	\$ 19,623	\$ 45,787	0.3	1.62	\$ 52,917	\$ 76,220
	S-102	Chip thickness screen	1	\$ 115,123	1.75	\$ 115,123	\$ 86,342	\$ 201,465	0.3	1.62	\$ 232,838	\$ 335,372
	S-103	Chip screen system chutes	1	\$ 54,766	1.75	\$ 54,766	\$ 41,075	\$ 95,841	0.6	1.62	\$ 128,014	\$ 184,387
T-101	Rainwater collection and settling system	1	\$ 21,906	1.75	\$ 21,906	\$ 16,430	\$ 38,336	0.6	1.62	\$ 51,205	\$ 73,753	
<b>Area 100 Total</b>											<b>\$ 5,702,898</b>	

## APENDIX II Continued

Section	Equip. No.	Description	Quantity(Req. & Spares)	1997 Unit cost	Install. Factor	Total cost	1997 Unit Install.	1997 Total Install.	Scaling Factor	Size Ratio	Total cost after scale	Total cost for 2013
A200 Hydrolysis and lime addition	A-206	Sterilization tank agitator	1	\$ 13,497	1.2	\$ 13,497	\$ 2,699	\$ 16,196	0.51	1.62	\$ 20,714	\$ 29,836
	A-209	Overliming tank agitator	1	\$ 16,573	1.3	\$ 16,573	\$ 4,972	\$ 21,545	0.51	1.62	\$ 27,555	\$ 39,689
	C-201	Screw conveyor	1	\$ 10,866	1.3	\$ 10,866	\$ 3,260	\$ 14,126	0.78	1.62	\$ 20,579	\$ 29,642
	C-222	Gypsum conveyor	1	\$ 1,789	1.3	\$ 1,789	\$ 537	\$ 2,326	1	1.62	\$ 3,768	\$ 5,427
	C-225	Lime solids feeder	1	\$ 3,407	1.3	\$ 3,407	\$ 1,022	\$ 4,429	0.6	1.62	\$ 5,916	\$ 8,521
	C-226	Lime conveyor	1	\$ 1,195	1.3	\$ 1,195	\$ 359	\$ 1,554	1	1.62	\$ 2,517	\$ 3,625
	H-201	Fermentation feed cooler	2	\$ 169,550	1.3	\$ 339,100	\$ 50,865	\$ 440,830	1	1.62	\$ 714,145	\$ 1,028,627
	H-202	Fermentation feed chiller	2	\$ 119,554	1.3	\$ 239,108	\$ 35,866	\$ 310,840	1	1.62	\$ 503,561	\$ 725,311
	M-201	Acid impregnator no. 1	2	\$ 350,000	1.3	\$ 700,000	\$ 105,000	\$ 910,000	0	1.62	\$ 910,000	\$ 1,310,730
	M-204	Acid impregnator no. 2	2	\$ 350,000	1.3	\$ 700,000	\$ 105,000	\$ 910,000	0	1.62	\$ 910,000	\$ 1,310,730
	M-224	Lime unloading pit	1	\$ 13,280	1.75	\$ 13,280	\$ 9,960	\$ 23,240	0.71	1.62	\$ 32,733	\$ 47,148
	P-201	Sulfuric acid pump	1	\$ 6,516	2.8	\$ 6,516	\$ 11,729	\$ 18,245	0.79	1.62	\$ 26,709	\$ 38,470
	P-209	Neutralized hydrolyzate slurry pump	1	\$ 16,245	2.8	\$ 16,245	\$ 29,241	\$ 45,486	0.79	1.62	\$ 66,588	\$ 95,911
	P-222	Neutralized hydrolyzate liquid pump	1	\$ 16,673	2.8	\$ 16,673	\$ 30,011	\$ 46,684	0.79	1.62	\$ 68,342	\$ 98,437
	P-223	Pneumatic lime unloader	1	\$ 54,057	1.4	\$ 54,057	\$ 21,623	\$ 75,680	0.5	1.62	\$ 96,325	\$ 138,742
	R-201	First stage hydrolysis reactor	1	\$ 210,430	1.3	\$ 210,430	\$ 63,129	\$ 273,559	0.6	1.62	\$ 365,393	\$ 526,298
	R-202	Second stage hydrolysis reactor	1	\$ 174,230	1.3	\$ 174,230	\$ 52,269	\$ 226,499	0.6	1.62	\$ 302,535	\$ 435,760
	S-201	First stage pre-reactor screw press	1	\$ 1,564,000	1.3	\$ 1,564,000	\$ 469,200	\$ 2,033,200	0	1.62	\$ 2,033,200	\$ 2,928,544
	S-202	Second stage pre-reactor screw press	1	\$ 1,976,000	1.3	\$ 1,976,000	\$ 592,800	\$ 2,568,800	0	1.62	\$ 2,568,800	\$ 3,700,002
	S-203	Inter stage pre-reactor screw press	2	\$ 1,500,000	1.3	\$ 3,000,000	\$ 450,000	\$ 3,900,000	0	1.62	\$ 3,900,000	\$ 5,617,413
	S-205	Avid vent desiccant filter	1	\$ 547	1.6	\$ 547	\$ 328	\$ 875	0.6	1.62	\$ 1,169	\$ 1,684
	S-222	Rotary drum filter	1	\$ 106,645	2	\$ 106,645	\$ 106,645	\$ 213,290	0.39	1.62	\$ 257,443	\$ 370,811
	T-201	Sulfuric acid process storage tank	1	\$ 4,066	1.4	\$ 4,066	\$ 1,626	\$ 5,692	0.71	1.62	\$ 8,018	\$ 11,548
	T-203	Blowdown tank #1	1	\$ 21,557	1.2	\$ 21,557	\$ 4,311	\$ 25,868	0.93	1.62	\$ 40,515	\$ 58,357
	T-204	First stage low pressure flash tank	1	\$ 19,423	2.6	\$ 19,423	\$ 31,077	\$ 50,500	0.93	1.62	\$ 79,093	\$ 113,923
	T-205	Second stage flash tank	1	\$ 13,894	2.5	\$ 13,894	\$ 20,841	\$ 34,735	0.71	1.62	\$ 48,924	\$ 70,468
T-206	Second stage low pressure flash tank	1	\$ 11,432	2.5	\$ 11,432	\$ 17,148	\$ 28,580	0.71	1.62	\$ 40,255	\$ 57,982	
T-209	Overliming tank	1	\$ 55,422	1.4	\$ 55,422	\$ 22,169	\$ 77,591	0.71	1.62	\$ 109,286	\$ 157,412	
T-2220	Lime storage bin	1	\$ 77,726	1.3	\$ 77,726	\$ 23,318	\$ 101,044	0.46	1.62	\$ 126,150	\$ 181,701	
W-203	Inter stage washer	2	\$ 350,000	1.3	\$ 700,000	\$ 105,000	\$ 910,000	0	1.62	\$ 910,000	\$ 1,310,730	
<b>Area 200 Total</b>											<b>\$ 20,453,479</b>	



## APENDIX II Continued

Section	Equip. No.	Description	Quantity(Req. & Spares)	1997 Unit cost	Install. Factor	Total cost	1997 Unit Install.	1997 Total Install.	Scaling Factor	Size Ratio	Total cost after scale	Total cost for 2013
A300 Production Fermentation	A-300	First stage #1 fermentor agitator	2	\$ 19,341	1.4	\$ 38,682	\$ 7,736	\$ 54,155	0.51	1.62	\$ 69,261	\$ 99,761
	A-301	Second stage #1 fermentor agitator	2	\$ 17,249	1.35	\$ 34,498	\$ 6,037	\$ 46,572	0.51	1.62	\$ 59,564	\$ 85,793
	A-302	First stage #2 fermentor agitator	2	\$ 18,804	1.5	\$ 37,608	\$ 9,402	\$ 56,412	0.51	1.62	\$ 72,148	\$ 103,919
	F-300	1st stage fermentor no. 1	1	\$ 294,847	2.8	\$ 294,847	\$ 530,725	\$ 825,572	1	1.62	\$ 1,337,426	\$ 1,926,378
	F-302	1st stage fermentor no. 2	1	\$ 308,815	2.8	\$ 308,815	\$ 555,867	\$ 864,682	1	1.62	\$ 1,400,785	\$ 2,017,638
	H-300	First stage #1 fermentor heat exchanger	1	\$ 426,000	2.8	\$ 426,000	\$ 766,800	\$ 1,192,800	0.78	1.62	\$ 1,737,758	\$ 2,503,001
	H-302	First stage #2 fermentor heat exchanger	1	\$ 9,100	2.8	\$ 9,100	\$ 16,380	\$ 25,480	0.78	1.62	\$ 37,121	\$ 53,468
	H-304	Distillation feed preheater	1	\$ 161,363	1.8	\$ 161,363	\$ 129,090	\$ 290,453	0.83	1.62	\$ 433,485	\$ 624,375
	P-300	First stage #1 fermentor pump	1	\$ 5,574	3	\$ 5,574	\$ 11,148	\$ 16,722	0.79	1.62	\$ 24,480	\$ 35,260
	P-302	First stage #2 fermentor pump	1	\$ 7,086	2.9	\$ 7,086	\$ 13,463	\$ 20,549	0.79	1.62	\$ 30,083	\$ 43,330
	P-304	Yeast recycle pump	1	\$ 7,086	3.5	\$ 7,086	\$ 17,715	\$ 24,801	0.79	1.62	\$ 36,307	\$ 52,295
<b>Area 300 Total</b>											<b>\$ 7,545,217</b>	

## APENDIX II Continued

Section	Equip. No.	Description	Quantity(Req. & Spares)	1997 Unit cost	Install. Factor	Total cost	1997 Unit Install.	1997 Total Install.	Scaling Factor	Size Ratio	Total cost after scale	Total cost for 2013
A500 Beer Distillation, Rectification, and Dehydration	D-501	Beer column	1	\$ 371,000	2.1	\$ 371,000	\$ 408,100	\$ 779,100	0.78	1.62	\$ 1,135,050	\$ 1,634,883
	D-502	Rectification column	1	\$ 242,679	2.1	\$ 242,679	\$ 266,947	\$ 509,626	0.78	1.62	\$ 742,460	\$ 1,069,412
	E-501	1st effect evaporator	2	\$ 214,404	2.1	\$ 428,808	\$ 235,844	\$ 900,497	0.68	1.62	\$ 1,250,122	\$ 1,800,628
	E-502	2nd effect evaporator	1	\$ 214,391	2.1	\$ 214,391	\$ 235,830	\$ 450,221	0.68	1.62	\$ 625,023	\$ 900,260
	E-503	3rd effect evaporator	1	\$ 214,391	2.1	\$ 214,391	\$ 235,830	\$ 450,221	0.68	1.62	\$ 625,023	\$ 900,260
	E-504	4th effect evaporator	1	\$ 214,391	2.1	\$ 214,391	\$ 235,830	\$ 450,221	0.68	1.62	\$ 625,023	\$ 900,260
	E-505	5th effect evaporator	1	\$ 214,391	2.1	\$ 214,391	\$ 235,830	\$ 450,221	0.68	1.62	\$ 625,023	\$ 900,260
	H-501	Reboiler	2	\$ 78,129	2.1	\$ 156,258	\$ 85,942	\$ 328,142	0.68	1.62	\$ 455,546	\$ 656,151
	H-502	Reboiler	2	\$ 13,881	2.1	\$ 27,762	\$ 15,269	\$ 58,300	0.68	1.62	\$ 80,936	\$ 116,577
	H-504	Overhead condenser	2	\$ 4,937	2.1	\$ 9,874	\$ 5,431	\$ 20,735	0.68	1.62	\$ 28,786	\$ 41,462
	H-505	Overhead condenser	2	\$ 42,405	2.1	\$ 84,810	\$ 46,646	\$ 178,101	0.68	1.62	\$ 247,250	\$ 356,130
	H-512	Feed/bottoms exchanger	1	\$ 22,043	2.1	\$ 22,043	\$ 24,247	\$ 46,290	0.68	1.62	\$ 64,263	\$ 92,562
	H-517	Evaporator condenser	2	\$ 59,797	2.1	\$ 119,594	\$ 65,777	\$ 251,147	0.68	1.62	\$ 348,657	\$ 502,193
	M-503	Ethanol dehydration package	1	\$ 1,291,368	1	\$ 1,291,368	\$ -	\$ 1,291,368	0.7	1.62	\$ 1,810,133	\$ 2,607,247
	P-501	Bottoms pump	1	\$ 51,163	2.8	\$ 51,163	\$ 92,093	\$ 143,256	0.79	1.62	\$ 209,716	\$ 302,067
	P-503	Reflux	1	\$ 340	2.8	\$ 340	\$ 612	\$ 952	0.79	1.62	\$ 1,394	\$ 2,007
	P-504	Bottoms pump	1	\$ 4,386	2.8	\$ 4,386	\$ 7,895	\$ 12,281	0.79	1.62	\$ 17,978	\$ 25,895
	P-505	Reflux	1	\$ 4,196	2.8	\$ 4,196	\$ 7,553	\$ 11,749	0.79	1.62	\$ 17,199	\$ 24,773
	P-511	1st effect pump	2	\$ 22,943	2.8	\$ 45,886	\$ 41,297	\$ 128,481	0.79	1.62	\$ 188,085	\$ 270,911
	P-512	2nd effect pump	2	\$ 23,722	2.8	\$ 47,444	\$ 42,700	\$ 132,843	0.79	1.62	\$ 194,472	\$ 280,110
	P-513	3rd effect pump	2	\$ 23,381	2.8	\$ 46,762	\$ 42,086	\$ 130,934	0.79	1.62	\$ 191,676	\$ 276,083
	P-514	4th effect pump	2	\$ 23,381	2.8	\$ 46,762	\$ 42,086	\$ 130,934	0.79	1.62	\$ 191,676	\$ 276,083
	P-515	5th effect pump	2	\$ 23,381	2.8	\$ 46,762	\$ 42,086	\$ 130,934	0.79	1.62	\$ 191,676	\$ 276,083
	P-516	Condensate pump	1	\$ 10,747	2.8	\$ 10,747	\$ 19,345	\$ 30,092	0.79	1.62	\$ 44,052	\$ 63,450
	P-517	Scrubber bottoms pump	1	\$ 1,254	2.8	\$ 1,254	\$ 2,257	\$ 3,511	0.79	1.62	\$ 5,140	\$ 7,404
	T-503	Overhead receiver	1	\$ 1,030	2.1	\$ 1,030	\$ 1,133	\$ 2,163	0.93	1.62	\$ 3,388	\$ 4,880
T-505	Overhead receiver	1	\$ 21,519	2.1	\$ 21,519	\$ 23,671	\$ 45,190	0.72	1.62	\$ 63,958	\$ 92,122	
T-512	CO2 scrubber	1	\$ 50,230	2.1	\$ 50,230	\$ 55,253	\$ 105,483	0.78	1.62	\$ 153,675	\$ 221,348	
<b>Area 500 Total</b>											<b>\$ 14,601,499</b>	

