ABSTRACT

LIFE CYCLE ASSESSMENT OF ETHANOL PRODUCED FROM LIGNOCELLULOSIC BIOMASS: TECHNO-ECONOMIC AND ENVIRONMENTAL EVALUATION

Poritosh Roy
University of Guelph, 2014

Advisor:
Dr. Animesh Dutta

The life cycle (LC) of ethanol derived from lignocellulosic biomass (hereafter referred to biomass: wheat straw, sawdust & miscanthus) by both enzymatic hydrolysis and thermochemical [gasification-biosynthesis pathway; torrefied/non-torrefied, with/without chemical looping gasification (CLG)] conversion processes has been evaluated, considering various scenarios. A follow-up study has also been conducted to identify the potential locations for ethanol industries in Ontario. Life cycle assessment (LCA) methodologies have been used to evaluate the LC of ethanol to determine if environmentally preferable and economically viable ethanol can be produced in Ontario, Canada. A novel continuous stirred tank bioreactor has also been developed (consisting of an innovative gas supply and an effluent extraction process) for syngas fermentation into ethanol.

The net energy consumption, GHG emissions and production cost of ethanol were found to be dependent on ethanol yield, feedstock cost, processing plant capacity and assumptions. This study revealed that environmental benefit can be gained from biomasses, the economic viability and biomass logistics of agri- and forest residues remain doubtful, unless a nominal subsidy (for example FiT) is provided. The CLG process seems to be useful to reduce net energy consumption and GHG emissions for both torrefied and non-torrefied miscanthus. Consequently,
miscanthus has emerged as a promising feedstock for ethanol industries (both enzymatic hydrolysis and biosynthesis) even if it is grown on marginal land in Ontario, avoids any sort of competition with food crops for higher quality land, avoids the food vs fuel debate, and improves farm income and the rural economy. Eastern Ontario has emerged as the best option for miscanthus based ethanol industry.

This study also revealed that syngas can be fermented with *Clostridium Ljungdahlii* into ethanol by using the developed bioreactor. It is worthy to note that careful consideration has to be placed on the land use changes, soil quality and their rebound effects if biomass, especially agri-residues are to be put to use in the ethanol industry. The information generated in this study has emerged to be novel and may help the stakeholders in their decision making processes, help meeting the ethanol demand, and achieving GHG emissions target of Canada.
This thesis is dedicated to my loved Parents (Late Sahadeb Roy & Late Bimola Roy), who are always remembered and in the center of all kind of inspiration in the life of the author.
Acknowledgements

The author wishes to express his deepest sense of gratitude to his advisor Dr. Animesh Dutta, School of Engineering, University of Guelph, Ontario, Canada for the institutional support and scholastic supervision, constructive criticism and constant encouragement during the entire period of this study.

He extend heartfelt gratitude to Dr. Bill Deen, Department of Plant Agricultural, Dr. Brajesh Dubey and Dr. Shohel Mahmud, School of Engineering, University University of Guelph, not only for serving in the Advisory Committee and extending their valuable time to review this manuscript, but also for their thoughtful remarks, useful suggestions and constructive criticism during this study. He also likes to thank Prof. Amar Mohanty and Dr. Fantahun M. Defersha for their service in the qualifying examination committee and constructive suggestions. The author is also thankful to Dr. Douglas M. Joy, Graduate Coordinator for his fruitful suggestion during the qualifying examination. The author also likes to thank Dr. Sheng Chang and Mr. Richard Chen for their support in preparing the membrane separator used in this study.

The author wishes to extend his appreciation to Mr. Michael Speagle for his ever-ready-to-help in the laboratory activities and experimental setups. He also likes to thank Mrs. Carly Fennell and Mrs. Joanne Ryks, Mr. Ryan Smith, and Mr. John Whiteside for extending their helping hand, especially for the syngas fermentation study and computer related issues, respectively. He would like to thank all the members of Dr. Dutta’s research team: Dr. Bimal Acharya, Mr. Harpreet Kambo, Mr. Stefan Goupal, Mr. Jamie Minarat, Mr. MD Tushar, Dr. Mathias Leon and Mr. Subhash Paul for their generous help and friendly companion during this study. He is also indebted to Ontario Graduate Scholarship (OGS) Program for awarding the prestigious scholarship during this study. The author also acknowledges for the Dean’s scholarship from the University of Guelph.

The author feels proud to acknowledge his beloved wife Rita Roy who made a fruitful life for the author during the entire period of this study and for her constant encouragement. He is also thankful to his daughter Riya Roy for her love, which gives all kind of inspiration. The author is also grateful to all of his family members and relatives for their moral support, enduring patience and positive encouragement throughout his study in the University of Guelph, Ontario, Canada. Finally, he wishes to express his sincere appreciation to those who have contributed directly or indirectly for the successful completion of this study.
Table of Contents

Cover .............................................................................................................................. i
Abstract ...................................................................................................................... ii
Dedication ................................................................................................................... iv
Acknowledgements ................................................................................................... v
Table of Contents ....................................................................................................... vi
List of Tables ............................................................................................................. vi
List of Figures ........................................................................................................... xii
Chapter 1: Introduction .............................................................................................. 1
  1.1. Rationale ........................................................................................................... 1
  1.2. Objectives ......................................................................................................... 5
  1.3. Scope and limitation of this research ................................................................. 6
  1.4 Novelty of the research ...................................................................................... 7
    1.4.1 Bioreactor development .............................................................................. 7
    1.4.2 Chemical looping gasification (CLG) ............................................................ 7
    1.4.3 Life cycle assessment .................................................................................. 8
  1.5 Contribution of this research ............................................................................. 8
  1.6 Publications from this research ......................................................................... 10
    1.6.1 Publications in peer reviewed journals ...................................................... 10
    1.6.2 Submitted manuscripts .............................................................................. 10
    1.6.3 Publications: Research presentations ......................................................... 10
Chapter 2: Literature Review .................................................................................... 11
  2.1 Ethanol production via biochemical conversion process (enzymatic hydrolysis) ........ 11
    2.1.1 Pretreatment ................................................................................................ 11
    2.1.2 Fermentation .............................................................................................. 12
    2.1.3 Distillation and purification ....................................................................... 13
    2.1.4 Waste management ................................................................................. 14
  2.2 Life cycle assessment (LCA) of ethanol produced by biochemical conversion process .......... 16
    2.2.1 LCA of ethanol produced from agri-residues .............................................. 16
    2.2.2 LCA of ethanol from energy crops, woody biomass and forest residues .......... 19
    2.2.3 Land, water and other approaches in LCA of ethanol ............................... 22
Chapter 5: Life cycle assessment of ethanol derived from sawdust ........................................ 62

5.1 Introduction .......................................................................................... 62

5.2 Methodology ....................................................................................... 62

5.2.1 System boundary and assumptions .................................................. 62

5.2.2 Ethanol production ........................................................................... 64

5.2.3 Cost analysis .................................................................................... 65

5.2.4 Data collection .................................................................................. 65

5.2.5 Ethanol production via gasification process ...................................... 24

5.2.5.1 Gasification ............................................................................... 24

5.2.5.2 Gas cleanup .............................................................................. 28

5.2.5.3 Syngas synthesis into ethanol .................................................... 28

2.4 Life cycle cost analysis (LCCA) .......................................................... 32

2.4.1 Life cycle costing of ethanol produced by biochemical process .......... 33

2.4.2 Life cycle costing of ethanol produced by thermochemical process .... 37

Chapter 3: Life Cycle Assessment (LCA) Methodologies .............................. 41

3.1 LCA Methodologies ............................................................................ 41

3.1.1 Goal definition and scoping ............................................................. 42

3.1.2 Life cycle inventory (LCI) analysis ................................................... 45

3.1.3 Impact assessment .......................................................................... 46

3.1.4 Interpretation ................................................................................... 46

3.2 Life cycle cost analysis (LCCA) ............................................................ 47

Chapter 4: Life Cycle Assessment of Ethanol produced from Wheat Straw ..... 49

4.1 Introduction .......................................................................................... 49

4.2 Materials and methods ......................................................................... 49

4.2.1 System boundary ............................................................................ 49

4.2.2 Biochemical conversion process ..................................................... 50

4.2.3 Cost analysis ................................................................................... 52

4.2.4 Data collection ................................................................................ 52

4.3 Results and discussion .......................................................................... 53

4.3.1 Energy consumption, CO₂ emission and production cost .................. 53

4.3.2 Sensitivity analysis .......................................................................... 56

4.4 Conclusion ........................................................................................... 61
Chapter 6: Evaluation of the Life Cycle of Ethanol derived from Miscanthus in Ontario......74
6.1 Introduction ........................................................................................................................................74
6.2 Methodology ......................................................................................................................................75
   6.2.1 Study area, system boundary and assumptions .................................................................75
   6.2.2 Miscanthus cultivation ........................................................................................................78
   6.2.3 Transportation .....................................................................................................................80
   6.2.4 Ethanol production .............................................................................................................80
   6.2.5 Cost analysis .......................................................................................................................82
6.3 Results and discussion ....................................................................................................................82
   6.3.1 Net energy consumption ....................................................................................................82
   6.3.2 Greenhouse gas emission (CO$_2$e) ................................................................................83
   6.3.3 Net production cost ............................................................................................................84
   6.3.4 Sensitivity analysis ............................................................................................................86
6.4 Conclusion ......................................................................................................................................90