## APENDIX II Continued

Section	Equip. No.	Description	Quantity(Req. & Spares)	1997 Unit cost	Install. Factor	Total cost	1997 Unit Install.	1997 Total Install.	Scaling Factor	Size Ratio	Total cost after scale	Total cost for 2013
A600 Lignin Separation & Wastewater Treatment	A-602	Equalization Basin Agitator	1	\$ 19,894	1.2	\$ 19,894	\$ 3,979	\$ 23,873	0.51	1.62	\$ 30,532	\$ 43,977
	A-608	Anaerobic Digester Agitator	4	\$ 30,300	1.2	\$ 121,200	\$ 6,060	\$ 145,440	0.51	1.62	\$ 186,010	\$ 267,922
	A-608	Aerobic digester aerator	16	\$ 31,250	1.4	\$ 500,000	\$ 12,500	\$ 700,000	1	1.62	\$ 1,134,000	\$ 1,633,371
	A-630	Recycled water tank agitator	1	\$ 3,311	1.3	\$ 3,311	\$ 993	\$ 4,304	0.51	1.62	\$ 5,505	\$ 7,929
	C-601	Lignin wet cake screw	1	\$ 12,456	1.4	\$ 12,456	\$ 4,982	\$ 17,438	0.78	1.62	\$ 25,406	\$ 36,593
	C-614	Aerobic sludge screw	1	\$ 2,466	1.4	\$ 2,466	\$ 986	\$ 3,452	0.78	1.62	\$ 5,030	\$ 7,245
	H-602	Anaerobic digester feed cooler	1	\$ 175,000	2.1	\$ 175,000	\$ 192,500	\$ 367,500	0.68	1.62	\$ 510,185	\$ 734,851
	M-604	Nutrient feed system	1	\$ 31,400	2.58	\$ 31,400	\$ 49,612	\$ 81,012	1	1.62	\$ 131,239	\$ 189,032
	M-606	Biogas handling system	1	\$ 11,702	1.68	\$ 11,702	\$ 7,957	\$ 19,659	0.6	1.62	\$ 26,259	\$ 37,822
	M-612	Filter aid addition system	1	\$ 3,000	1.2	\$ 3,000	\$ 600	\$ 3,600	1	1.62	\$ 5,832	\$ 8,400
	P-602	Anaerobic digester feed pump	2	\$ 6,568	2.8	\$ 13,136	\$ 11,822	\$ 36,781	0.79	1.62	\$ 53,844	\$ 77,555
	P-606	Aerobic digester feed pump	2	\$ 6,179	2.8	\$ 12,358	\$ 11,122	\$ 34,602	0.79	1.62	\$ 50,655	\$ 72,962
	P-608	Aerobic sludge recycle pump	1	\$ 4,686	2.8	\$ 4,686	\$ 8,435	\$ 13,121	0.79	1.62	\$ 19,208	\$ 27,666
	P-610	Aerobic sludge pum	1	\$ 4,686	2.8	\$ 4,686	\$ 8,435	\$ 13,121	0.79	1.62	\$ 19,208	\$ 27,666
	P-611	Aerobic digestion outlet pump	2	\$ 6,157	2.8	\$ 12,314	\$ 11,083	\$ 34,479	0.79	1.62	\$ 50,475	\$ 72,702
	P-614	Sludge filtrate recycle pump	2	\$ 2,568	2.8	\$ 5,136	\$ 4,622	\$ 14,381	0.79	1.62	\$ 21,052	\$ 30,323
	P-616	Treated water pump	2	\$ 6,150	2.8	\$ 12,300	\$ 11,070	\$ 34,440	0.79	1.62	\$ 50,417	\$ 72,619
	P-630	Recycle water pump	2	\$ 738	2.8	\$ 1,476	\$ 1,328	\$ 4,133	0.79	1.62	\$ 6,050	\$ 8,714
	S-600	Bar screen	1	\$ 90,468	1.2	\$ 90,468	\$ 18,094	\$ 108,562	0.6	1.62	\$ 145,006	\$ 208,861
	S-601	Beer columns bottom centrifuge	3	\$ 659,550	1.2	\$ 1,978,650	\$ 131,910	\$ 2,374,380	0.6	1.62	\$ 3,171,460	\$ 4,568,051
	S-614	Aerobic sludge belt filter press	1	\$ 650,223	1.8	\$ 650,223	\$ 520,178	\$ 1,170,401	0.72	1.62	\$ 1,656,478	\$ 2,385,928
	T-602	Equilization basin	1	\$ 245,733	1.42	\$ 245,733	\$ 103,208	\$ 348,941	0.51	1.62	\$ 446,277	\$ 642,801
	T-606	Anaerobic digester	4	\$ 881,081	1.04	\$ 3,524,324	\$ 35,243	\$ 3,665,297	0.51	1.62	\$ 4,687,722	\$ 6,752,017
	T-608	Aerobic digester	1	\$ 635,173	1	\$ 635,173	\$ -	\$ 635,173	1	1.62	\$ 1,028,980	\$ 1,482,104
	T-610	Clarifier	1	\$ 122,335	1.96	\$ 122,335	\$ 117,442	\$ 239,777	0.51	1.62	\$ 306,662	\$ 441,704
	T-630	Recycle water tank	1	\$ 6,146	1.4	\$ 6,146	\$ 2,458	\$ 8,604	0.745	1.62	\$ 12,326	\$ 17,753
	XXX	Flare	1	\$ 13,000	1.58	\$ 13,000	\$ 7,540	\$ 20,540	1	1.62	\$ 33,275	\$ 47,928
											<b>Area 600 Total</b>	<b>\$ 19,904,497</b>

## APENDIX II Continued

Section	Equip. No	Description	Quantity(Req. & Spares)	1997 Unit cost	Install. Factor	Total cost	1997 Unit Install.	1997 Total Install.	Scaling Factor	Size Ratio	Total cost after scale	Total cost for 2013
A700 Storage	A-701	In-line ethanol denaturant mixer	1	\$ 1,202	1	\$ 1,202	\$ -	\$ 1,202	0.48	1.62	\$ 1,515	\$ 2,182
	P-701	Ethanol product pump	2	\$ 3,718	2.8	\$ 7,436	\$ 6,692	\$ 20,821	0.79	1.62	\$ 30,480	\$ 43,902
	P-703	Sulfuric acid pump	1	\$ 5,430	2.8	\$ 5,430	\$ 9,774	\$ 15,204	0.79	1.62	\$ 22,257	\$ 32,059
	P-704	Firewater pump	1	\$ 8,659	2.8	\$ 8,659	\$ 15,586	\$ 24,245	0.79	1.62	\$ 35,493	\$ 51,123
	P-706	Ammonia pump	0	\$ 2,344	2.8	\$ -	\$ -	\$ -	0.79	1.62	\$ -	\$ -
	P-708	Diesel pump	1	\$ 6,100	2.8	\$ 6,100	\$ 10,980	\$ 17,080	0.79	1.62	\$ 25,004	\$ 36,014
	P-710	Gasoline pump	1	\$ 2,118	2.8	\$ 2,118	\$ 3,812	\$ 5,930	0.79	1.62	\$ 8,682	\$ 12,505
	P-720	CSL pump	1	\$ 1,895	2.8	\$ 1,895	\$ 3,411	\$ 5,306	0.79	1.62	\$ 7,768	\$ 11,188
	T-701	Ethanol product storage tank	2	\$ 101,922	1.4	\$ 203,844	\$ 40,769	\$ 285,382	0.85	1.62	\$ 430,045	\$ 619,420
	T-703	Sulfuric acid storage tank	1	\$ 33,094	1.2	\$ 33,094	\$ 6,619	\$ 39,713	0.51	1.62	\$ 50,791	\$ 73,157
	T-704	Firewater storage tank	1	\$ 102,111	1.4	\$ 102,111	\$ 40,844	\$ 142,955	0.85	1.62	\$ 215,421	\$ 310,284
	T-706	Ammonia storage tank	0	\$ 144,058	1.4	\$ -	\$ -	\$ -	0.72	1.62	\$ -	\$ -
	T-708	Diesel storage tank	1	\$ 14,400	1.4	\$ 14,400	\$ 5,760	\$ 20,160	0.51	1.62	\$ 25,784	\$ 37,138
	T-710	Gasoline storage tank	1	\$ 26,739	1.4	\$ 26,739	\$ 10,696	\$ 37,435	0.51	1.62	\$ 47,877	\$ 68,960
	T-720	CSL storage tank	1	\$ 18,975	1.4	\$ 18,975	\$ 7,590	\$ 26,565	0.79	1.62	\$ 38,889	\$ 56,014
	<b>Area 700 Total</b>											<b>\$ 1,353,947</b>

## APENDIX II Continued

Section	Equip. No.	Description	Quantity(Req. & Spares)	1997 Unit cost	Install. Factor	Total cost	1997 Unit Install.	1997 Total Install.	Scalling Factor	Size Ratio	Total cost after scale	Total cost for 2013
A800 Boiler Feed Drying, Combustor & Turbo Generator	H-811	BFW Preheater	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	M-802	Combustion airfan	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	M-803	Fluidized bed combustion reactor	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	M-804	Combustion gas baghouse	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	M-811	Turbine/Generator	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	M-820	Deminerlizer	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	M-822	Condensate Polisher	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	M-830	Hydrazine addition package	1	\$ 11,156	1.4	\$ 11,156	\$ 4,462	\$ 15,618	0.6	1.62	\$ 20,862	\$ 30,048
	M-832	Ammonia addition package	1	\$ 11,156	1.4	\$ 11,156	\$ 4,462	\$ 15,618	0.6	1.62	\$ 20,862	\$ 30,048
	M-834	Phosphate addition package	1	\$ 11,156	1.4	\$ 11,156	\$ 4,462	\$ 15,618	0.6	1.62	\$ 20,862	\$ 30,048
	P-804	Condensate pump	2	\$ 3,395	4	\$ 6,790	\$ 10,185	\$ 27,160	0.79	1.62	\$ 39,760	\$ 57,269
	P-811	Turbine condensate pump	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	P-824	Deaerator feed pump	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	P-826	BFW pump	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	P-828	Blowdown pump	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	P-830	Hydrazine transfer pump	1	\$ 1,042	4	\$ 1,042	\$ 3,126	\$ 4,168	0.79	1.62	\$ 6,102	\$ 8,789
	T-804	Condensate collection tank	1	\$ 3,257	4	\$ 3,257	\$ 9,771	\$ 13,028	0.71	1.62	\$ 18,350	\$ 26,430
	T-824	Condensate surge drum	1	\$ 11,741	3	\$ 11,741	\$ 23,482	\$ 35,223	0.72	1.62	\$ 49,851	\$ 71,804
	T-826	Deaerator	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	T-828	Blowdown flash drum	0	\$ -	0	\$ -	\$ -	\$ -	0	1.62	\$ -	\$ -
	T-830	Hydrazine drum	1	\$ 4,249	4	\$ 4,249	\$ 12,747	\$ 16,996	0.93	1.62	\$ 26,619	\$ 38,341
	Misc. Transformers	1	\$ 250,000	1.5	\$ 250,000	\$ 125,000	\$ 375,000	0	1.62	\$ 375,000	\$ 540,136	
	Misc. Piping	1	\$ 300,000	1.5	\$ 300,000	\$ 150,000	\$ 450,000	0	1.62	\$ 450,000	\$ 648,163	
<b>Area 800 Total</b>											<b>\$ 1,481,076</b>	

## APENDIX II Continued

Section	Equip. No.	Description	Quantity(Req. & Spares)	1997 Unit cost	Install. Factor	Total cost	1997 Unit Install.	1997 Total Install.	Scaling Factor	Size Ratio	Total cost after scale	Total cost for 2013
A1000 Cooling water & Instrument Air	A-1018	Sterilization tank agitator	1	\$ 13,504	1.3	\$ 13,504	\$ 4,051	\$ 17,555	0.51	1.62	\$ 22,452	\$ 32,339
	A-1020	Cleaning tank agitator	1	\$ 13,504	1.3	\$ 13,504	\$ 4,051	\$ 17,555	0.51	1.62	\$ 22,452	\$ 32,339
	H-1010	Water sterilizer	1	\$ 1,501	1.4	\$ 1,501	\$ 600	\$ 2,101	0.68	1.62	\$ 2,917	\$ 4,202
	M-1002	Cooling tower system	1	\$ 814,399	1.2	\$ 814,399	\$ 162,880	\$ 977,279	0.78	1.62	\$ 1,423,771	\$ 2,050,746
	M-1004	Plant air compressor	3	\$ 44,012	1.3	\$ 132,036	\$ 13,204	\$ 171,647	0.34	1.62	\$ 202,242	\$ 291,301
	M-1006	Fermentor air compressor package	3	\$ 380,151	1.3	\$ 1,140,453	\$ 114,045	\$ 1,482,589	0.34	1.62	\$ 1,746,851	\$ 2,516,098
	M-1008	Chilled water package	3	\$ 380,000	1.2	\$ 1,140,000	\$ 76,000	\$ 1,368,000	0.8	1.62	\$ 2,012,325	\$ 2,898,477
	P-1002	Cooling water pump	2	\$ 156,935	2.8	\$ 313,870	\$ 282,483	\$ 878,836	0.79	1.62	\$ 1,286,544	\$ 1,853,090
	P-1010	Sterile water pump	2	\$ 2,101	2.8	\$ 4,202	\$ 3,782	\$ 11,766	0.79	1.62	\$ 17,224	\$ 24,809
	P-1012	Make-up water pump	2	\$ 4,535	2.8	\$ 9,070	\$ 8,163	\$ 25,396	0.79	1.62	\$ 37,178	\$ 53,549
	P-1014	Process water circulating pump	3	\$ 5,188	2.8	\$ 15,564	\$ 9,338	\$ 43,579	0.79	1.62	\$ 63,796	\$ 91,890
	P-1016	CIP/CS supply pump	2	\$ 2,801	2.8	\$ 5,602	\$ 5,042	\$ 15,686	0.79	1.62	\$ 22,962	\$ 33,074
	P-1018	CIP/CS supply pump	2	\$ 2,802	2.8	\$ 5,604	\$ 5,044	\$ 15,691	0.79	1.62	\$ 22,971	\$ 33,086
	S-1004	Instrument air dryer	2	\$ 7,777	1.3	\$ 15,554	\$ 2,333	\$ 20,220	0.6	1.62	\$ 27,008	\$ 38,901
	T-1004	Plant air receiver	1	\$ 6,721	1.3	\$ 6,721	\$ 2,016	\$ 8,737	0.72	1.62	\$ 12,366	\$ 17,811
	T-1005	Instrument air receiver	1	\$ -	0	\$ -	\$ -	\$ -	N/A	1.62	\$ -	\$ -
	T-1010	Process water tank	1	\$ 13,206	1.4	\$ 13,206	\$ 5,282	\$ 18,488	0.71	1.62	\$ 26,041	\$ 37,508
	T-1014	Process water tank	1	\$ 119,645	1.4	\$ 119,645	\$ 47,858	\$ 167,503	0.51	1.62	\$ 214,228	\$ 308,565
	T-1016	Sterile rinse water tank	1	\$ 13,206	1.4	\$ 13,206	\$ 5,282	\$ 18,488	0.71	1.62	\$ 26,041	\$ 37,508
	T-1018	Sterilization tank	1	\$ 29,013	1.4	\$ 29,013	\$ 11,605	\$ 40,618	0.71	1.62	\$ 57,211	\$ 82,404
T-1020	Cleaning tank	1	\$ 16,407	1.4	\$ 16,407	\$ 6,563	\$ 22,970	0.71	1.62	\$ 32,353	\$ 46,600	
											<b>Area 1000 Total</b>	<b>\$ 10,484,299</b>
											<b>Total Install. Cost</b>	<b>\$ 81,526,913</b>

**Appendix III. Individual Equipment Cost Summary (Scenario II)** (Only the additional equipment compared with Scenario I is listed here, any other equipment are all the same as in Scenario I)

Section	Equip. No	Description	Quantity(Req. & Spares)	1997 Unit cost	Install. Factor	Total cost	1997 Unit Install.	1997 Total Install.	Scaling Factor	Size Ratio	Total cost after scale	Total cost for 2013	
A200 Hydrolysis and lime addition	A-206	Sterilization tank agitator	1	\$ 13,497	1.2	\$ 13,497	\$ 2,699	\$ 16,196	0.51	1.62	\$ 20,714	\$ 29,836	
	A-209	Overliming tank agitator	1	\$ 16,573	1.3	\$ 16,573	\$ 4,972	\$ 21,545	0.51	1.62	\$ 27,555	\$ 39,689	
	C-201	Screw conveyor	1	\$ 10,866	1.3	\$ 10,866	\$ 3,260	\$ 14,126	0.78	1.62	\$ 20,579	\$ 29,642	
	C-222	Gypsum conveyor	1	\$ 1,789	1.3	\$ 1,789	\$ 537	\$ 2,326	1	1.62	\$ 3,768	\$ 5,427	
	C-225	Lime solids feeder	1	\$ 3,407	1.3	\$ 3,407	\$ 1,022	\$ 4,429	0.6	1.62	\$ 5,916	\$ 8,521	
	C-226	Lime conveyor	1	\$ 1,195	1.3	\$ 1,195	\$ 359	\$ 1,554	1	1.62	\$ 2,517	\$ 3,625	
	H-201	Fermentation feed cooler	2	\$ 169,550	1.3	\$ 339,100	\$ 50,865	\$ 440,830	1	1.62	\$ 714,145	\$ 1,028,627	
	H-202	Fermentation feed chiller	2	\$ 119,554	1.3	\$ 239,108	\$ 35,866	\$ 310,840	1	1.62	\$ 503,561	\$ 725,311	
	M-201	Acid impregnator no. 1	2	\$ 350,000	1.3	\$ 700,000	\$ 105,000	\$ 910,000	0	1.62	\$ 910,000	\$ 1,310,730	
	M-204	Acid impregnator no. 2	2	\$ 350,000	1.3	\$ 700,000	\$ 105,000	\$ 910,000	0	1.62	\$ 910,000	\$ 1,310,730	
	M-224	Lime unloading pit	1	\$ 13,280	1.75	\$ 13,280	\$ 9,960	\$ 23,240	0.71	1.62	\$ 32,733	\$ 47,148	
	P-201	Sulfuric acid pump	1	\$ 6,516	2.8	\$ 6,516	\$ 11,729	\$ 18,245	0.79	1.62	\$ 26,709	\$ 38,470	
	P-209	Neutralized hydrolyzate slurry pump	1	\$ 16,245	2.8	\$ 16,245	\$ 29,241	\$ 45,486	0.79	1.62	\$ 66,588	\$ 95,911	
	P-222	Neutralized hydrolyzate liquid pump	1	\$ 16,673	2.8	\$ 16,673	\$ 30,011	\$ 46,684	0.79	1.62	\$ 68,342	\$ 98,437	
	P-223	Pneumatic lime unloader	1	\$ 54,057	1.4	\$ 54,057	\$ 21,623	\$ 75,680	0.5	1.62	\$ 96,325	\$ 138,742	
	P-225	ISEP elution pump	1	\$ 7,900	2.8	\$ 7,900	\$ 14,220	\$ 22,120	0.79	1.00	\$ 22,120	\$ 31,861	
	P-226	ISEP reload pump	1	\$ 8,700	2.8	\$ 8,700	\$ 15,660	\$ 24,360	0.79	1.00	\$ 24,360	\$ 35,087	
	P-227	ISEP hydrolyzate feed pump	1	\$ 10,700	2.8	\$ 10,700	\$ 19,260	\$ 29,960	0.79	1.00	\$ 29,960	\$ 43,153	
	R-201	First stage hydrolysis reactor	1	\$ 210,430	1.3	\$ 210,430	\$ 63,129	\$ 273,559	0.6	1.62	\$ 365,393	\$ 526,298	
	R-202	Second stage hydrolysis reactor	1	\$ 174,230	1.3	\$ 174,230	\$ 52,269	\$ 226,499	0.6	1.62	\$ 302,535	\$ 435,760	
	S-201	First stage pre-reactor screw press	1	\$ 1,564,000	1.3	\$ 1,564,000	\$ 469,200	\$ 2,033,200	0	1.62	\$ 2,033,200	\$ 2,928,544	
	S-202	Second stage pre-reactor screw press	1	\$ 1,976,000	1.3	\$ 1,976,000	\$ 592,800	\$ 2,568,800	0	1.62	\$ 2,568,800	\$ 3,700,002	
	S-203	Inter stage pre-reactor screw press	2	\$ 1,500,000	1.3	\$ 3,000,000	\$ 450,000	\$ 3,900,000	0	1.62	\$ 3,900,000	\$ 5,617,413	
	S-205	Avid vent desicant filter	1	\$ 547	1.6	\$ 547	\$ 328	\$ 875	0.6	1.62	\$ 1,169	\$ 1,684	
	S-221	ISEP	1	\$ 2,058,000	1.2	\$ 2,058,000	\$ 411,600	\$ 2,469,600	0.33	1.00	\$ 2,469,600	\$ 3,557,119	
	S-222	Rotary drum filter	1	\$ 106,645	2	\$ 106,645	\$ 106,645	\$ 213,290	0.39	1.62	\$ 257,443	\$ 370,811	
	T-201	Sulfuric acid process storage tank	1	\$ 4,066	1.4	\$ 4,066	\$ 1,626	\$ 5,692	0.71	1.62	\$ 8,018	\$ 11,548	
	T-203	Blowdown tank #1	1	\$ 21,557	1.2	\$ 21,557	\$ 4,311	\$ 25,868	0.93	1.62	\$ 40,515	\$ 58,357	
	T-204	First stage low pressure flash tank	1	\$ 19,423	2.6	\$ 19,423	\$ 31,077	\$ 50,500	0.93	1.62	\$ 79,093	\$ 113,923	
	T-205	Second stage flash tank	1	\$ 13,894	2.5	\$ 13,894	\$ 20,841	\$ 34,735	0.71	1.62	\$ 48,924	\$ 70,468	
	T-206	Second stage low pressure flash tank	1	\$ 11,432	2.5	\$ 11,432	\$ 17,148	\$ 28,580	0.71	1.62	\$ 40,255	\$ 57,982	
	T-209	Overliming tank	1	\$ 55,422	1.4	\$ 55,422	\$ 22,169	\$ 77,591	0.71	1.62	\$ 109,286	\$ 157,412	
	T-2220	Lime storage bin	1	\$ 77,726	1.3	\$ 77,726	\$ 23,318	\$ 101,044	0.46	1.62	\$ 126,150	\$ 181,701	
	W-203	Inter stage washer	2	\$ 350,000	1.3	\$ 700,000	\$ 105,000	\$ 910,000	0	1.62	\$ 910,000	\$ 1,310,730	
												<b>Area 200 Total</b>	<b>\$ 24,120,699</b>