Chapter 7: Identification of suitable plant location for ethanol industry in Ontario, Canada...91
7.1 Introduction ......................................................................................................................................91
7.2 Materials and methods ................................................................................................................91
   7.2.1 Study area .............................................................................................................................91
   7.2.2 System boundary ................................................................................................................91
   7.2.3 Transportation, ethanol production and cost analysis .........................................................92
7.3 Results and discussion ..................................................................................................................93
   7.3.1 Net energy consumption .....................................................................................................93
   7.3.2 Greenhouse gas emission (CO$_2$e) ..................................................................................94
   7.3.3 Production cost ................................................................................................................97
   7.3.4 Sensitivity analysis ............................................................................................................98
7.4 Conclusion ....................................................................................................................................102

Chapter 8: Development of a Continuous Stirred Tank Bioreactor for Syngas Fermentation 103
8.1 Introduction ................................................................................................................. 103
8.2 Materials and Methods ............................................................................................. 104
  8.2.1 Reactor development ......................................................................................... 104
  8.2.2 Microorganism and media ................................................................................ 106
  8.2.3 Syngas fermentation ......................................................................................... 106
  8.2.4 Analytical method ............................................................................................. 109
8.3 Results and discussion .............................................................................................. 109
  8.3.1 pH and temperature profile during syngas fermentation .................................. 109
  8.3.2 Ethanol and other alcoholic compounds ......................................................... 110
8.4 Conclusion .................................................................................................................. 111

Chapter 9: Evaluation of the Life Cycle of Ethanol derived from Biosyngas Fermentation.... 112
9.1 Introduction ............................................................................................................... 112
9.2 Materials and methods ............................................................................................. 113
  9.2.1 System boundary and assumptions ................................................................. 113
  9.2.2 Pretreatment (torrefaction) ............................................................................. 113
  9.2.3 Ultimate analysis ............................................................................................ 114
  9.2.4 Gasification and syngas cleaning .................................................................... 114
  9.2.5 Syngas fermentation ....................................................................................... 115
  9.2.6 Separation (distillation & purification) ............................................................ 116
  9.2.7 Waste management ....................................................................................... 117
  9.2.8 Cost analysis .................................................................................................. 117
  9.2.9 Data collection ................................................................................................ 117
9.3 Results and discussion .............................................................................................. 117
  9.3.1 Net energy consumption ............................................................................... 117
  9.3.2 GHG emission (CO₂e) .................................................................................. 119
  9.3.3 Production cost .............................................................................................. 120
  9.3.4 Sensitivity analysis ....................................................................................... 121
9.4 Conclusion .................................................................................................................. 127

Chapter 10: Conclusions and Recommendations .......................................................... 128
10.1 Conclusions .............................................................................................................. 128
  10.1.1 Evaluation of the LC of ethanol produced by enzymatic hydrolysis process .... 128
  10.1.2 Evaluation of the LC of ethanol produced by gasification-biosynthesis process .... 129
10.1.3 Continuous stirred tank bioreactor ........................................................................................................ 130
10.2 Recommendations ........................................................................................................................................ 130
10.2.1 Life cycle assessment .............................................................................................................................. 130
10.2.2 Improvement of bioreactor ...................................................................................................................... 130

Chapter 11: References ........................................................................................................................................ 132

Appendices ............................................................................................................................................................ 170

A-2-1 The schematic diagram of chemical looping gasification (CLG) system.................................................. 170
A-2-2 Brief summary of microorganisms identified and used for syngas fermentation .................................. 171
A-2-3 Syngas fermentation parameters and ethanol yield .............................................................................. 175
A-6-1 Land classification in Ontario .................................................................................................................. 177
A-6-2 On-farm inputs for miscanthus cultivation in different regions .............................................................. 178
A-6-3 On-farm energy and other inputs for miscanthus cultivation ................................................................. 180
A-6-4 Estimated emission from farm input and carbon sequestration ......................................................... 182
A-6-5 Calculation of energy consumption and material cost of enzyme production ................................. 183
A-8-1 Membrane separator ................................................................................................................................. 184
A-8-2 Membrane support .................................................................................................................................. 184
A-8-3 List of materials/accessories for the developed bioreactor ................................................................. 185
A-8-4 List of materials/accessories for anaerobic gas chamber ................................................................... 186
A-8-5 List of chemicals and their amount used for broth media ................................................................. 186
A-8-6 Photograph of the incubator .............................................................................................................. 187
A-8-7 Calibration curve of the pump ............................................................................................................... 187
A-8-8 Photographs of overall experimental setup ...................................................................................... 188
A-9-1 Experimental setup of torrefaction process adopted in this study .................................................. 189
A-9-2 Composition of flue gas from biomass torrefaction process ............................................................. 189
A-9-3 Energy consumption in the torrefaction of biomass (for 45 min) ...................................................... 190
A-9-4 Flash 200 CHNS-O, Organic Elemental Analyzer ........................................................................... 190
A-9-5 Photograph of thermo gravimetric analyzer (TGA) ........................................................................ 191
A-9-6 Photograph of Fourier transform infrared spectroscopy (FT-IR) ...................................................... 191
A-9-7 TGA/FT-IR experimental parameters ............................................................................................... 192
A-9-8 Comparison among various raw biomasses ......................................................................................... 192
A- 9-9 Comparison among various torrefied biomasses................................. 193
A- 9-10 Comparison among various raw biomasses degraded with CaO............... 193
A- 9-11 Comparison among various torrefied biomasses degraded with CaO.......... 194
A- 9-12 Comparison among raw and torrefied with or without CaO (miscanthus)..... 194
A-9-13 Cold gas efficiency (CGE) calculation for steam gasification ................... 195
A-9-14 Summary of ASPEN simulation parameters ........................................ 195
A-9-15 Summary of ASPEN simulation parameters and CLG block diagram ......... 196
A-9-16 CLG simulation flowsheet .................................................................. 197
A-9-17 Product gas compositions (simulated) and CGE .................................. 198
List of Tables

Table 1.1 Projected biofuel production in major biofuel producing countries and in the world .................................. 2
Table 1.2 Lignocellulosic ethanol plants in Canada and their capacity ................................................................. 3
Table 2.1 Pretreatment processes of biomass ............................................................................................................. 12
Table 2.2 Brief summary of energy consumption in distillation processes .............................................................. 15
Table 2.3 The LC GHG emission/energy consumption of ethanol produced by thermochemical conversion process .......................................................................................................................... 33
Table 2.4 Tax credits on ethanol in various provinces in Canada ............................................................................. 34
Table 2.5 Summary of the reported cost of ethanol produced from different feedstocks (biochemical conversion) .................................................................................................................................. 38
Table 2.6 Summary of the reported cost of ethanol from different feedstock and energy efficiency (thermochemical conversion) ....................................................................................................... 40
Table 3.1 Mill residues production in Canada in 2004 (ODt: Oven dry tonnes) .................................................... 43
Table 3.2 Volatile matter, fixed carbon, and ash content in selected biomass (dry basis) ........................................ 43
Table 3.3 Potential feedstocks and their major components ....................................................................................... 44
Table 3.4 Chemical composition of different feedstock .......................................................................................... 44
Table 4.1 Summary of parameters for which data are collected from the literature ................................................ 53
Table 4.2 Summary of the reported cost of ethanol produced from different feedstock ........................................ 55
Table 4.3 Ethanol yield from wheat straw ................................................................................................................ 56
Table 5.1 Scenarios of this study. ............................................................................................................................. 63
Table 5.2 Summary of parameters for which data are collected from literature ....................................................... 66
Table 6.1 Land areas in Ontario, ha ....................................................................................................................... 77
Table 6.2 Land classes, soil types and miscanthus yield ......................................................................................... 77
Table 6.3 Scenarios of this study. ............................................................................................................................. 78
Table 6.4 Summary of parameters for which data are collected from literature ..................................................... 79
Table 7.1 Land area under different tillable land classes and various regions in Ontario, ha .............................. 92
Table 7.2 Scenarios of this study ............................................................................................................................. 92
Table 9.1 Components of different feedstock ....................................................................................................... 114
Table 9.2 Ethanol yield from biosyngas fermentation ............................................................................................ 116
Table 9.3 Summary of parameters for which data are collected from literature or estimated ........................................ 118
List of Figures