**Appendix IV. Individual Equipment Cost Summary (Scenario III)** (All the equipment listed below have been scaled up accordingly due to the increased feedstock input)

Section	Equip. No.	Description	Quantity(Req. & Spares)	1997 Unit cost	Install. Factor	Total cost	1997 Unit Install.	1997 Total Install.	Scaling Factor	Size Ratio	Total cost after scale	Total cost for 2013
A100 Wood chip feed handling	C-101	Chip conveyor to storage	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
	C-102	Chip stackers	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
	C-103	Reclaim conveyor	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
	C-104	Conveyor to screening	1	\$ 240,713	1.75	\$ 240,713	\$ 180,535	\$ 421,248	0.3	3.24	\$ 599,347	\$ 863,277
	C-105	Conveyor to chip silo	1	\$ 209,315	1.75	\$ 209,315	\$ 156,986	\$ 366,301	0.3	3.24	\$ 521,170	\$ 750,673
	C-106	Chip conveyor to process	1	\$ 209,315	1.75	\$ 209,315	\$ 156,986	\$ 366,301	0.3	3.24	\$ 521,170	\$ 750,673
	C-107	Lignin conveyor to BF conveyor	1	\$ 250,000	1.75	\$ 250,000	\$ 187,500	\$ 437,500	0.3	3.24	\$ 622,471	\$ 896,583
	M-101	Truck scale	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
	M-102	Truck dumper	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
	M-103	Chip receiving hopper	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
	M-104	Bulldozer	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
	M-105	Tramp iron magnet	1	\$ 8,000	1.75	\$ 8,000	\$ 6,000	\$ 14,000	0	3.24	\$ 14,000	\$ 20,165
	M-106	Air density separation system	1	\$ 86,306	1.75	\$ 86,306	\$ 64,730	\$ 151,036	0.5	3.24	\$ 271,840	\$ 391,548
	M-107	Chip slicer	1	\$ 136,915	1.75	\$ 136,915	\$ 102,686	\$ 239,601	0.6	3.24	\$ 485,032	\$ 698,622
	M-108	Chip silo	1	\$ 383,363	1.75	\$ 383,363	\$ 287,522	\$ 670,885	0.6	3.24	\$ 1,358,094	\$ 1,956,147
	M-109	Vibrating silo discharger	1	\$ 78,493	1.75	\$ 78,493	\$ 58,870	\$ 137,363	0.3	3.24	\$ 195,438	\$ 281,502
	M-110	Silo discharge feeder	1	\$ 31,397	1.75	\$ 31,397	\$ 23,548	\$ 54,945	0.3	3.24	\$ 78,175	\$ 112,600
	M-111	Belt scale	1	\$ 5,233	1.75	\$ 5,233	\$ 3,925	\$ 9,158	0.3	3.24	\$ 13,030	\$ 18,767
	S-101	Disc scalping screen	1	\$ 26,164	1.75	\$ 26,164	\$ 19,623	\$ 45,787	0.3	3.24	\$ 65,145	\$ 93,833
	S-102	Chip thickness screen	1	\$ 115,123	1.75	\$ 115,123	\$ 86,342	\$ 201,465	0.3	3.24	\$ 286,643	\$ 412,869
S-103	Chip screen system chutes	1	\$ 54,766	1.75	\$ 54,766	\$ 41,075	\$ 95,841	0.6	3.24	\$ 194,013	\$ 279,449	
T-101	Rainwater collection and settling system	1	\$ 21,906	1.75	\$ 21,906	\$ 16,430	\$ 38,336	0.6	3.24	\$ 77,604	\$ 111,778	
<b>Area 100 Total</b>											<b>\$ 7,638,487</b>	



## Appendix IV Continued

Section	Equip. No.	Description	Quantity(Req. & Spares)	1997 Unit cost	Install. Factor	Total cost	1997 Unit Install.	1997 Total Install.	Scaling Factor	Size Ratio	Total cost after scale	Total cost for 2013
A200 Hydrolysis and lime addition	A-206	Sterilization tank agitator	1	\$ 13,497	1.2	\$ 13,497	\$ 2,699	\$ 16,196	0.51	3.24	\$ 29,496	\$ 42,484
	A-209	Overliming tank agitator	1	\$ 16,573	1.3	\$ 16,573	\$ 4,972	\$ 21,545	0.51	3.24	\$ 39,236	\$ 56,514
	C-201	Screw conveyor	1	\$ 10,866	1.3	\$ 10,866	\$ 3,260	\$ 14,126	0.78	3.24	\$ 35,333	\$ 50,892
	C-222	Gypsum conveyor	1	\$ 1,789	1.3	\$ 1,789	\$ 537	\$ 2,326	1	3.24	\$ 7,534	\$ 10,852
	C-225	Lime solids feeder	1	\$ 3,407	1.3	\$ 3,407	\$ 1,022	\$ 4,429	0.6	3.24	\$ 8,966	\$ 12,914
	C-226	Lime conveyor	1	\$ 1,195	1.3	\$ 1,195	\$ 359	\$ 1,554	1	3.24	\$ 5,032	\$ 7,249
	H-201	Fermentation feed cooler	2	\$ 169,550	1.3	\$ 339,100	\$ 50,865	\$ 440,830	1	3.24	\$ 1,428,040	\$ 2,056,895
	H-202	Fermentation feed chiller	2	\$ 119,554	1.3	\$ 239,108	\$ 35,866	\$ 310,840	1	3.24	\$ 1,006,947	\$ 1,450,369
	M-201	Acid impregnator no. 1	2	\$ 350,000	1.3	\$ 700,000	\$ 105,000	\$ 910,000	0	3.24	\$ 910,000	\$ 1,310,730
	M-204	Acid impregnator no. 2	2	\$ 350,000	1.3	\$ 700,000	\$ 105,000	\$ 910,000	0	3.24	\$ 910,000	\$ 1,310,730
	M-224	Lime unloading pit	1	\$ 13,280	1.75	\$ 13,280	\$ 9,960	\$ 23,240	0.71	3.24	\$ 53,539	\$ 77,115
	P-201	Sulfuric acid pump	1	\$ 6,516	2.8	\$ 6,516	\$ 11,729	\$ 18,245	0.79	3.24	\$ 46,175	\$ 66,509
	P-209	Neutralized hydrolyzate slurry pump	1	\$ 16,245	2.8	\$ 16,245	\$ 29,241	\$ 45,486	0.79	3.24	\$ 115,119	\$ 165,814
	P-222	Neutralized hydrolyzate liquid pump	1	\$ 16,673	2.8	\$ 16,673	\$ 30,011	\$ 46,684	0.79	3.24	\$ 118,152	\$ 170,182
	P-223	Pneumatic lime unloader	1	\$ 54,057	1.4	\$ 54,057	\$ 21,623	\$ 75,680	0.5	3.24	\$ 136,212	\$ 196,194
	R-201	First stage hydrolysis reactor	1	\$ 210,430	1.3	\$ 210,430	\$ 63,129	\$ 273,559	0.6	3.24	\$ 553,774	\$ 797,635
	R-202	Second stage hydrolysis reactor	1	\$ 174,230	1.3	\$ 174,230	\$ 52,269	\$ 226,499	0.6	3.24	\$ 458,509	\$ 660,419
	S-201	First stage pre-reactor screw press	1	\$ 1,564,000	1.3	\$ 1,564,000	\$ 469,200	\$ 2,033,200	0	3.24	\$ 2,033,200	\$ 2,928,544
	S-202	Second stage pre-reactor screw press	1	\$ 1,976,000	1.3	\$ 1,976,000	\$ 592,800	\$ 2,568,800	0	3.24	\$ 2,568,800	\$ 3,700,002
	S-203	Inter stage pre-reactor screw press	2	\$ 1,500,000	1.3	\$ 3,000,000	\$ 450,000	\$ 3,900,000	0	3.24	\$ 3,900,000	\$ 5,617,413
	S-205	Avid vent desiccant filter	1	\$ 547	1.6	\$ 547	\$ 328	\$ 875	0.6	3.24	\$ 1,772	\$ 2,552
	S-222	Rotary drum filter	1	\$ 106,645	2	\$ 106,645	\$ 106,645	\$ 213,290	0.39	3.24	\$ 337,329	\$ 485,876
	T-201	Sulfuric acid process storage tank	1	\$ 4,066	1.4	\$ 4,066	\$ 1,626	\$ 5,692	0.71	3.24	\$ 13,114	\$ 18,889
	T-203	Blowdown tank #1	1	\$ 21,557	1.2	\$ 21,557	\$ 4,311	\$ 25,868	0.93	3.24	\$ 77,180	\$ 111,167
	T-204	First stage low pressure flash tank	1	\$ 19,423	2.6	\$ 19,423	\$ 31,077	\$ 50,500	0.93	3.24	\$ 150,670	\$ 217,019
	T-205	Second stage flash tank	1	\$ 13,894	2.5	\$ 13,894	\$ 20,841	\$ 34,735	0.71	3.24	\$ 80,020	\$ 115,258
	T-206	Second stage low pressure flash tank	1	\$ 11,432	2.5	\$ 11,432	\$ 17,148	\$ 28,580	0.71	3.24	\$ 65,841	\$ 94,835
	T-209	Overliming tank	1	\$ 55,422	1.4	\$ 55,422	\$ 22,169	\$ 77,591	0.71	3.24	\$ 178,749	\$ 257,463
	T-2220	Lime storage bin	1	\$ 77,726	1.3	\$ 77,726	\$ 23,318	\$ 101,044	0.46	3.24	\$ 173,510	\$ 249,918
	W-203	Inter stage washer	2	\$ 350,000	1.3	\$ 700,000	\$ 105,000	\$ 910,000	0	3.24	\$ 910,000	\$ 1,310,730
											<b>Area 200 Total</b>	<b>\$ 23,553,163</b>

## Appendix IV Continued

Section	Equip. No.	Description	Quantity(Req. & Spares)	1997 Unit cost	Install. Factor	Total cost	1997 Unit Install.	1997 Total Install.	Scalling Factor	Size Ratio	Total cost after scale	Total cost for 2013
A300 Production Fermentation	A-300	First stage #1 fermentor agitator	2	\$ 19,341	1.4	\$ 38,682	\$ 7,736	\$ 54,155	0.51	3.24	\$ 98,623	\$ 142,052
	A-301	Second stage #1 fermentor agitator	2	\$ 17,249	1.35	\$ 34,498	\$ 6,037	\$ 46,572	0.51	3.24	\$ 84,814	\$ 122,163
	A-302	First stage #2 fermentor agitator	2	\$ 18,804	1.5	\$ 37,608	\$ 9,402	\$ 56,412	0.51	3.24	\$ 102,733	\$ 147,973
	F-300	1st stage fermentor no. 1	1	\$ 294,847	2.8	\$ 294,847	\$ 530,725	\$ 825,572	1	3.24	\$ 2,674,386	\$ 3,852,084
	F-302	1st stage fermentor no. 2	1	\$ 308,815	2.8	\$ 308,815	\$ 555,867	\$ 864,682	1	3.24	\$ 2,801,081	\$ 4,034,572
	H-300	First stage #1 fermentor heat exchanger	1	\$ 426,000	2.8	\$ 426,000	\$ 766,800	\$ 1,192,800	0.78	3.24	\$ 2,983,552	\$ 4,297,396
	H-302	First stage #2 fermentor heat exchanger	1	\$ 9,100	2.8	\$ 9,100	\$ 16,380	\$ 25,480	0.78	3.24	\$ 63,733	\$ 91,799
	H-304	Distillation feed preheater	1	\$ 161,363	1.8	\$ 161,363	\$ 129,090	\$ 290,453	0.83	3.24	\$ 770,488	\$ 1,109,782
	P-300	First stage #1 fermentor pump	1	\$ 5,574	3	\$ 5,574	\$ 11,148	\$ 16,722	0.79	3.24	\$ 42,321	\$ 60,958
	P-302	First stage #2 fermentor pump	1	\$ 7,086	2.9	\$ 7,086	\$ 13,463	\$ 20,549	0.79	3.24	\$ 52,008	\$ 74,910
P-304	Yeast recycle pump	1	\$ 7,086	3.5	\$ 7,086	\$ 17,715	\$ 24,801	0.79	3.24	\$ 62,768	\$ 90,409	
<b>Area 300 Total</b>											<b>\$ 14,024,098</b>	

## Appendix IV Continued

Section	Equip. No.	Description	Quantity(Req. & Spares)	1997 Unit cost	Install. Factor	Total cost	1997 Unit Install.	1997 Total Install.	Scaling Factor	Size Ratio	Total cost after scale	Total cost for 2013
A500 Beer Distillation, Rectification, and Dehydration	D-501	Beer column	1	\$ 371,000	2.1	\$ 371,000	\$ 408,100	\$ 779,100	0.78	3.24	\$ 1,948,764	\$ 2,806,926
	D-502	Rectification column	1	\$ 242,679	2.1	\$ 242,679	\$ 266,947	\$ 509,626	0.78	3.24	\$ 1,274,728	\$ 1,836,070
	E-501	1st effect evaporator	2	\$ 214,404	2.1	\$ 428,808	\$ 235,844	\$ 900,497	0.68	3.24	\$ 2,002,633	\$ 2,884,516
	E-502	2nd effect evaporator	2	\$ 214,391	2.1	\$ 428,782	\$ 235,830	\$ 900,442	0.68	3.24	\$ 2,002,511	\$ 2,884,341
	E-503	3rd effect evaporator	2	\$ 214,391	2.1	\$ 428,782	\$ 235,830	\$ 900,442	0.68	3.24	\$ 2,002,511	\$ 2,884,341
	E-504	4th effect evaporator	2	\$ 214,391	2.1	\$ 428,782	\$ 235,830	\$ 900,442	0.68	3.24	\$ 2,002,511	\$ 2,884,341
	E-505	5th effect evaporator	2	\$ 214,391	2.1	\$ 428,782	\$ 235,830	\$ 900,442	0.68	3.24	\$ 2,002,511	\$ 2,884,341
	H-501	Reboiler	1	\$ 78,129	2.1	\$ 78,129	\$ 85,942	\$ 164,071	0.68	3.24	\$ 364,881	\$ 525,560
	H-502	Reboiler	1	\$ 13,881	2.1	\$ 13,881	\$ 15,269	\$ 29,150	0.68	3.24	\$ 64,827	\$ 93,375
	H-504	Overhead condenser	1	\$ 4,937	2.1	\$ 4,937	\$ 5,431	\$ 10,368	0.68	3.24	\$ 23,057	\$ 33,210
	H-505	Overhead condenser	1	\$ 42,405	2.1	\$ 42,405	\$ 46,646	\$ 89,051	0.68	3.24	\$ 198,041	\$ 285,251
	H-512	Feed/bottoms exchanger	1	\$ 22,043	2.1	\$ 22,043	\$ 24,247	\$ 46,290	0.68	3.24	\$ 102,946	\$ 148,279
	H-517	Evaporator condenser	2	\$ 59,797	2.1	\$ 119,594	\$ 65,777	\$ 251,147	0.68	3.24	\$ 558,532	\$ 804,488
	M-503	Ethanol dehydration package	1	\$ 1,291,368	1	\$ 1,291,368	\$ -	\$ 1,291,368	0.7	3.24	\$ 2,940,211	\$ 4,234,969
	P-501	Bottoms pump	1	\$ 51,163	2.8	\$ 51,163	\$ 92,093	\$ 143,256	0.79	3.24	\$ 362,564	\$ 522,224
	P-503	Reflux	1	\$ 340	2.8	\$ 340	\$ 612	\$ 952	0.79	3.24	\$ 2,409	\$ 3,470
	P-504	Bottoms pump	1	\$ 4,386	2.8	\$ 4,386	\$ 7,895	\$ 12,281	0.79	3.24	\$ 31,081	\$ 44,768
	P-505	Reflux	1	\$ 4,196	2.8	\$ 4,196	\$ 7,553	\$ 11,749	0.79	3.24	\$ 29,735	\$ 42,829
	P-511	1st effect pump	2	\$ 22,943	2.8	\$ 45,886	\$ 41,297	\$ 128,481	0.79	3.24	\$ 325,169	\$ 468,361
	P-512	2nd effect pump	2	\$ 23,722	2.8	\$ 47,444	\$ 42,700	\$ 132,843	0.79	3.24	\$ 336,210	\$ 484,264
	P-513	3rd effect pump	2	\$ 23,381	2.8	\$ 46,762	\$ 42,086	\$ 130,934	0.79	3.24	\$ 331,377	\$ 477,302
	P-514	4th effect pump	2	\$ 23,381	2.8	\$ 46,762	\$ 42,086	\$ 130,934	0.79	3.24	\$ 331,377	\$ 477,302
	P-515	5th effect pump	2	\$ 23,381	2.8	\$ 46,762	\$ 42,086	\$ 130,934	0.79	3.24	\$ 331,377	\$ 477,302
	P-516	Condensate pump	1	\$ 10,747	2.8	\$ 10,747	\$ 19,345	\$ 30,092	0.79	3.24	\$ 76,158	\$ 109,695
	P-517	Scrubber bottoms pump	1	\$ 1,254	2.8	\$ 1,254	\$ 2,257	\$ 3,511	0.79	3.24	\$ 8,886	\$ 12,800
	T-503	Overhead receiver	1	\$ 1,030	2.1	\$ 1,030	\$ 1,133	\$ 2,163	0.93	3.24	\$ 6,453	\$ 9,295
	T-505	Overhead receiver	1	\$ 21,519	2.1	\$ 21,519	\$ 23,671	\$ 45,190	0.72	3.24	\$ 105,337	\$ 151,723
T-512	CO2 scrubber	1	\$ 50,230	2.1	\$ 50,230	\$ 55,253	\$ 105,483	0.78	3.24	\$ 263,845	\$ 380,032	
											<b>Area 500 Total</b>	<b>\$ 28,851,379</b>

## Appendix IV Continued

Section	Equip. No.	Description	Quantity(Req. & Spares)	1997 Unit cost	Install. Factor	Total cost	1997 Unit Install.	1997 Total Install.	Scaling Factor	Size Ratio	Total cost after scale	Total cost for 2013	
A600 Lignin Separation & Wastewater Treatment	A-602	Equalization Basin Agitator	1	\$ 19,894	1.2	\$ 19,894	\$ 3,979	\$ 23,873	0.51	3.24	\$ 43,475	\$ 62,620	
	A-608	Anaerobic Digester Agitator	4	\$ 30,300	1.2	\$ 121,200	\$ 6,060	\$ 145,440	0.51	3.24	\$ 264,864	\$ 381,500	
	A-608	Aerobic digester aerator	16	\$ 31,250	1.4	\$ 500,000	\$ 12,500	\$ 700,000	1	3.24	\$ 2,267,605	\$ 3,266,172	
	A-630	Recycled water tank agitator	1	\$ 3,311	1.3	\$ 3,311	\$ 993	\$ 4,304	0.51	3.24	\$ 7,839	\$ 11,291	
	C-601	Lignin wet cake screw	1	\$ 12,456	1.4	\$ 12,456	\$ 4,982	\$ 17,438	0.78	3.24	\$ 43,619	\$ 62,827	
	C-614	Aerobic sludge screw	1	\$ 2,466	1.4	\$ 2,466	\$ 986	\$ 3,452	0.78	3.24	\$ 8,635	\$ 12,438	
	H-602	Anaerobic digester feed cooler	1	\$ 175,000	2.1	\$ 175,000	\$ 192,500	\$ 367,500	0.68	3.24	\$ 817,291	\$ 1,177,194	
	M-604	Nutrient feed system	1	\$ 31,400	2.58	\$ 31,400	\$ 49,612	\$ 81,012	1	3.24	\$ 262,433	\$ 377,999	
	M-606	Biogas handling system	1	\$ 11,702	1.68	\$ 11,702	\$ 7,957	\$ 19,659	0.6	3.24	\$ 39,797	\$ 57,322	
	M-612	Filter aid addition system	1	\$ 3,000	1.2	\$ 3,000	\$ 600	\$ 3,600	1	3.24	\$ 11,662	\$ 16,797	
	P-602	Anaerobic digester feed pump	2	\$ 6,568	2.8	\$ 13,136	\$ 11,822	\$ 36,781	0.79	3.24	\$ 93,088	\$ 134,080	
	P-606	Aerobic digester feed pump	2	\$ 6,179	2.8	\$ 12,358	\$ 11,122	\$ 34,602	0.79	3.24	\$ 87,574	\$ 126,139	
	P-608	Aerobic sludge recycle pump	1	\$ 4,686	2.8	\$ 4,686	\$ 8,435	\$ 13,121	0.79	3.24	\$ 33,207	\$ 47,830	
	P-610	Aerobic sludge pum	1	\$ 4,686	2.8	\$ 4,686	\$ 8,435	\$ 13,121	0.79	3.24	\$ 33,207	\$ 47,830	
	P-611	Aerobic digestion outlet pump	2	\$ 6,157	2.8	\$ 12,314	\$ 11,083	\$ 34,479	0.79	3.24	\$ 87,263	\$ 125,690	
	P-614	Sludge filtrate recycle pump	2	\$ 2,568	2.8	\$ 5,136	\$ 4,622	\$ 14,381	0.79	3.24	\$ 36,396	\$ 52,423	
	P-616	Treated water pump	2	\$ 6,150	2.8	\$ 12,300	\$ 11,070	\$ 34,440	0.79	3.24	\$ 87,163	\$ 125,547	
	P-630	Recycle water pump	2	\$ 738	2.8	\$ 1,476	\$ 1,328	\$ 4,133	0.79	3.24	\$ 10,460	\$ 15,066	
	S-600	Bar screen	1	\$ 90,468	1.2	\$ 90,468	\$ 18,094	\$ 108,562	0.6	3.24	\$ 219,765	\$ 316,541	
	S-601	Beer columns bottom centrifuge	3	\$ 659,550	1.2	\$ 1,978,650	\$ 131,910	\$ 2,374,380	0.6	3.24	\$ 4,806,532	\$ 6,923,146	
	S-614	Aerobic sludge belt filter press	1	\$ 650,223	1.8	\$ 650,223	\$ 520,178	\$ 1,170,401	0.72	3.24	\$ 2,728,178	\$ 3,929,565	
	T-602	Equilization basin	1	\$ 245,733	1.42	\$ 245,733	\$ 103,208	\$ 348,941	0.51	3.24	\$ 635,464	\$ 915,299	
	T-606	Anaerobic digester	4	\$ 881,081	1.04	\$ 3,524,324	\$ 35,243	\$ 3,665,297	0.51	3.24	\$ 6,674,957	\$ 9,614,357	
	T-608	Aerobic digester	1	\$ 635,173	1	\$ 635,173	\$ -	\$ 635,173	1	3.24	\$ 2,057,602	\$ 2,963,692	
	T-610	Clarifier	1	\$ 122,335	1.96	\$ 122,335	\$ 117,442	\$ 239,777	0.51	3.24	\$ 436,663	\$ 628,953	
	T-630	Recycle water tank	1	\$ 6,146	1.4	\$ 6,146	\$ 2,458	\$ 8,604	0.745	3.24	\$ 20,655	\$ 29,750	
	XXX	Flare	1	\$ 13,000	1.58	\$ 13,000	\$ 7,540	\$ 20,540	1	3.24	\$ 66,538	\$ 95,839	
												<b>Area 600 Total</b>	<b>\$ 31,517,906</b>