Figure 1.1 Contribution of this study ........................................................................................................... 9
Figure 2.1 Schematic diagram of ethanol production process from syngas.................................................. 27
Figure 3.1 Stages of an LCA (ISO, 2006) .................................................................................................. 42
Figure 3.2 System boundary of this study ................................................................................................. 45
Figure 3.3 Structure of the LCIA method based on endpoint modeling (LIME2) ..................................... 47
Figure 4.1 Schematic diagrams of the life cycle of wheat straw and the system boundary of this study .... 50
Figure 4.2 Schematic diagram of ethanol production process from biomass ........................................... 51
Figure 4.3 Energy, emission and cost breakdown of the life cycle of ethanol produced from wheat straw... 54
Figure 4.4 Effect of ethanol yield on net energy consumption, emission and production cost of ethanol .... 57
Figure 4.5 Effect of feedstock cost on the production cost of ethanol ....................................................... 58
Figure 4.6 Effect of plant capacity on the production cost and emission of the life cycle of ethanol ........ 58
Figure 4.7 Effect of feedstock cost on the emission of the life cycle of ethanol ....................................... 60
Figure 4.8 Effect of system boundary and the ethanol yield on life cycle GHG emission of ethanol ......... 60
Figure 4.9 Effect of carbon sequestration and ethanol yield on the life cycle GHG emission .................. 61
Figure 5.1 Schematic diagrams of the LC of sawdust and the system boundary of this study .................. 64
Figure 5.2 Energy breakdown of the life cycle of ethanol ....................................................................... 67
Figure 5.3 Emission breakdown of the life cycle of ethanol ..................................................................... 68
Figure 5.4 Effect of carbon sequestration on the net emission of the life cycle of ethanol ..................... 69
Figure 5.5 Cost breakdown of the life cycle of ethanol ............................................................................. 70
Figure 5.6 Effect of the change in energy consumption at different stages on net energy consumption .... 71
Figure 5.7 Effect of the change in energy consumption at different stages on net emission (kg-CO₂ e/L) .... 71
Figure 5.8 Effect of the change in energy consumption at different stages on net cost ($/L) ...................... 72
Figure 5.9 Effect of the changes in feedstock- and fixed cost on the production cost of ethanol ............ 72
Figure 6.1 Transportation fuel consumption and contribution of ethanol in Canada .............................. 75
Figure 6.2 Different regions in Ontario, Canada ....................................................................................... 76
Figure 6.3 Different regions and land classes in Ontario, Canada ............................................................. 76
Figure 6.4 Schematic diagrams of the life cycle of sawdust and the system boundary of this study .......... 80
Figure 6.5 Energy breakdown of the life cycle of ethanol derived from miscanthus ............................... 83
Figure 6.6 Emission breakdown of the life cycle of ethanol derived from miscanthus ............................ 84
Figure 6.7 Cost breakdown of the life cycle of ethanol ............................................................................ 85
Figure 6.8 Effect of the variation in transportation distance and pretreatment energy consumption on the net energy consumption (MJ/L) .............................................................................................. 87
Figure 6.9 Effect of the variation in transportation distance and pretreatment energy consumption on the net emission and production cost .................................................................................. 88
Figure 6.10 Effect of feedstock and fixed cost (S/L) ................................................................. 88
Figure 6.11 Effect of carbon dynamics on the net emission of the life cycle of ethanol ....................... 89
Figure 7.1 Feedstock transportation distance at different location in Ontario .................................... 93
Figure 7.2 Energy breakdown of the life cycle of ethanol (Southern Ontario) .................................. 94
Figure 7.3 Net energy consumption at different location in Ontario ................................................. 95
Figure 7.4 Emission breakdown of the life cycle of ethanol (Southern Ontario) ................................. 96
Figure 7.5 Net emissions at different location in Ontario ............................................................... 96
Figure 7.6 Cost breakdown of the life cycle of ethanol (Southern Ontario) ...................................... 97
Figure 7.7 Net production cost at different location in Ontario ...................................................... 98
Figure 7.8 Effect of ethanol plant capacity on production cost and emission ..................................... 99
Figure 7.9 Effect of ethanol plant capacity on production cost and emission ................................... 100
Figure 7.10 Effect of the variation of different parameters on net energy consumption (MJ/L) .......... 101
Figure 7.11 Effect of the variation of different parameters on net emission ....................................... 101
Figure 8.1 Photograph of the developed reactor .............................................................................. 104
Figure 8.2 Schematic diagram of the gas chamber (not to scale) ...................................................... 105
Figure 8.3 Photograph of the developed gas chamber ......................................................................... 105
Figure 8.4 Photograph of the experimental setup .............................................................................. 108
Figure 8.5 Schematic diagram of the experimental setup of this study ............................................. 108
Figure 8.6 pH and temperature profile of the fermentation broth .................................................... 110
Figure 8.7 Mass spectra of the effluent ............................................................................................ 111
Figure 9.1 Schematic diagram of the system boundary of this study ................................................ 113
Figure 9.2 Energy consumption at various stages of the LC of ethanol ........................................... 119
Figure 9.3 Emission at different stages of the LC of ethanol ............................................................ 120
Figure 9.4 Production cost at different stages of the LC of ethanol ................................................ 121
Figure 9.5 Effect of transportation and pretreatment on net energy consumption ............................ 122
Figure 9.6 Effect of transportation and pretreatment on emission and cost ....................................... 123
Figure 9.7 Effect of the variation of gasification and heat recovery on net energy consumption (MJ/L) .... 123
Figure 9.8 Effect of the variation of gasification and heat recovery on emission and cost .................. 124
Figure 9.9 Effect of the variation of fermentation and distillation on net energy consumption (MJ/L) .... 125
Figure 9.10 Effect of variation of fermentation and distillation on emission and cost ....................... 125
Figure 9.11 Effect of variation of fixed and feedstock cost on production cost ($/L) ............................. 126
Figure 9.12 Effect of CGE on GHG emissions and production cost .................................................. 126
Chapter 1

Introduction

1.1. Rationale

The global energy demand was 424 EJ/year in 2000 and is increasing at the rate of 2.2% per year (Lal, 2009) and the world’s total primary energy supply was reported to be 479 EJ in 2005 (GBEP, 2007). With existing technologies and consumption patterns, global energy demand could double by 2050 due to the combination of population and economic growth (UNEP, 2007). Greenhouse gas (GHG) emissions, which have increased remarkably due to tremendous energy use liable for global warming, and perhaps the most serious problem that humankind faces today. The growing concerns about climate change, rising costs of fossil fuels and the geo-political uncertainty associated with possible interruption of current fossil fuel-based energy supplies have motivated individuals, organizations and nations to seek clean and renewable substitutes. Liquid biofuels (ethanol and biodiesel) are widely recognized alternatives to fossil fuels. Table 1.1 represents the projected biofuel production in different regions. Renewable energy not only reduces the reliance on foreign oil and improves energy security, but also provides significant environmental benefits and enhances rural economies (Kim & Dale, 2003; Spatari et al., 2005; Farrell et al., 2006). In contrast, this rapid expansion affects virtually every aspect of the field crop sectors and there remain an inevitable conflict between the increasing diversion of crops or crop land for fuel instead of food (Liew et al., 2013). Biofuels contain low sulphur, noted to be nontoxic, biodegradable and can reduce harmful GHG, carbon monoxide, hydrocarbons and particulate matter (Mata et al., 2010).

The transportation sector in Canada accounts for about 25% of the nation's energy use and the major part of this energy (99%) comes from fossil fuels (NRC, 2013). In 2009, Canada committed to reduce total GHG emissions by 17% from 2005 levels by 2020. The Renewable Energy Regulation (SOR/2010-189) was enacted (came-into-force from July 1, 2011) in Canada which requires fuel producers and importers of gasoline to have renewable fuel content of at least 5% distillates (by volume) that they produce and import yearly (Environment Canada, 2010), which generates a considerable demand on biofuels. The Government of Canada also offers $0.10/L and $0.26/L operating incentive for ethanol and biodiesel, respectively, for up to seven consecutive years (Biofuelnet, 2013). Consequently, the interest in biofuels is expanding. The cellulosic ethanol processing plants in Canada and their production capacity is reported in
Table 1.2. First generation biofuels are produced from food or feed grains, and thus compete with food or feed and contribute to higher food prices (Yang et al., 2009; Kazi et al., 2010a; Mueller et al., 2011; Liew et al., 2013). Consequently, production of second/third generation biofuels from lignocellulosic biomass (hereafter referred to biomass) has been emphasized, because it does not compete with food or feed (Zaldivar et al., 2001; Gray et al., 2006; Hahn-Hägerdal et al., 2006; Cardona & Sánchez, 2007; Sánchez & Cardona, 2008).

Table 1.1 Projected biofuel production in major biofuel producing countries and in the world

<table>
<thead>
<tr>
<th>Country/Region</th>
<th>Biofuels</th>
<th>Projected production or consumption in different years, L (×10⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>2013</td>
</tr>
<tr>
<td>World</td>
<td>Ethanol</td>
<td>113853.8</td>
</tr>
<tr>
<td></td>
<td>Biodiesel</td>
<td>28507.8</td>
</tr>
<tr>
<td>Brazil</td>
<td>Ethanol</td>
<td>28684.5</td>
</tr>
<tr>
<td></td>
<td>Biodiesel</td>
<td>2587.0</td>
</tr>
<tr>
<td>USA</td>
<td>Ethanol</td>
<td>55769.8</td>
</tr>
<tr>
<td></td>
<td>Biodiesel</td>
<td>6057.5</td>
</tr>
<tr>
<td>Canada</td>
<td>Ethanol</td>
<td>1605.0</td>
</tr>
<tr>
<td></td>
<td>Biodiesel</td>
<td>487.8</td>
</tr>
<tr>
<td>Europe</td>
<td>Ethanol</td>
<td>7048.5</td>
</tr>
<tr>
<td></td>
<td>Biodiesel</td>
<td>11287.6</td>
</tr>
<tr>
<td>Argentina</td>
<td>Ethanol</td>
<td>497.3</td>
</tr>
<tr>
<td></td>
<td>Biodiesel</td>
<td>2697.1</td>
</tr>
</tbody>
</table>

Data source: OECD-FAO, 2013

Several methods have been used in producing biofuels from biomass. Ethanol has been produced by either biochemical processes (hydrolysis) or thermochemical processes (gasification/pyrolysis of biomass to syngas followed by biosynthesis or chemical synthesis). Traditionally, ethanol production from biomass involves different steps of pretreatment, acid/enzymatic hydrolysis (saccharification), fermentation and distillation. However, the commercialization of ethanol production from biomass has been hindered mainly by the prohibitive cost of the expensive and inefficient pretreatment, and saccharification and distillation methods. Each process has its strengths and weaknesses. Biosynthesis of syngas results in poor mass transfer.
properties of gaseous substrates and low ethanol yield (Munasinghe & Khanal, 2010). Conversely, higher ethanol yield was reported in this process (Clausen & Gaddy, 1993). Biosynthesis is a two-stage process consisting of biomass gasification followed by microbial fermentation of syngas into ethanol. This process may offer distinct advantages (utilization of whole biomass including lignin, irrespective of biomass quality, elimination of complex pretreatment steps and costly enzymes, higher specificity of biocatalysts, independence of the \( \text{H}_2/\text{CO} \) ratio, aseptic operation of syngas fermentation, bioreactor operation at ambient conditions, no issue with inorganic catalyst poisoning due to trace sulphur containing gas) over both hydrolysis-fermentation and gasification-catalytic synthesis (high pressure, temperature, expensive metallic catalyst and complex gas cleaning). Traditional fermentations rely on carbohydrates as the carbon and energy sources for the microbial growth; however, syngas fermentation utilizes microorganisms (especially, the \textit{Clostridium} family) capable of metabolizing syngas into ethanol and other valuable chemicals in an inexpensive liquid substrate. However, poor mass transfer between gaseous and liquid substrates is one of the most significant challenges for this process.