## Appendix IV Continued

Section	Equip. No.	Description	Quantity(Req. & Spares)	1997 Unit cost	Install. Factor	Total cost	1997 Unit Install.	1997 Total Install.	Scaling Factor	Size Ratio	Total cost after scale	Total cost for 2013
A700 Storage	A-701	In-line ethanol denaturant mixer	1	\$ 1,202	1	\$ 1,202	\$ -	\$ 1,202	0.48	3.24	\$ 2,113	\$ 3,044
	P-701	Ethanol product pump	2	\$ 3,718	2.8	\$ 7,436	\$ 6,692	\$ 20,821	0.79	3.24	\$ 52,695	\$ 75,900
	P-703	Sulfuric acid pump	1	\$ 5,430	2.8	\$ 5,430	\$ 9,774	\$ 15,204	0.79	3.24	\$ 38,479	\$ 55,424
	P-704	Firewater pump	1	\$ 8,659	2.8	\$ 8,659	\$ 15,586	\$ 24,245	0.79	3.24	\$ 61,362	\$ 88,383
	P-706	Ammonia pump	1	\$ 2,344	2.8	\$ 2,344	\$ 4,219	\$ 6,563	0.79	3.24	\$ 16,611	\$ 23,925
	P-708	Diesel pump	1	\$ 6,100	2.8	\$ 6,100	\$ 10,980	\$ 17,080	0.79	3.24	\$ 43,227	\$ 62,263
	P-710	Gasoline pump	1	\$ 2,118	2.8	\$ 2,118	\$ 3,812	\$ 5,930	0.79	3.24	\$ 15,009	\$ 21,619
	P-720	CSL pump	1	\$ 1,895	2.8	\$ 1,895	\$ 3,411	\$ 5,306	0.79	3.24	\$ 13,429	\$ 19,342
	T-701	Ethanol product storage tank	2	\$ 101,922	1.4	\$ 203,844	\$ 40,769	\$ 285,382	0.85	3.24	\$ 775,041	\$ 1,116,340
	T-703	Sulfuric acid storage tank	1	\$ 33,094	1.2	\$ 33,094	\$ 6,619	\$ 39,713	0.51	3.24	\$ 72,322	\$ 104,170
	T-704	Firewater storage tank	1	\$ 102,111	1.4	\$ 102,111	\$ 40,844	\$ 142,955	0.85	3.24	\$ 388,239	\$ 559,205
	T-706	Ammonia storage tank	1	\$ 144,058	1.4	\$ 144,058	\$ 57,623	\$ 201,681	0.72	3.24	\$ 470,114	\$ 677,135
	T-708	Diesel storage tank	1	\$ 14,400	1.4	\$ 14,400	\$ 5,760	\$ 20,160	0.51	3.24	\$ 36,714	\$ 52,881
	T-710	Gasoline storage tank	1	\$ 26,739	1.4	\$ 26,739	\$ 10,696	\$ 37,435	0.51	3.24	\$ 68,173	\$ 98,194
	T-720	CSL storage tank	1	\$ 18,975	1.4	\$ 18,975	\$ 7,590	\$ 26,565	0.79	3.24	\$ 67,233	\$ 96,839
	<b>Area 700 Total</b>											<b>\$</b>

## Appendix IV Continued

Section	Equip. No	Description	Quantity(Req. & Spares)	1997 Unit cost	Install. Factor	Total cost	1997 Unit Install.	1997 Total Install.	Scaling Factor	Size Ratio	Total cost after scale	Total cost for 2013
A800 Boiler Feed Drying, Combustor & Turbo Generator	H-811	BFW Preheater	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
	M-802	Combustion airfan	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
	M-803	Fluidized bed combustion reactor	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
	M-804	Combustion gas baghouse	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
	M-811	Turbine/Generator	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
	M-820	Deminerlizer	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
	M-822	Condensate Polisher	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
	M-830	Hydrazine addition package	1	\$ 11,156	1.4	\$ 11,156	\$ 4,462	\$ 15,618	0.6	3.24	\$ 31,617	\$ 45,540
	M-832	Ammonia addition package	1	\$ 11,156	1.4	\$ 11,156	\$ 4,462	\$ 15,618	0.6	3.24	\$ 31,617	\$ 45,540
	M-834	Phosphate addition package	1	\$ 11,156	1.4	\$ 11,156	\$ 4,462	\$ 15,618	0.6	3.24	\$ 31,617	\$ 45,540
	P-804	Condensate pump	2	\$ 3,395	4	\$ 6,790	\$ 10,185	\$ 27,160	0.79	3.24	\$ 68,739	\$ 99,008
	P-811	Turbine condensate pump	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
	P-824	Deaerator feed pump	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
	P-826	BFW pump	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
	P-828	Blowdown pump	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
	P-830	Hydrazine transfer pump	1	\$ 1,042	4	\$ 1,042	\$ 3,126	\$ 4,168	0.79	3.24	\$ 10,549	\$ 15,194
	T-804	Condensate collection tank	1	\$ 3,257	4	\$ 3,257	\$ 9,771	\$ 13,028	0.71	3.24	\$ 30,013	\$ 43,230
	T-824	Condensate surge drum	1	\$ 11,741	3	\$ 11,741	\$ 23,482	\$ 35,223	0.72	3.24	\$ 82,104	\$ 118,259
	T-826	Deaerator	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
	T-828	Blowdown flash drum	0	\$ -	0	\$ -	\$ -	\$ -	0	3.24	\$ -	\$ -
T-830	Hydrazine drum	1	\$ 4,249	4	\$ 4,249	\$ 12,747	\$ 16,996	0.93	3.24	\$ 50,709	\$ 73,039	
	Misc. Transformers	1	\$ 250,000	1.5	\$ 250,000	\$ 125,000	\$ 375,000	0	3.24	\$ 375,000	\$ 540,136	
	Misc. Piping	1	\$ 300,000	1.5	\$ 300,000	\$ 150,000	\$ 450,000	0	3.24	\$ 450,000	\$ 648,163	
<b>Area 800 Total</b>											<b>\$ 1,673,648</b>	

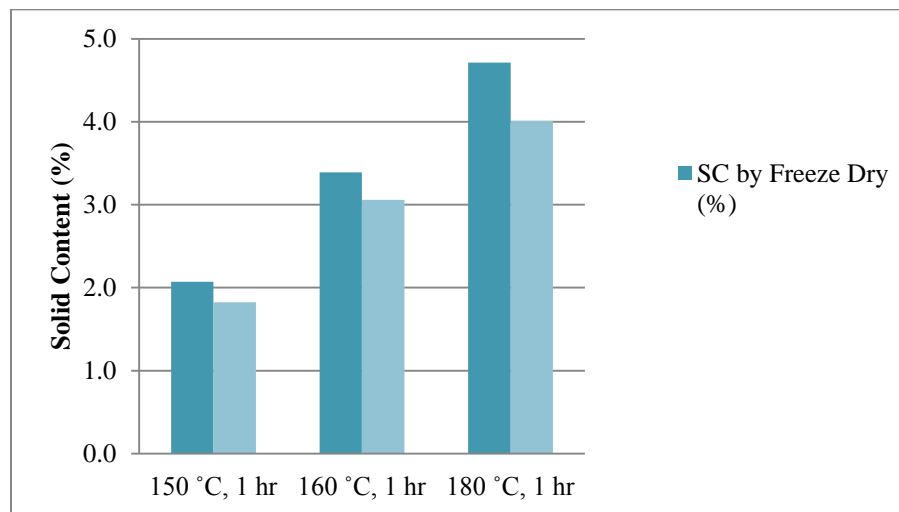
## Appendix IV Continued

Section	Equip. No.	Description	Quantity(Req. & Spares)	1997 Unit cost	Install. Factor	Total cost	1997 Unit Install.	1997 Total Install.	Scalling Factor	Size Ratio	Total cost after scale	Total cost for 2013
A1000 Cooling water & Instrument Air	A-1018	Sterilization tank agitator	1	\$ 13,504	1.3	\$ 13,504	\$ 4,051	\$ 17,555	0.51	3.24	\$ 31,970	\$ 46,049
	A-1020	Cleaning tank agitator	1	\$ 13,504	1.3	\$ 13,504	\$ 4,051	\$ 17,555	0.51	3.24	\$ 31,970	\$ 46,049
	H-1010	Water sterilizer	1	\$ 1,501	1.4	\$ 1,501	\$ 600	\$ 2,101	0.68	3.24	\$ 4,673	\$ 6,731
	M-1002	Cooling tower system	1	\$ 814,399	1.2	\$ 814,399	\$ 162,880	\$ 977,279	0.78	3.24	\$ 2,444,469	\$ 3,520,921
	M-1004	Plant air compressor	3	\$ 44,012	1.3	\$ 132,036	\$ 13,204	\$ 171,647	0.34	3.24	\$ 255,974	\$ 368,695
	M-1006	Fermentor air compressor package	3	\$ 380,151	1.3	\$ 1,140,453	\$ 114,045	\$ 1,482,589	0.34	3.24	\$ 2,210,957	\$ 3,184,579
	M-1008	Chilled water package	3	\$ 380,000	1.2	\$ 1,140,000	\$ 76,000	\$ 1,368,000	0.8	3.24	\$ 3,503,172	\$ 5,045,837
	P-1002	Cooling water pump	2	\$ 156,935	2.8	\$ 313,870	\$ 282,483	\$ 878,836	0.79	3.24	\$ 2,224,224	\$ 3,203,689
	P-1010	Sterile water pump	2	\$ 2,101	2.8	\$ 4,202	\$ 3,782	\$ 11,766	0.79	3.24	\$ 29,777	\$ 42,890
	P-1012	Make-up water pump	2	\$ 4,535	2.8	\$ 9,070	\$ 8,163	\$ 25,396	0.79	3.24	\$ 64,274	\$ 92,578
	P-1014	Process water circulating pump	3	\$ 5,188	2.8	\$ 15,564	\$ 9,338	\$ 43,579	0.79	3.24	\$ 110,294	\$ 158,863
	P-1016	CIP/CS supply pump	2	\$ 2,801	2.8	\$ 5,602	\$ 5,042	\$ 15,686	0.79	3.24	\$ 39,698	\$ 57,180
	P-1018	CIP/CS supply pump	2	\$ 2,802	2.8	\$ 5,604	\$ 5,044	\$ 15,691	0.79	3.24	\$ 39,712	\$ 57,200
	S-1004	Instrument air dryer	2	\$ 7,777	1.3	\$ 15,554	\$ 2,333	\$ 20,220	0.6	3.24	\$ 40,932	\$ 58,957
	T-1004	Plant air receiver	1	\$ 6,721	1.3	\$ 6,721	\$ 2,016	\$ 8,737	0.72	3.24	\$ 20,366	\$ 29,335
	T-1005	Instrument air receiver	1	\$ -	0	\$ -	\$ -	\$ -	N/A	3.24	\$ -	\$ -
	T-1010	Process water tank	1	\$ 13,206	1.4	\$ 13,206	\$ 5,282	\$ 18,488	0.71	3.24	\$ 42,592	\$ 61,349
	T-1014	Process water tank	1	\$ 119,645	1.4	\$ 119,645	\$ 47,858	\$ 167,503	0.51	3.24	\$ 305,044	\$ 439,373
	T-1016	Sterile rinse water tank	1	\$ 13,206	1.4	\$ 13,206	\$ 5,282	\$ 18,488	0.71	3.24	\$ 42,592	\$ 61,349
	T-1018	Sterilization tank	1	\$ 29,013	1.4	\$ 29,013	\$ 11,605	\$ 40,618	0.71	3.24	\$ 93,574	\$ 134,780
T-1020	Cleaning tank	1	\$ 16,407	1.4	\$ 16,407	\$ 6,563	\$ 22,970	0.71	3.24	\$ 52,916	\$ 76,219	
											<b>Area 1000 Total</b>	<b>\$ 16,692,622</b>
											<b>Total Install. Cost</b>	<b>\$ 127,005,967</b>

## Appendix V. The Comparison between Freeze Dry and Oven Dry for Solid Content Measurement of Filtrates (Chapter 4)

A certain amount of filtrates (5mL) from auto-hydrolysis of mixed softwood at different conditions were subjected to both freeze dry and oven dry to study the effect of different measurement methods on the result of solid content in the filtrate.

Conditions	SC by Freeze Dry (%)	SC by Oven Dry (%)	Differential (%)
150 °C, 1 hr	2.1	1.8	13.6
160 °C, 1 hr	3.4	3.1	10.8
180 °C, 1 hr	4.7	4.0	17.4





## **Appendix V Continued**

It was determined that the solid content obtained was at least 10% higher by using the freeze dry method, compared with the standard oven dry method, mainly due to the evaporation of volatile components from the filtrate during the oven dry process.

**Appendix VI. Sugar Conversion Calculation Index (From mono-sugars to polymers)**

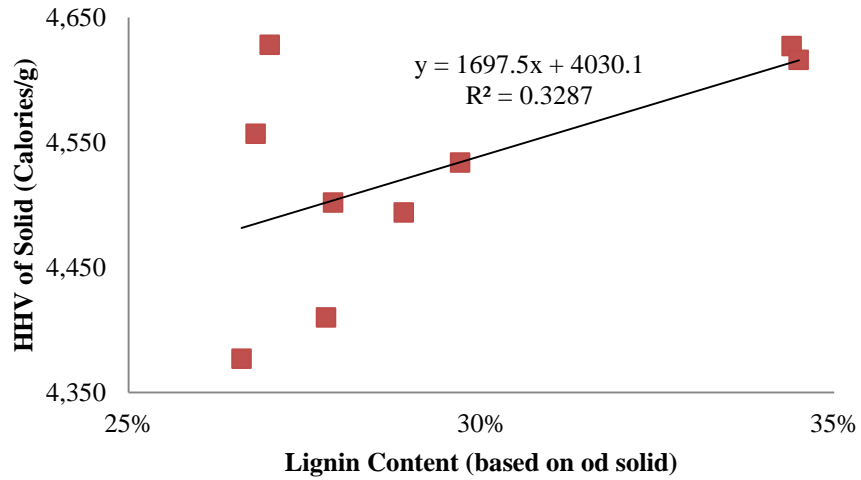
<b>Sugar</b>	<b>Calculation Index</b>	<b>MW of Monomer</b>	<b>MW of repeat unit of polymer</b>
*Arabinose	0.88	150	132
Rhamnose	0.90	180	162
Galactose	0.90	180	162
Glucose	0.90	180	162
Xylose	0.88	150	132
Mannose	0.90	180	162

\*Example calculation:

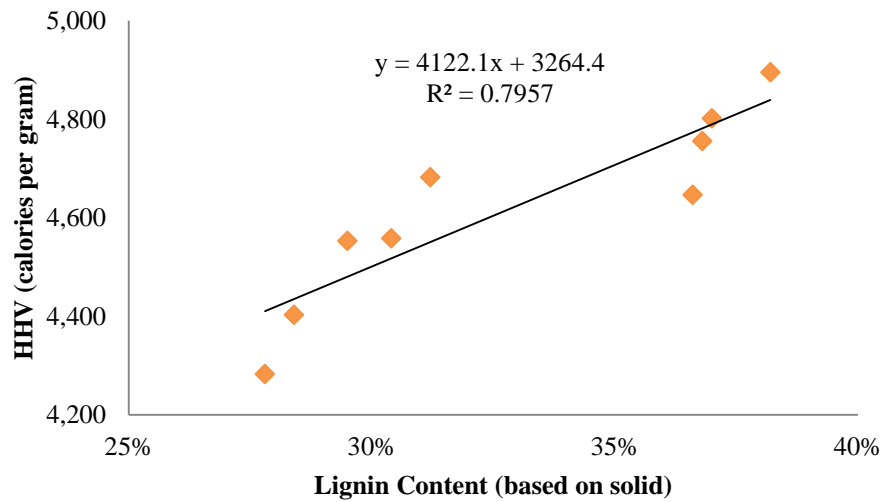
To convert 100 grams of arabinose into arabinan:

$$\text{Arabinan} = 100 \times 0.88 = 88 \text{ grams}$$

## Appendix VII. Higher Heating Value versus Lignin Content of the Solids



Hardwood HHV vs. Lignin Content (Chapter 3)

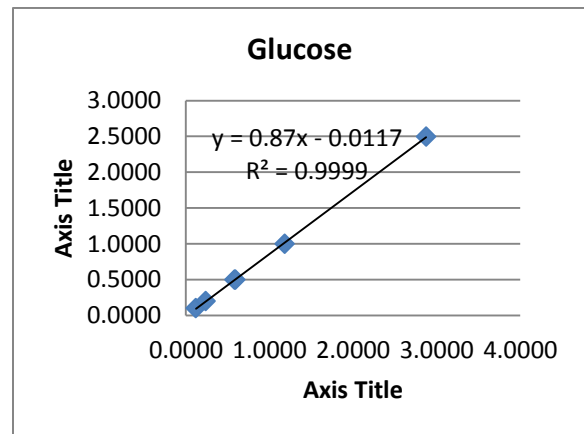
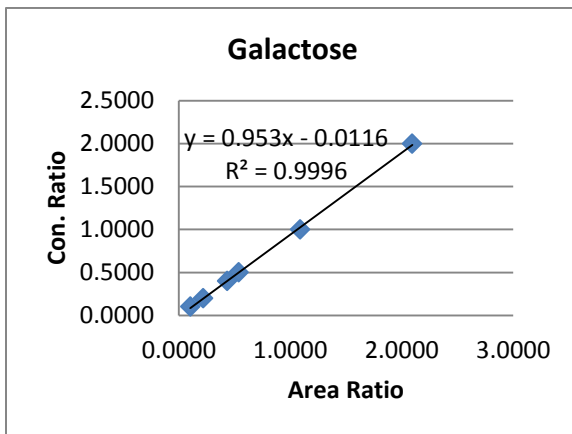
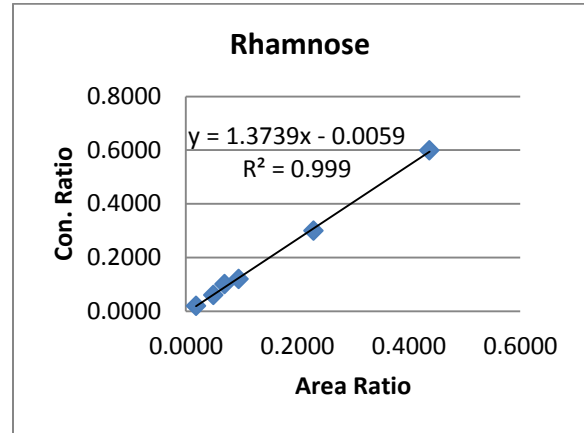
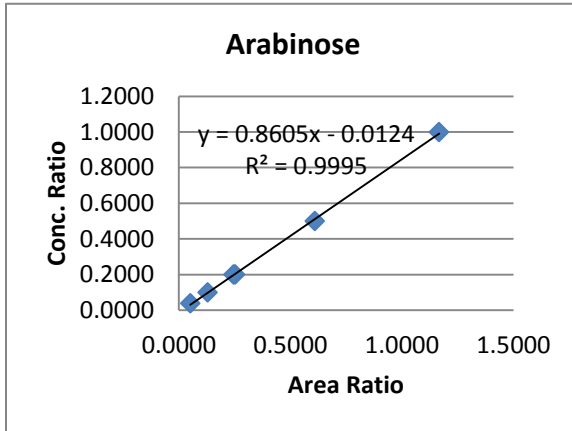


Softwood HHV vs. Lignin Content (Chapter 4)

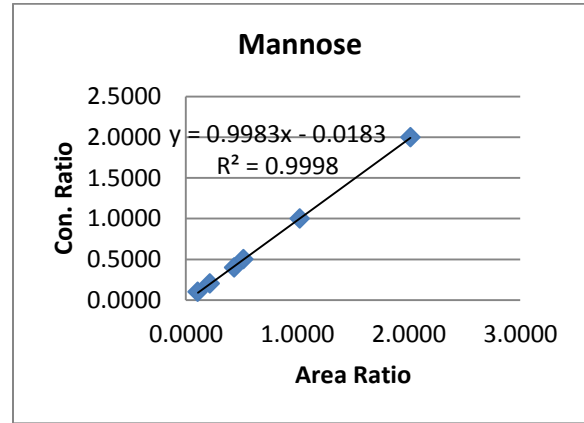
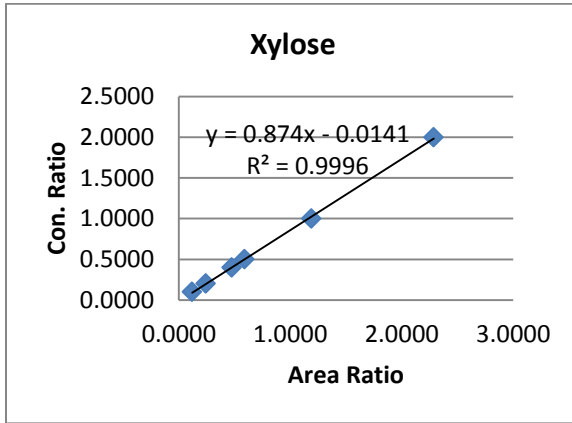
## **Appendix VII Continued**

See detailed HHV and Lignin measurement method in Chapter 3 Section 3.3.6 and 3.3.5, respectively.

## Appendix VIII. Sugar Calibrations by Ion Chromatography



## Appendix VIII Continued

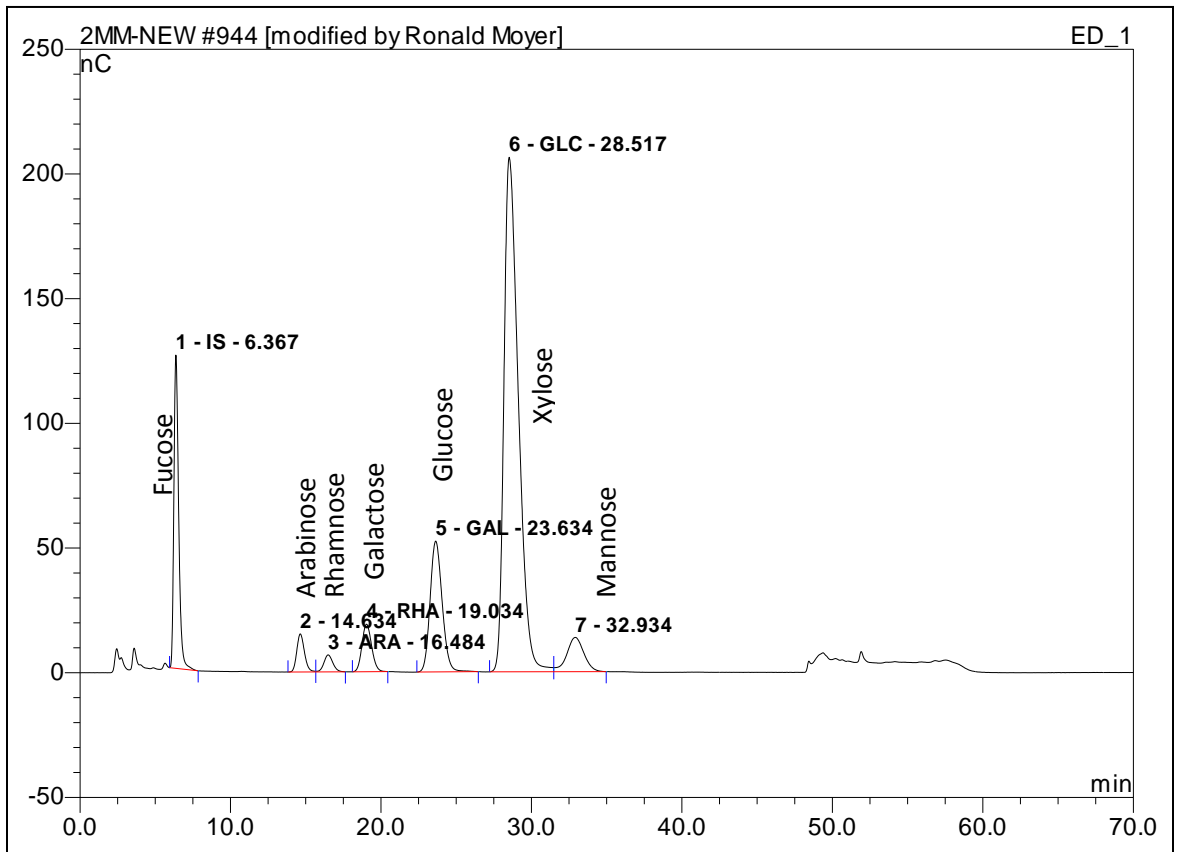


See detailed description of the HPLC and column used in Chapter 5 Section 5.3.4. All the sugars standards were obtained from Fisher, Scientific, Fair Lawn, New Jersey. Standard sugar solutions (totally 6) were made according to the table below.