Table 1.2 Lignocellulosic ethanol plants in Canada and their capacity

<table>
<thead>
<tr>
<th>Company</th>
<th>Location</th>
<th>Feedstock</th>
<th>Capacity, (10^6) L/y</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enerkem Inc.</td>
<td>Westbury, QC</td>
<td>Wood waste from used utility poles, RDF</td>
<td>5</td>
<td>Existing</td>
</tr>
<tr>
<td>Iogen Corp.</td>
<td>Ottawa, ON</td>
<td>Wheat Straw, Oat Straw, Barley Straw, Bagasse</td>
<td>2</td>
<td>Existing</td>
</tr>
<tr>
<td>Enerkem/GreenField - Varennes cellulosic Ethanol LP</td>
<td>Varennes, QC</td>
<td>RDF, C&amp;D debris</td>
<td>38</td>
<td>Proposed</td>
</tr>
<tr>
<td>Mascoma Corp. Drayton Valley</td>
<td>Drayton Valley, AB</td>
<td>Hardwood</td>
<td>72</td>
<td>Proposed</td>
</tr>
<tr>
<td>Nipawin Biomass Ethanol New Generation Co-operative Ltd.</td>
<td>Nipawin, SK</td>
<td>Wood waste, Straw</td>
<td>100</td>
<td>Proposed</td>
</tr>
<tr>
<td>Woodland Biofuel Inc.</td>
<td>Sarnia, ON</td>
<td>Wood waste</td>
<td>0.5</td>
<td>Proposed</td>
</tr>
</tbody>
</table>

Source: EPM, 2014
Although the thermochemical process produces ethanol in large quantities, it requires expensive catalysts and high operating pressure (Subramani and Gangwal, 2008). Many researchers have studied ethanol production processes from syngas either by biosynthesis or catalytic synthesis process (Ruth, 2005; Martchamadol, 2007; Clausen & Gaddy, 2008; Munasinghe & Khanal, 2010) except for few examples (Foust et al., 2009; Mu et al., 2010). Bioenergy systems have also been modeled with Aspen Plus and evaluated to estimate production cost and environmental impacts of bioenergy. GHG emissions and production cost of biofuels were reported to be dependent on both technical and economic parameters, such as the cost and choice of feedstock, conversion technologies and value of coproducts/byproducts (Wyman, 1994; Ballerini et al., 1994; Wooley et al., 1999a; Aden et al., 2002; Mabee et al., 2006; Aden, 2008; Dutta et al., 2010a; Balat, 2011). Thus, a wide variation was reported in the case of GHG emissions and production cost. The cost of cellulase was the major expense when producing lignocellulosic ethanol with conventional technology (Singh & Kumar, 2010) and contributed about 40–55% of the enzymatic ethanol production cost. Distillation, enzyme production and pretreatment were reported to be the main contributor to energy consumption and GHG emissions in the LC of ethanol produced by conventional technology (Roy et al., 2012a,b; Orikasa et al., 2009). The cost effective and innovative fermentation strategies integrated in the technology chain of gasification and gas cleaning combined with syngas fermentation, and catalytic synthesis could significantly improve the overall economics of ethanol from biomass.

Life cycle assessment (LCA) is a tool for evaluating environmental effects of a product, process, or activity throughout its LC. The key objective of an LCA study is to provide as complete a portrait as possible of energy consumption, environmental impacts, economic viability and their rebound effects, hence enable effective planning for a sustainable society. This study evaluated the LC of ethanol to estimate net energy consumption and GHG emissions to identify the hotspots, improve the production process, and determine if environmentally friendly ethanol can be produced from biomass. It is also known that environmental information generated through an LCA, while useful, does not always provide a sufficient basis for making a sound decision on an investment. The cost analysis along with the estimation of GHG emissions broadens the process of making sound decisions. Therefore, the production cost of ethanol has also been estimated with both fixed costs (straight line depreciation on installation, labor, maintenance and interest on investment) and variable costs (feedstock, yeast/bacteria, utilities
and waste management). The Aspen Plus process modeling has also been used for steady-state simulation (for syngas composition and syngas production to calculate the cold gas efficiency). Sensitivity analyses were also conducted to determine the acceptability, profitability and risk on investment if any. Finally, the results were interpreted to communicate to the stakeholder, environmental activist and policy makers, which may help investor and policy maker’s decision and draw more investment in this sector.

1.2. Objectives

The goal of this research was to investigate the technical feasibility of ethanol derived from biomass (crop/forest residues and energy crops) by hybrid thermochemical and biochemical/chemical processing, considering innovative technologies [enzymatic hydrolysis: pretreatment (CaCCO: calcium capturing by carbonation), vacuum extractive fermentation and distillation; biosynthesis: with/without chemical looping gasification (CLG) of torrefied and non-torrefied biomass]. At first, the conventional ethanol production processes were evaluated to have the baseline information and then Aspen Plus simulation software has been used to gather required data (especially for the gasification processes). Finally, the LC of ethanol produced by the above mentioned innovative technologies have been evaluated by using the LCA methodologies (centering on net energy consumption, GHG emissions and production cost) to determine the environmentally preferable and economically viable energy pathway for Ontario, Canada. This study developed/identified environmentally preferable and economically viable innovative technology (either biochemical or thermochemical) for lignocellulosic ethanol, which is renewable and clean, thus help in reducing GHG emissions from the present energy sector in Canada, may enable to compete economically and technologically in the world ethanol markets, and contribute to improve rural economy in Ontario, Canada.

The specific objectives of this study were:

i. Evaluate the LC of ethanol produced by conventional /traditional technology (enzymatic hydrolysis).

ii. Develop a bioreactor for syngas fermentation into ethanol.

iii. Evaluate the LC of ethanol produced from syngas (biosynthesis). Both torrefied and non-torrefied biomass were used for a novel CLG and steam gasification (without CLG) processes.

iv. Determine the LC cost of ethanol.
1.3. **Scope and limitation of this research**

This research consists of four individual objectives, the scope of those are explained below.

i. Three types of feedstocks (wheat straw, sawdust and miscanthus) have been selected for enzymatic hydrolysis process. The LC of ethanol produced from these feedstocks by enzymatic hydrolysis process was evaluated based on the estimated and literature data. Ontario specific data were collected from the literature for miscanthus cultivation. All those data were neither site nor country specific nor from the same plant size. The plant capacity was considered to be 20000 kL/yr. The yearly operation period and life span of the processing plant was assumed to be 350 days and 20 years, respectively (Dutta et al., 2011; Huang et al., 2009; Wu et al., 2006). Some optimistic literature data has also been used in this study, especially the enzyme production.

ii. Mass transfer between liquid and gaseous substrates hinders the syngas fermentation into ethanol. The bioreactor has been developed as a part of this study to improve the mass transfer by incorporating an innovative gas supply system. In addition to this, a membrane separation system has also been added to the reactor to extract the effluent excluding the microorganism. The reactor has been tested with only CO instead of syngas (60%CO; 35%H\textsubscript{2} and 5%CO\textsubscript{2}) to prove the concept.

iii. The torrefied and non-torrefied biomass have been considered for gasification (with or without CLG) processes. Thermal degradation experiments have been conducted with TGA to determine the effectiveness of CLG. Aspen Plus simulation at equilibrium condition has been used to generate data for syngas composition and volume to calculate the cold gas efficiency, thus the ethanol yield. The estimated and literature data have been used to evaluate the LC of ethanol produced by gasification-biosynthesis process considering the plant capacity of 20000 kL/yr.

iv. The production cost has been determined based on both the fixed and variable costs. The life span of an ethanol plant and an operation period was assumed to be 20 years and 350 days per year, respectively (Dutta et al., 2011; Huang et al., 2009; Wu et al., 2006). Both the estimated and literature data have been used to determine the production cost.
1.4 Novelty of the research

This research consists of both analytical and theoretical analysis (LCA: policy analysis) which are thought to be a novel approach.

1.4.1 Bioreactor development

A novel continuous stir-tank bioreactor (consists of innovative gas supply and effluent extraction processes) has been developed to produce ethanol from syngas by using microorganism. Innovative systems for syngas supply and ethanol extraction have also been developed to improve gas-liquid mass transfer and reuse of microorganism. The research also attempted to produce ethanol from syngas by using the developed bioreactor.

1.4.2 Chemical looping gasification (CLG)

Biomass characteristics have been determined at the laboratory, and those properties were applied for further studies. A macro-reactor (QWM: Quartz wool matrix) was used for the torrefaction process. The thermal degradation properties were also determined. The weight loss and heat flow during the degradation process were monitored in a micro-reactor (TGA-FTIR).

The CLG concept consists of two fluidized bed reactors (operate parallelly), which were functioning as calciner and gasifier. In the calciner, limestone was calcined. Lime was then circulated to the reactor (gasifier), where the lime sorbent was carbonated in parallel with the gasification reactions, tying up most of the CO$_2$ as CaCO$_3$. The CaCO$_3$ was then recirculated to the calciner, acting as a regenerator. This looping concept has definite economic promise, and was particularly attractive in the gasification processes, where it has added benefits - shifting the equilibrium to yield more hydrogen, releasing heat in the reactor (where the main reactions were endothermic), reducing loss of activity, and decreasing tar formation, at the same time capturing CO$_2$ produced during gasification.

Aspen Plus (V7.3) simulation software has been used to determine the syngas productivity and gas composition at equilibrium condition for treated (torrefied) and untreated feedstock with (CLG: chemical looping gasification) or without CO$_2$ capture. The novelty of the CLG process lies in the generation of relatively pure H$_2$ from biomass on a continuous basis, while CO$_2$ produces as a byproduct using steam as the gasifying agent. Another unique feature of the process is internal regeneration of the sorbent, fouled in the gasifier. The technology served the twin purpose of regenerating the sorbent, and generation of relatively clean syngas which is a novel approach. Utilization of torrefied biomass in ethanol production process is also known to
be a novel idea and is a novelty of this research. Thus, it will open up a new area of research on H₂-enriched gas production from biomass with in-process CO₂ capture. The specific new information generated by this study are as follows:

- Torrefied and non-torrefied feedstock has been used in the CLG process.
- Torrefied feedstock produced relatively better quality syngas.
- The use of torrefied feedstock in ethanol production process.

### 1.4.3 Life cycle assessment

The research evaluated the life cycle (LC) of ethanol produced from various feedstocks (wheat straw, sawdust and miscanthus), identified the feedstock and locations for ethanol industry in Ontario, Canada; especially, from energy crop (miscanthus) by using hybrid enzymatic hydrolysis and biosynthesis (syngas fermentation) processes. Both the technoeconomic and environmental evaluation were carried out by adopting the life cycle assessment (LCA) methodologies. The LCA methodologies also identify hotspots, and help to improve the production process. The main hotspots identified are either pretreatment, feedstock or gasification in the case of GHG emissions, depending on the type of feedstock, and scenario or the conversion technology. The LCA study on the ethanol production process which incorporated the torrefaction and the chemical looping gasification (CLG) is also a novel approach. The novel information generated in this study would be useful to researchers, investors and policy makers which might help Ontario compete economically and technologically in the world ethanol markets, and contribute to improve rural economies in Canada. The specific new and novel information generated by this study are as follows:

- This study generated new information on lignocellulosic ethanol in the context of Ontario.
- Identified the potential location for miscanthus based ethanol industry in Ontario.
- Life cycle of ethanol from torrefied and non-torrefied feedstocks with or without CLG has also been evaluated, which is a novel work of this kind.

### 1.5 Contribution of this research

The following diagram briefly represents the plan, background and contribution of this study (Fig. 1.1).
Research on torrefied biomass thermal degradation with or without CaO is limited.

Syngas fermentation with microorganism in an innovative reactor is scarce.

Steam gasification with or without CLG of treated or untreated biomass is scarce.

Studies on innovative gas supply and effluent extraction is limited.

Life cycle of ethanol from lignocellulosic biomass, wheat straw, sawdust, and miscanthus which received limited attention.

LCA of syngas fermentation (biosynthesis) is scarce.

Biomass characterization
Torrefaction of biomass in QWM fluidized bed reactor
Thermal degradation with or without CaO in a micro-gasifier (TGA)
Syngas fermentation with microorganism for ethanol

Syngas composition and syngas productivity are simulated by ASPEN Plus simulation software.

A novel bioreactor has been developed which consists of innovative gas supply and effluent extraction methods.

LCA and LCCA of ethanol produced from wheat straw, sawdust, miscanthus by enzymatic hydrolysis process

LCA and LCCA of ethanol derived from syngas (gasification-biosynthesis path) from treated or untreated biomass with or without CLG.

(QWM: quartz wool matrix, TGA: Thermo gravimetric analysis, LCCA: life cycle cost analysis)

Figure 1.1 Contribution of this study
1.6 Publications from this research

1.6.1 Publications in peer reviewed journals


1.6.2 Submitted manuscripts


1.6.3 Publications: Research presentations

Chapter 2

Literature Review

2.1. Ethanol production via biochemical conversion process (enzymatic hydrolysis)

2.1.1. Pretreatment

Pretreatment (either physical or chemical or both) is a prerequisite for biological conversion of biomasses (Lynd et al., 2008; Yang & Wyman, 2008) to make them more amenable to cellulose hydrolysis. Table 2.1 summarizes some pretreatment processes of biomass. Physical pretreatment refers to the size reduction of feedstock to increase enzyme-accessible surface areas (Zhu et al., 2009b) and chemical pretreatments remove or modify key chemical components that interfere with biomass cellulose saccharification, mainly hemicelluloses and lignin (Zhu et al., 2009a; Zhu & Pan, 2010). The potential pretreatment methods are: acid hydrolysis (concentrated or diluted), liquid hot water extraction, steam explosion, dilute acid-steam explosion, ammonia fiber explosion, lime pretreatment, etc. (Holtzapple et al., 1991; Mosier, et al., 2005a,b; Wyman et al., 2005; Yang & Wyman, 2008; Huang et al., 2009; Banerjee et al., 2010a; Manzanares et al., 2012). The acid pretreatments are reported to be toxic, hazardous, and corrosive, and require expensive reactors resistant to corrosion and also causes difficulties in waste management streams (Yang & Wyman, 2008).

High energy requirement and inhibitors generation are reported to be major drawback of steam explosion method (Hendriks & Zeeman, 2009; Banerjee et al., 2010a). The cost of ammonia, its handling, and recovery, and high energy consumption in recompression are the main bottlenecks in the process (Banerjee et al., 2010a). On the other hand, the alkaline pretreatment is reported to be more suitable and effective for herbaceous crops and agricultural residues (Bjerre et al., 1996; Chang et al., 2001; Rabelo et al., 2009). The hot water pretreatment avoids the formation of inhibitors and catalyze hydrolysis of cellulosic materials (Mosier et al., 2005a; Yu et al., 2010). It is also reported that cost of lime is relatively low and safer reagent compared with other alkalis and ammonia (Kaar & Holtzapple, 2000; Saha & Cotta, 2008). The CaCCO (calcium capturing by carbonation) process has also been developed to facilitate the pretreatment of biomass (Park et al., 2010; Shiroma et al., 2011). The author also noted that this pretreatment can also be applied at room temperature (7 days and 10% lime) to facilitate the conversion process. Pretreatment process contributes about 18–20% of the total cost of
biological production of cellulosic ethanol, which is greater than any other single step of the LC of ethanol (Aden et al., 2002; Yang & Wyman, 2008; Wooley et al., 1999b). Although the pretreatment to biomasses may vary depending on their characteristics (for example sawdust from softwood vs hardwood), the hotwater pretreatment (with 10% lime) has been adopted for this study (Park et al., 2010; Shiroma et al., 2011).

Table 2.1 Pretreatment processes of biomass

<table>
<thead>
<tr>
<th>Methods</th>
<th>Processes</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Physical</td>
<td>Milling: ball, hammer, two-roll, colloid, vibro etc.</td>
<td>High energy demand</td>
</tr>
<tr>
<td></td>
<td>Irradiation: microwave, electron-beam, gamma ray</td>
<td>Cannot remove lignin</td>
</tr>
<tr>
<td></td>
<td>Others: torrefaction, extrusion, pyrolysis, high pressure steam, hotwater etc.,</td>
<td>No chemicals are used</td>
</tr>
<tr>
<td>Physico-</td>
<td>Explosion: steam, ammonia fiber (AFEX), CO₂, SO₂</td>
<td></td>
</tr>
<tr>
<td>chemical</td>
<td>Alkali: NaOH, NH₄, (NH₄)₂S, Ca(OH)₂, RT-CaCCO, ammonia recycled percolation (ARP), liquid ammonia</td>
<td>Low cost</td>
</tr>
<tr>
<td></td>
<td>Gas: NO₂, ClO₂, SO₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acid: H₂SO₄, HCl, H₃PO₄</td>
<td>Complex downstream</td>
</tr>
<tr>
<td></td>
<td>Oxidizing: Hydrogen peroxide, wet oxidation, ozone</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Solvent extraction: Ethanol-water, benzene-water, ethylene glycol, butanol-water, swelling agents</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SPORL: Acid with sulfite or bisulfite</td>
<td></td>
</tr>
<tr>
<td>Biological</td>
<td>Fungi, actinomycetes</td>
<td>Low energy requirement, low treatment rate</td>
</tr>
</tbody>
</table>

Source: Taherzadeh & Karimi, 2008; Zhu et al., 2009a; Shiroma et al., 2011; Wilkins, 2011; Yoon et al., 1995.

2.1.2. Fermentation

Fermentation is the chemical decomposition process of a substance by bacteria, yeasts, or other microorganisms. This process is usually used in the preparation of alcohol, wine and liquor. The complex organic compounds, such as glucose, are broken down by the action of enzymes into simpler compounds in an anaerobic environment, known as an energy generating process, where organic compound act as both electron donor and acceptors (Stanbury, 2000). Microbial fermentation is classified into five groups based on the produce: microbial cell or biomass, microbial metabolites, microbial enzymes, recombinant products and biotransformation.
(Stanbury, 2000). Biochemical conversion process of biomass consists of four biological steps: enzyme production, enzymatic hydrolysis, hexose fermentation and pentose fermentation.