Conc. (mg/ml)	Fucose	Arabinose	Rhamnose	Galactose	Glucose	Xylose	Mannose
STD 1	0.1001	0.0200	0.0020	0.0100	0.0500	0.0100	0.0200
STD 2	0.1001	0.0100	0.0060	0.0200	0.0100	0.0200	0.0400
STD 3	0.1001	0.0040	0.0120	0.0400	0.0200	0.0400	0.0100
STD 4	0.1001	0.1000	0.0100	0.0500	0.2500	0.0500	0.1000
STD 5	0.1001	0.0500	0.0300	0.1000	0.0500	0.1000	0.2000
STD 6	0.1001	0.0200	0.0600	0.2000	0.1000	0.2000	0.0500

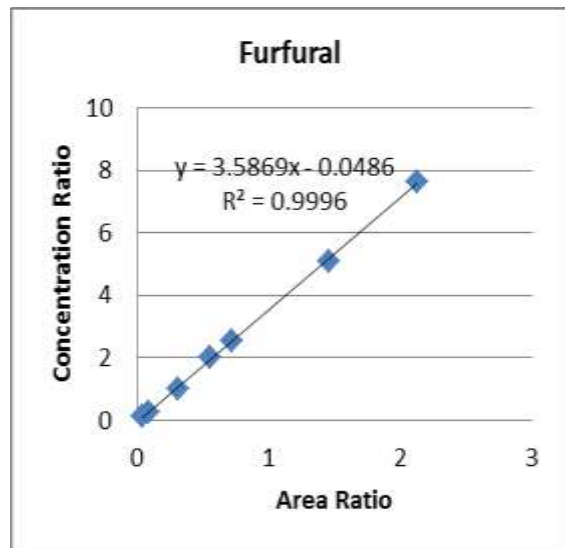
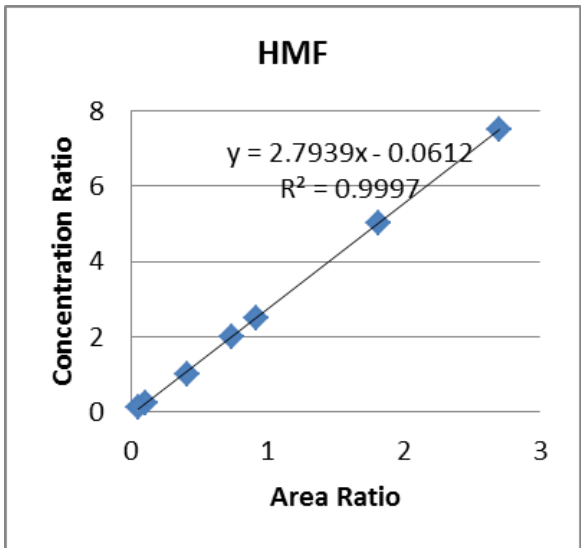
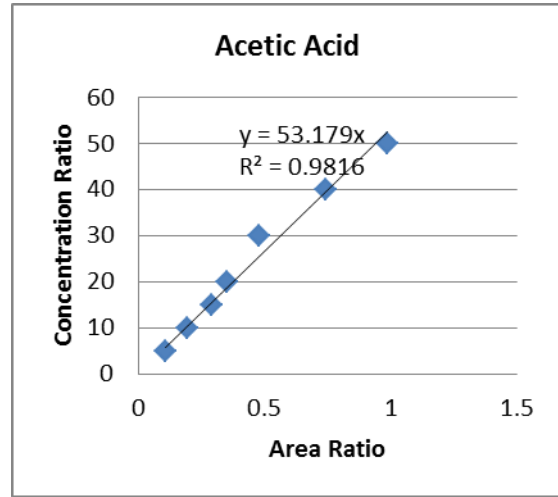
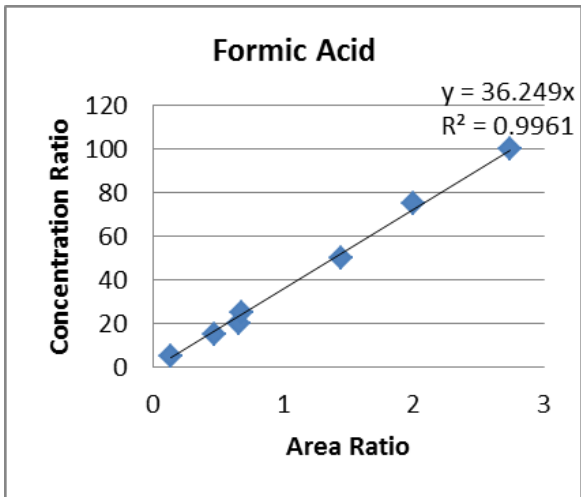
# Appendix IX. Sugar Calibration Chromatography by Ion Chromatography

See detailed description of the HPLC and column used in Chapter 5 Section 5.3.4. All the sugars standards were obtained from Fisher, Scientific, Fair Lawn, New Jersey. Graph below shows the sugar calibration chromatograph obtained by Standard Sugar Solution #6 (see table in Appendix VIII)



# Appendix X. Calibration Lines and Chromatography for Byproducts

## Measurement Obtained by HPLC (Chapter 5)





## Appendix X Continued

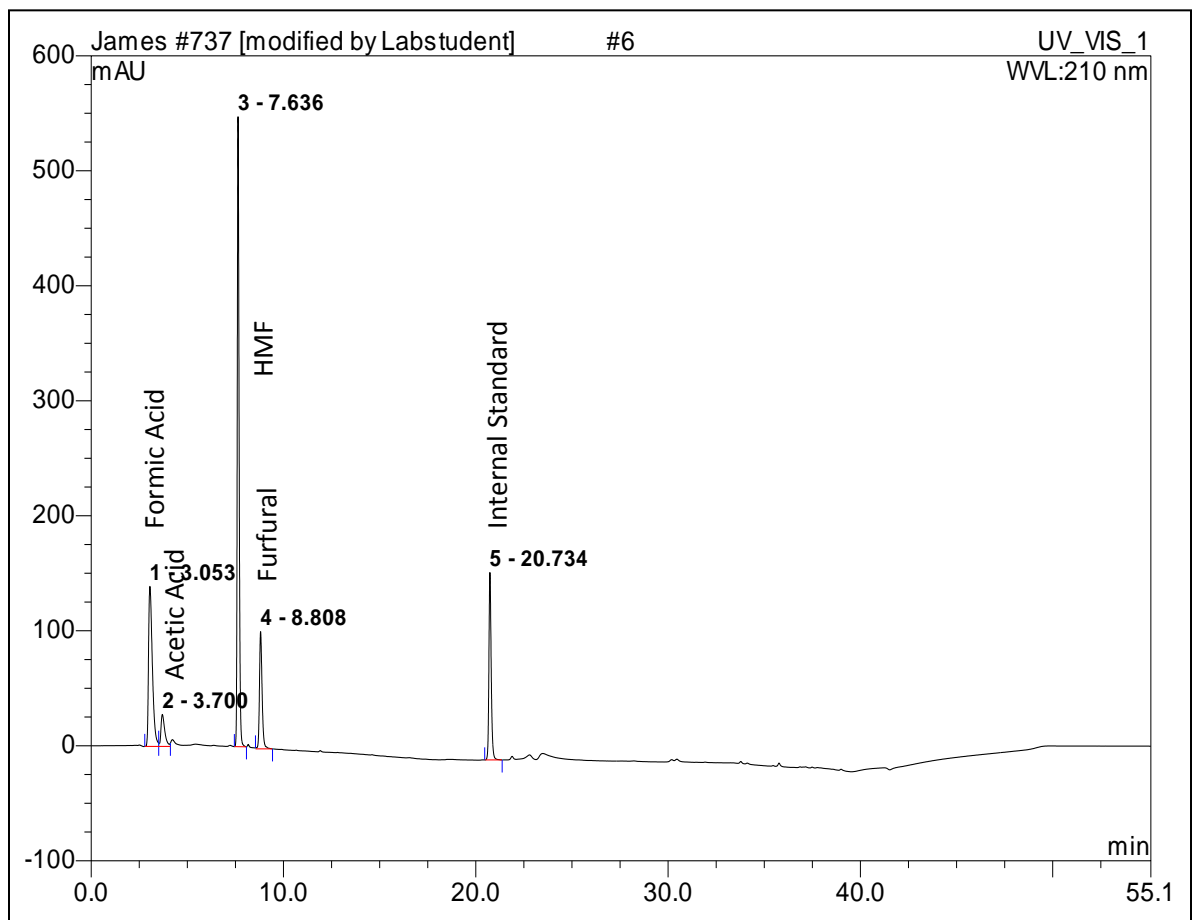
See detailed description of the HPLC and column used in Chapter 5 Section 5.3.5.

Standard byproduct solutions (totally 7) were made according to the table below.

<b>Con. (mg/mL)</b>	<b>Formic Acid</b>	<b>Acetic Acid</b>	<b>HMF</b>	<b>Furfural</b>	<b>IS</b>
<b>#1</b>	0.800	2.000	0.040	0.010	0.040
<b>#2</b>	1.001	1.200	0.201	0.080	0.040
<b>#3</b>	4.002	0.400	0.080	0.005	0.040
<b>#4</b>	3.002	0.200	0.010	0.040	0.040
<b>#5</b>	0.200	0.800	0.005	0.306	0.040
<b>#6</b>	2.001	0.600	0.301	0.102	0.040
<b>#7</b>	0.600	1.601	0.100	0.204	0.040

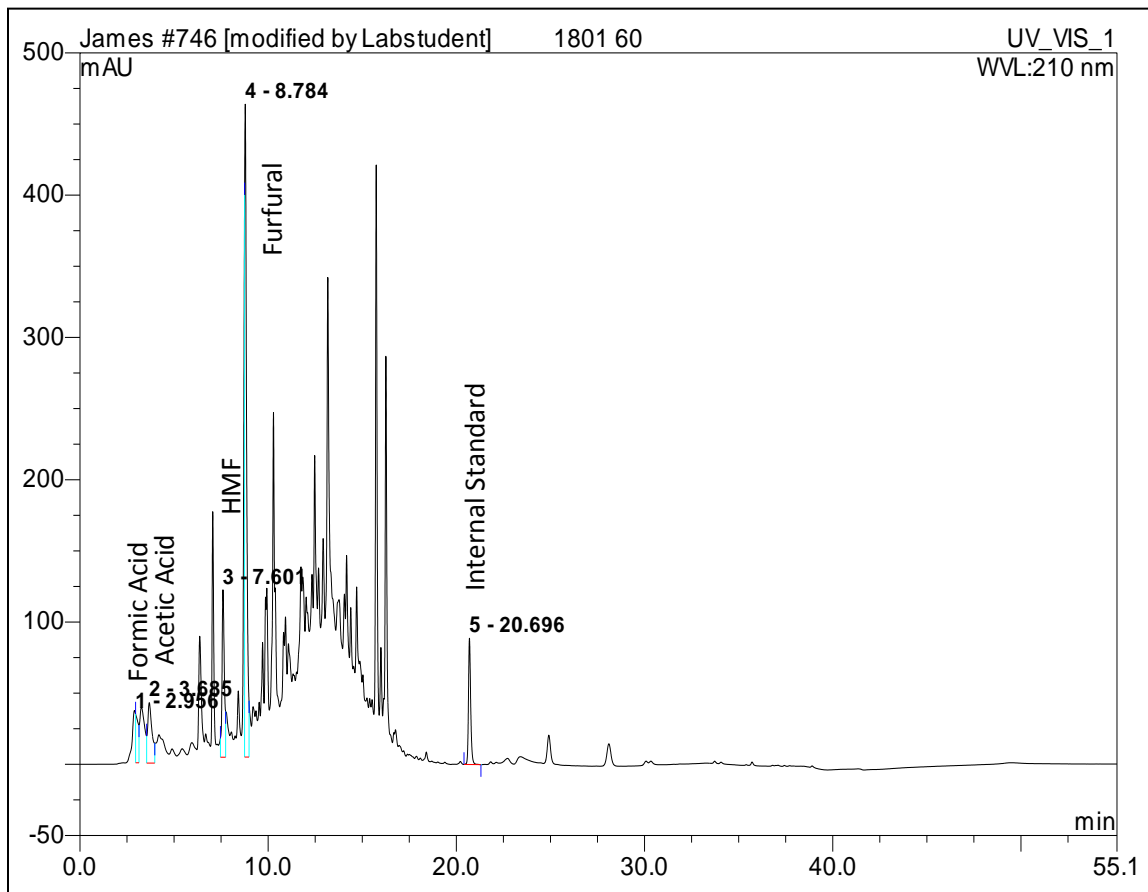
## Appendix X Continued

See detailed description of the HPLC and column used in Chapter 5 Section 5.3.5. Graph below shows the byproduct calibration chromatograph obtained by Standard Byproduct Solution #6 (see table in Appendix X).



## Appendix XI. Chromatography for Byproducts Measurement of Filtrate Obtained by HPLC (Chapter 5)

See detailed description of the HPLC and column used in Chapter 5 Section 5.3.5. The graph below shows the chromatograph of the byproducts measurement of the filtrate obtained at 60 minute of auto-hydrolysis of mixed hardwood at 180°C.



## Appendix XII. Standardization of Bomb Calorimeter

<b>Trials</b>	<b>#1</b>	<b>#2</b>	<b>#3</b>	<b>#4</b>	<b>Mean</b>	<b>Std.</b>
<b>W<sup>a</sup> (calories/°C)</b>	2416	2422	2423	2415	2419	3.9

<sup>a</sup> Energy equivalent of the calorimeter in calories per °C, this factor represents the energy required to raise the temperature of the calorimeter one degree

Before the heat of combustion measurement, 4 trials of standardization were carried out by combustion of benzoic acid to find out the energy equivalent factor of the calorimeter system. The standardization results are presented in table above. Detailed description of the bomb calorimeter and the method used can be found in Chapter 3 Section 3.3.6.