Fermentation of the pretreated biomass can be carried out in a variety of ways: separate hydrolysis and fermentation (SHF), simultaneous saccharification and fermentation (SSF), simultaneous saccharification and co-fermentation (SSCF), and consolidated bioprocessing (CBP) (Bisaria & Ghose, 1981; Boyle et al., 1997; McAloon et al., 2000; Lynd et al., 2005; Olson et al., 2012). Sugars produces in cellulose hydrolysis or saccharification are simultaneously fermented into ethanol in the SSF which greatly reduces inhibition to hydrolysis (Boyle et al., 1997; Krishna et al., 1998). Among these process SSF and SSCF are preferred because both unit operation can be completed in the same tank, reducing the cost (Wright et al., 1988; Olofsson et al., 2008; Balan et al., 2012). The conventional alcoholic fermentation is a typical inhibitory process, with cells growth rate affected by cellular, substrate and product concentration (Rivera et al., 2006) and must be maintained between 7–10°GL to prevent inhibitory effects (Junqueira et al., 2009a,b), beyond that reduce yield and productivity of the process (Silva et al., 1999). Vacuum extractive fermentation process allows simultaneous removal of produced ethanol from the fermentor, yields a highly concentrated wine, as a result reduces the amount of vinasse and energy consumption in fermentation and the subsequent distillation steps (Silva et al., 1999; Junqueira et al., 2009a,b).

2.1.3. Distillation and purification

Distillation is a process of separating a mixture of liquids based on the difference in boiling point temperature of components in a liquid mixture. Azeotropes are formed when the mixture has a vapor pressure lower than that of either binary component; such as ethanol boils at 78.5°C and water at 100°C and the azeotrope at 78.5°C. This technology as such cannot be used to separate azeotropes because they have the same composition in the vapour and liquid phase. Usually, azeotrops are separated based on the pressure-swing or extractive distillation using an additive, which are noted to be energy intensive. Pervaporation process significantly reduces the investment and operating cost (Sommer et al., 2002; Van Hoof et al., 2004; Yuan et al., 2011). Retrofit-extractive distillation achieved significant energy and cost savings compared to the conventional extractive distillation process (Duc Long & Lee, 2013). Liquid-liquid extraction and extractive distillation saves both energy and cost (Avilés Martínez, 2011).
The hydrous ethanol produced in the distillation undergoes purification stages to achieve anhydrous ethanol (99.5%). The industrial separation methods are azeotropic distillation with cyclohexane/benzene/pentane, extractive distillation with monoethyleneglycol (MEG)/gasoline/glycerol/salt-solvent mixtures, and adsorption with molecular sieves and processes that include the use of pervaporation membranes (Lynn & Hanson, 1986; Ulrich & Pavel, 1988; Pinto et al., 2000; Fu, 2004a,b; Gil et al., 2008; Dias et al., 2009; Gil et al., 2012). Some of these methods are no longer in use due to the high operating costs, operative problems and high energy consumption (Gil et al., 2008). MEG is a fossil and toxic solvent. Bioglycerol as a byproduct of biodiesel production process reported to be cheap and is not harmful to humans or to the environment, a suitable agent for the separation of ethanol–water mixtures (Lee & Pahl, 1985). Bioglycerol can be safely used to produce anhydrous ethanol for use in food or pharmaceutical industries (Dias et al., 2009). Zacchi and Axelsson (1989) noted that energy consumption in the distillation process significantly depend on the ethanol concentration in the feed material to a certain concentration and seems have no effect beyond 7.5% (wt).

Internally heated integrated distillation column (HIDiC) is noted to be a promising option to reduce energy consumption in the distillation process and reduce 60% of distillation energy compared with the conventional column system without raising capital cost (Olujic et al., 2003; Nakaiwa & Ohmori, 2009). Self-heat recuperation technology in azeotropic distillation process also reduced distillation energy consumption compared with the conventional azeotropic distillation (Kansha et al., 2009). Membrane-assisted vapor stripping process reduced at least 43% distillation energy requirement. Energy requirement varied from 2.5–8.9 MJ/kg of fuel grade depending on the ethanol concentration in the solution (Vane & Alvarez, 2008). Table 2.2 represents a brief summary of distillation parameters, energy consumption and cost.

2.1.4. Waste management

The stillage from the distillation column is sent to multieffect evaporator for partial dewatering. The main residual solid from lignocellulosic ethanol industry is lignin, and amount dependent of the feedstock, and pretreatment conditions. Usually, the waste stream is used to be separated into three feed streams: solids (lignin), biogas and syrup high in solids (Wooley et al., 1999; McAloon et al., 2000; Aden et al., 2002; Contreras et al., 2009; Greer, 2011). Lignin can be used to produce coproducts, such as high-octane hydrocarbon fuel additives and replace phenol in phenol formaldehyde resins (Hamelinck et al., 2005). Anaerobic digestion of the
wastewater produces a biogas high in methane. Biogas production is noted to be dependent on the COD level in the effluent entering the digester. The COD level is estimated to be 4800 mg/l (Shafiei et al., 2011). De Paoli et al. (2011) noted that biogas production is also dependent on the pretreatment conditions of biomass (178–554 L\textsubscript{N}\/kg volatile solids). The author also argued that ethanol residues can contribute about 5% of total energy consumption in Brazil. Methane production rate is reported to be 0.31–0.66 m\textsuperscript{3}/kg COD (Barta et al., 2010a; Greer, 2011; Gyenge et al., 2013). Biogas production from fermentation wort is reported to be 678 mL/kg slurry (Ofoefule et al., 2013). Burning these byproducts streams to generate either the heat or electricity required in the processes reduces not only the waste management costs, but may also lead to profit.

Table 2.2 Brief summary of energy consumption in distillation processes

<table>
<thead>
<tr>
<th>Methods</th>
<th>Ethanol concentration</th>
<th>Energy consumption</th>
<th>Cost</th>
<th>Remarks</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Membrane-assisted vapor stripping</td>
<td>1 wt%</td>
<td>8.9 MJ/kg</td>
<td>$0.098/L</td>
<td>Simulation</td>
<td>Vane &amp; Alvarez, 2008</td>
</tr>
<tr>
<td></td>
<td>5 wt%</td>
<td>2.5 MJ/kg</td>
<td>$0.042/L</td>
<td>Simulation</td>
<td>Van Hoof et al., 2004</td>
</tr>
<tr>
<td>Hybrid system (combining with pervaporation)</td>
<td>-</td>
<td>-</td>
<td>€0.130/kg</td>
<td>Experiment &amp; simulation</td>
<td></td>
</tr>
<tr>
<td>Vacuum extractive fermentation &amp; distillation</td>
<td>&gt;40 °GL</td>
<td>7.525 MJ/kg</td>
<td>-</td>
<td>Simulation</td>
<td>Junqueira, et al., 2009a</td>
</tr>
<tr>
<td>Extractive distillation (purification)</td>
<td>93 wt%</td>
<td>1.085 MJ/kg</td>
<td>-</td>
<td>Simulation</td>
<td>Dias et al., 2009</td>
</tr>
<tr>
<td>Conventional distillation</td>
<td>5.0 wt%</td>
<td>7.500 MJ/L</td>
<td>-</td>
<td>Simulation</td>
<td>Zacchi &amp; Axelsson, 1989</td>
</tr>
<tr>
<td></td>
<td>7.5 wt%</td>
<td>5.969 MJ/L</td>
<td>-</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The concentrated solids in syrup can be sent to the burner minimizing the load to the wastewater treatment. Utilization of excess solid residue for heat and power production had a considerable effect on the process economics (McAlloon et al., 2000; Sassner & Zacchi, 2008;
Sassner et al., 2008; Dutta et al., 2010a; Klein-Marcuschamer et al., 2010). Residual solid burning in the boiler produces ash as a waste. Ash recovered from biomass power industries can be dispersed on the field as fertilizer (Daugherty, 2001; Mani et al., 2010; Mandre et al., 2010). On the other hand ash disposal cost is reported to be $0.157–$2.2/t (Frederick Jr et al., 2008; Mani et al., 2010) depending on the transportation distance. Ash from biomass combustion in modern boilers or stoves primarily consists of non-combustible mineral constituents such as oxides or salts. Both fly ash and bottom ash have an economic value and could be used in cement, brick manufacturing, construction of roads and embankments (IRRI, 2007). Bottom ash from biomass can be used either as fertilizer or manufacturing of lightweight blocks (Pitman, 2006; BEC, 2011; Pérez-Villarejo et al., 2012). Nutrients and heavy metals leaching are reported in case of wood ash fertilization on peatland (Piirainen, 2005). On the other hand, fly ash is noted to be not only useful in the cement industry but also improve thermal and acoustic properties as well as the durability of concrete (Youngquist et al., 1996; Bhatti & Miller, 2003; Naik et al., 2006; Salas et al., 2009; Chatveera & Lertwattanaruk, 2011).

2.2. Life cycle assessment (LCA) of ethanol produced by biochemical conversion process

The enzymatic processes reduce global warming, acidification, eutrophication, photochemical ozone formation and energy use compared to traditional process, and LCA reveals in depth environmental properties of the processes have been studied (Jegannathan & Nielsen, 2013).

2.2.1. LCA of ethanol produced from agri-residues

Agri-residues are identified as the most abundant feedstock for lignocellulosic ethanol, have gained increasing attention as a renewable energy source. The life cycle (LC) of lignocellulosic ethanol extensively studied using the LCA methodology. Those studies noted that lignocellulosic ethanol can improve energy security and contributes significantly to abate GHG emissions (Fleming et al., 2006; González-García et al., 2009; Mabee & Saddler, 2010; Spatari et al., 2005; Vliet et al., 2009; Williams et al., 2009a; Wyman, 1994). The reduction in GHG emission is reported to be dependent on feedstock, conversion technology, utilization of coproducts and allocation methods (Spatari et al., 2005; Tilman et al., 2009; Luo et al., 2009a,b; Kaufman et al., 2010; Roy et al., 2012a,b). In contrast, greater GHG emissions are also reported compared to fossil alternative when the energy used to feed the biomass conversion process comes from carbon-intensive fossil sources (Fu et al., 2003).
Pourhashem et al. (2013) studied the alternate use of ethanol byproduct (lignin) and noted that the lowest emission from the LC of ethanol in case the lignin is used as a land amendment to replace the soil organic carbon followed by the replacement for coal and the highest for onsite electricity production. Enzyme is an important contributor to the net GHG emission of the LC of ethanol. The GHG emission from enzyme production is reported to be 0.26–0.40 kg CO₂ e/L for onsite and offsite production (Hong et al., 2013).

Although, biofuel production is beneficial to reduce fossil energy consumption and the global warming potential if biomass from cropping systems are utilized. The utilization of biomass for biofuels would also tend to increase acidification and eutrophication, primarily because significant nitrogen and phosphorus related environmental burdens are released from the soil during cultivation, if additional measures are not in place such as planting the cover crops (Kim & Dale, 2005). The lignocellulosic residues of banana fruit are also reported to be energetically feasible for ethanol production (Velásquez-Arredondo et al., 2010). Ethanol produced from grass clippings, corn stalks and other plants using future techniques is noted to be beneficial (Stolman, 2005). Bioenergy production from sugarcane bagasse revealed that the cogeneration option results in lower energy-related emissions (i.e. lower global warming, acidification and eutrophication potentials), however the fuel ethanol option is preferred in terms of resource conservation (since it is assumed to replace oil not coal), and scores better in terms of human and eco-toxicity if lead-bearing oxygenates are replaced (Botha and Blottnitz, 2006).

Ethanol produced from stover avoids 86–113% of GHG emissions, if E85 is used in fuel flexible vehicles instead of gasoline (Dutta et al., 2010; Stoeglehner & Narodoslawsky, 2009). The carbon neutrality of biomass and the use of residues may play an important role to abate more than 100% GHG emissions. Although fossil energy consumption is 102% lower and whereas hydrocarbon ozone precursors are reduced, emissions of CO, NOx, and SOx increased (Stoeglehner & Narodoslawsky, 2009). Emissions from stover ethanol are noted to be 65% lower for the near-term scenario (2010) due to the sharing of emissions with corn grains (Spatari et al., 2005). Emissions would be about 25–35% lower than the near-term scenario if the mid-term scenario (2020) is considered. The use of corn stover as a feedstock results in lower GHG emissions relative to conventional corn-grain ethanol (Kim & Dale, 2005, Williams et al., 2009), although this reduction is dependent on the allocation method used (Kaufman et al., 2010; Kim & Dale, 2005; Williams et al., 2009). The carbon intensity of ethanol is reportedly 10–44% that
of gasoline (Kaufman et al., 2010). The equipment capable of performing a single-pass harvest of stover becomes commercially available which help abating GHG emissions from stover harvest (Stoeglehner & Narodoslawsky, 2009). It is worthy to note that biomass combustions are assumed to be carbon neutral in all these studies.

Ozone layer and abiotic resources depletion decrease if gasoline is replaced by stover ethanol fuels (E10 and E85), which is not relevant to the allocation method. However, other impacts are larger except the global warming potential (GWP). The GWP reduces when mass/energy allocation is applied, but increases in the case of economic allocation (Luo et al., 2009a). In LCA studies, system boundaries cause a considerable variation since they not only vary according to start and end points (e.g. well to tank and well to wheel) but also over space and time in a way that can significantly affect energy and GHG balances (Botha & Blottnitz, 2006). The GWP of the lignocellulosic ethanol plant is noted as significantly (two fold) worse than that of the gasoline refinery, but its improved eco-efficiencies make it superior in terms of abiotic and ozone layer depletion potentials (Luo et al., 2010). In contrast, GHG savings from ethanol and Ethyl Tertiary Butyl Ether (ETBE) blending are reported to be positive, even the modification of the refinery sector is included (Croezen & Kampman, 2009).

Lignocellulosic ethanol produced by an enzymatic hydrolysis process shows that E10 improves the environmental performance in GHG emissions if the energy used in the steam generation process is derived from biomass instead of fossil fuel for pretreatment of feedstock, but has inferior performances in terms of acidification, eutrophication, winter smog, summer smog, carcinogenic substances, heavy metals, ozone layer depletion and solid waste (Fu et al., 2003). Bio-based products and fuels from straw may also be associated with environmental disadvantages due to land use or water eutrophication (Uihlein & Schebek, 2009). The environmental impacts predominantly result from the provision of hydrochloric acid and, to a smaller extent, from the provision of process heat. The optional acid and heat recoveries yield environmental impacts that are approximately 41% lower than those of the fossil counterparts. The net energy ratios (output energy divided by input energy from fossil fuels) of ethanol production systems from high yield rice plants are also noted to be positive, where whole rice plants are used (Koga & Tajima, 2011; Saga et al., 2010). Whole rice plant-based ethanol production systems improved energy efficiency and reduce GHG emission, because straw removals notably mitigate CH₄ emissions from the paddy field. The use of straw for energy
(CHP: combined heat and power) in ethanol production from wheat grains has significant benefits, but the eutrophication and atmospheric acidification impact categories were slightly unfavorable in some cases (Gabrielle & Gagnaire, 2008). The use of agricultural residues in a biorefinery saves GHG (50%) and reduces demand of fossil fuels (80%), where the best management practices are employed (Cherubini & Ulgati, 2010). However, biomass harvest rates must be carefully established to avoid any negative consequences on stability and productivity of land.

Although agri-residues are identified as abundant biomass resources, there debate is prevail regarding the actual amounts of residues could be removed from arable soils without any loss of quality, as well as the potential trade-offs in the overall energy chain compared to the use of fossil energy. The removal of wheat straw had little influence on environmental emissions from the field, and incorporating it in soil resulted in sequestration of only 5–10% of its C in the long term (Gabrielle & Gagnaire, 2008). It is noted that a certain portion of crop residues can be removed to produce ethanol without degrading the soil quality, which is dependent on the season, location, tillage and soil types (Nelson, 2002; Reijnders, 2008). Selecting residues that contain relatively high levels of available cellulose and hemicellulose for removal or returning suitable crop residues that are rich in refractory compounds may increase the scope for removal of crop residues for ethanol production (Reijnders, 2008). Sheehan et al. (2002) argued that up to 60% of the stover can be collected and converted into ethanol. However, Blanco-Canqui and Lal (2009) suggested that stover removal rate should be as low as 25%, beyond which soil fertility and structural stability would be negatively affected. In current agricultural practice, only 28% of the stover is harvested, and the rest is left on the field for soil fertility (Graham et al., 2007). Although biomass is recognised to be the most promising feedstock considering its great availability and low cost, the large-scale commercial production of lignocellulosic ethanol has yet to be implemented (Balat, 2011; Jensen et al., 2010), due to challenges and obstacles (cost, technology and environmental issues) needing to be overcome for the commercial production of lignocellulosic ethanol (Hatti-Kaul et al., 2007; Tan et al., 2008).

2.2.2. LCA of ethanol from energy crops, woody biomass and forest residues

The contribution of energy crops to total biomass energy is set to grow in the near future. The majority of LCA studies noted that bioenergy from energy crops reduces GWP and fossil energy consumption if the most common transportation biofuels are used to replace their
counterpart (Blottnitz & Curran, 2007; Cherubini & Jungmeier, 2010; Guo et al., 2010; Schmer et al., 2008; Sims et al., 2006) in all but a few studies (Pimente & Patzek, 2005; Searchinger et al., 2008). In contrast, acidification and eutrophication increased (Cherubini & Jungmeier, 2010), and including land use change effects in GHG balances, biofuels substituting fossil fuels may lead to increased negative impacts (Searchinger et al., 2008). Pimentel & Patzek (2005) reported that ethanol production from switchgrass and woody biomass requires 50 and 57% more fossil energy than the ethanol fuel produced, respectively. Cherubini et al. (2009) argued that these limitations could be partially overcome by developing second generation biofuels, derived from various lignocellulosic non-food crops and residues.

The estimated GHG emissions from cellulosic ethanol were 94% lower than those of gasoline, while genetic and agronomical improvement may further enhance the energy sustainability and biofuel yield of switchgrass (Schmer et al., 2008). Switchgrass fields are noted to be near-GHG neutral depending on the agricultural inputs (mainly N fertilization) and biomass yields. The use of ligneous biomass in cellulosic biorefinery is the main key to abetting GHG emissions rather than biofuels from annual crops, where processing energy is derived from fossil fuels (Farrell et al., 2006). Spatari et al. (2005) noted that emissions from energy crop (switchgrass) ethanol were 57% in the case of the near-term scenario (2010) and lower for an E85-fueled automobile compared to gasoline, on a CO₂ equivalent per kilometer basis. It could be 25–35% lower than those of the near-term scenario if the mid-term scenario (2020) were considered. Net energy gains from each hectare of biofuels are affected by the crop yield, conversion rate, and energy inputs to produce, deliver and process feedstock. The yearly net energy gain is noted to be greater than low-input switchgrass grown in small plots (Schmer et al., 2008).

Switchgrass is reported to be effective at storing soil organic carbon (SOC), not just near the soil surface, but also at depths below 30 cm where carbon is less susceptible to mineralization and loss (Liebig et al., 2005; Schmer et al., 2008; Wu al., 2008). Haney et al. (2010) noted that perennial grass systems had higher SOC and water extractable organic C (WEOC) than the annual corn system. Among perennial grass systems, switchgrass had the lowest SOC and WEOC. Nitrogen leaching is reported to be less for switchgrass than corn, but greater than in alfalfa–corn cropping systems (Vadas et al., 2008). Monti et al. (2009) analyzed the energy crops (switchgrass, giant reed and cynara) production in terms of energy and hectares,
and compared them with conventional wheat and maize rotation. The authors concluded that on average, 50% lower environmental impacts can be achieved by substituting conventional rotation with perennial crops. The benefits are reportedly dependent on biomass yield and the preference to a specific energy crop strongly depends on weighting sets that may change considerably in terms of space and time. In contrast, the switchgrass biochar-pyrolysis system is noted to be a net GHG emitter (+36 kg-CO$_2$/t feedstock) (Roberts et al., 2010).

Tilman et al. (2006) reported that biofuels derived from low-input high-diversity (LIHD) mixtures of native grassland perennials can provide more usable energy, greater GHG emission abatement, and less agri-chemical pollution than that of corn grain ethanol. LIHD biofuels are carbon negative because net ecosystem carbon dioxide sequestration (4.4 t/ha/year of carbon dioxide in soil and roots) is reported to be greater that the release during biofuel production (0.32 t/ha/year). LIHD biofuels can also be produced on agriculturally degraded lands and thus neither displaces food production nor cause any loss of biodiversity via habitat destruction. The environmental performance of ethanol produced from poplar biomass considering three ethanol applications (E10, E85 and E100) revealed that the impact potentials per kilometer driven by a mid-size passenger car, may help ease the exacerbation of global warming, and depletion of abiotic resources and the ozone layer by up to 62, 72 and 36%, respectively. However, acidification and eutrophication would intensify.

The economic and environmental aspects of high yield cropping systems are not necessarily conflicting, whereas under or over supply of nitrogen fertilizers leads to a decline in resource use efficiency (Brentrup et al., 2004a,b; Haas et al., 2001). Pedersen et al. (2005) reveal that in the USA, some long-term breeding of switchgrass has achieved large yields and may begin to contribute significantly to biofuel production. Genetically modified (GM) herbicide tolerant energy crops (sugar beet) are reported to be less harmful to the environment and human health than growing conventional crops, largely due to lower emissions from herbicide manufacture, transport and field operations (Bennett et al., 2004). These studies indicate that the social and environmental co-benefits, including carbon sequestration opportunities, will be drivers of future energy cropping uptake, although they must also be ecologically sustainable, environmentally acceptable and economically competitive with fossil fuels (Sims et al., 2006).
2.2.3. Land, water and other approaches in LCA of ethanol

The global population continues to grow geometrically, exerting great pressure on arable land, water, energy and biological resources to provide an adequate food supply while maintaining the ecosystem. The availability of land on which to grow biofuel crops without affecting food production or GHG emissions from land conversion is limited, hence land use efficiency should be maximized to achieve climate change goals. Although lignocellulosic ethanol supply chains are considered feasible for making GHG savings relative to gasoline, an important caveat is that if lignocellulosic ethanol production uses feedstock that cause indirect land-use change, or other resulting significant impacts, any benefit may be greatly offset (Slade et al., 2009). The effects of land use changes were noted as having a significant influence on the final GHG balance (about 50%) (Cherubini & Ulgiati, 2010). Jegannathan & Nielsen (2013) reported that land use savings can be achieved in industries where enzymatic processes save agricultural raw materials. On the other hand it becomes a trade-off where only fossil fuels and/or inorganic chemicals are conserved.

It is noted that converting croplands or grasslands to produce energy crops may actually lead to an increase rather than fall in GHG emissions (Fargione et al., 2008; Searchinger et al., 2008). The carbon debt (CO$_2$ emission) increases 17–420 folds compared to the gasoline if rainforests, peatlands, savannas, or grasslands are converted to produce food crop–based biofuels. In contrast, a little or no carbon debt is resulted if biofuels are produced from waste biomass or biomass grown on degraded and abandoned agricultural lands (Fargione et al., 2008). Brandão et al. (2011) studied the different land use systems for energy crops and noted that miscanthus is the optimal choice in terms of GHG emissions and soil quality compared to oilseed rape, short-rotation coppice willow and forest residues, but performed worse in the categories of acidification and eutrophication, while oilseed rape showed the worst performance across all categories. Stephenson et al. (2010) revealed that if willows are grown on idle arable land in the UK, or in Eastern Europe, and imported as wood chips into the UK to produce ethanol, this saves about 70–90% of GHG emissions compared to fossil-derived gasoline on an energy basis. In contrast, Searchinger et al. (2008) estimated GHG emissions from land-use changes by using a global agricultural model and reported that corn-based ethanol, instead of achieving 20% savings, nearly doubles GHG emissions over 30 years and increases GHGs for 167 years. Biofuels from switchgrass also increase emissions by 50%, if grown on U.S. corn lands. The
bioelectricity pathway outperforms the cellulosic ethanol across a range of feedstock, conversion technologies, and vehicle classes; producing 81% more transportation kilometers and 108% more emission offsets per unit area of cropland (Campbell et al., 2009).

Stoeglehner et al. (2009) noted that biofuels will only be able to contribute to a certain—may be relatively limited-extent, to an overall sustainable energy supply that will vary widely between regions, and the sustainability of biofuel production depends on the amount of land available. Direct land use changes, the choice of calculation methods, utilization of coproducts and the technical design of production systems affect the GHG balances and eutrophication for all biofuels (Börjesson & Tufvesson, 2010). The enhanced demand for biofuel crops under the EU Biofuel Directive has a strong impact on agriculture at a global and European level, while the incentive to increase production in the EU tends to increase land prices and farm income there and in other regions (Banse et al., 2011).

Several competing factors have need to be balanced, such as changes in land use (clearing tropical forests or using peatlands for crop cultivation) to negate any of the intended future climate benefits, and impacts on biodiversity. Also, developments in the agricultural sector for food and non-food crops will have important implications for water usage and its availability. The opportunity costs and rebound effects of land use changes must be addressed while considering any decision to assign land to biofuel feedstock (Pickett et al., 2008). Although biomass residues have been identified as a potential feedstock for bioenergy, the global mature forest area will decrease by 24% between 1990 and 2100, due to both population growth and wood biomass demand in developing regions, and may even disappear by 2100 in some developing regions, such as Centrally Planned Asia, Middle East and North Africa, and South Asia (Yamamoto et al., 2001). Consequently, the sustainability of biofuels depends on the selection of land on which feedstock are grown.

Reith et al. (2002) reported that the gross water consumption in the lignocellulosic ethanol production processes is 28–54 liters per liter of ethanol. The high water consumption results from the process water used in the Ca(OH)$_2$ pretreatment, washing of solids prior to enzymatic hydrolysis. In contrast, water consumption is noted to be only 0.3 L per liter of ethanol produced from agri-residues (corn stover or wheat straw), because the water requirement for crop production was attributed only to grains (Singh & Kumar, 2010). Biochemical or thermochemical conversion process of biomass into ethanol is expected to reduce GHG and air
pollutant emissions, but involve similar or potentially greater water demands and solid waste streams than conventional ethanol biorefineries. Despite current expectations, significant uncertainty remains regarding how well next-generation biofuels will fare in terms of different environmental and sustainability factors when derived on a commercial scale in the U.S. (Williams et al., 2009a). Although ethanol production consumes huge amounts of water, its impact on water resources is seldom included. The land to man ratio in developing countries is not as favorable as in developed countries, with far scarcer land resources creating serious problems in land resources management and possibly resulting in land degradation in such developing countries. The use of bioenergy also involves environmental challenges, for instance increased mono-cropping practices and greater fertilizer and pesticide use, which may jeopardize water and soil quality. Perhaps the main concern over land use change is the risk of large areas of natural forests and grasslands being converted to energy crop production, which not only threaten biodiversity and ecosystems, but also result in a possible increase in GHG emissions.

2.3. Ethanol production via gasification process

Thermochemical conversion technologies, including gasification and pyrolysis, heat biomass feedstock under low oxygen conditions to produce synthesis gas, or ‘syngas,’ which can be converted into various biofuels and biochemicals efficiently (Phillips et al., 2007; Brown, 2007; Henstra et al., 2007; Weber et al., 2010). The feedstock flexibility of gasification process gives advantages over other ethanol production processes from biomass. The bacterial fermentation noted to have advantages over catalytic conversion. The microbes are reported to be less sensitive to syngas impurities like sulfur and normally produce specific alcohols instead of mixtures (Munasinghe & Khanal 2010). The thermochemical processes are more effective especially in the case of plants with a high content of lignin (Möller et al., 2006).

2.3.1. Gasification

Gasification is reported to be very effective at converting non-carbohydrate biomass fractions and all other components of biomass into syngas with nearly equal efficiency and effectiveness (Phillips et al., 2007; Brown, 2007; Henstra et al., 2007; Weber et al., 2010; Aden et al., 2002; Wang & Yan, 2008; Pereira et al., 2012). Usually, feedstock is heated up to 700–1000°C in a gasification process where all components of feedstock are decomposed into syngas primarily containing H₂, CO, CO₂, CH₄, with very few residues (tar and ash). The syngas produced under anaerobic conditions is composed of 15–30% H₂, 10–65% CO, 1–20% CO₂, 0–
8% CH₄, and trace amounts of other gases depending on the type of feedstock (Wei et al., 2009; He & Zhang, 2011); however, with air gasification, the syngas may contain 40–50% N₂ (Hu et al., 2007; Wei et al., 2006; Rao et al., 2004; Eriksson et al., 2004; Datar et al., 2004; Clausen and Gaddy, 1993). The composition and quality of syngas from biomass are dependent on the type of gasifier, feedstock, gasifying agent, steam to biomass ratio, temperature, pressure, catalyst, etc. (He & Zhang, 2011; Carpenter et al., 2010). Gasification affects the calorific value of syngas. The increasing gasification pressure is noted to be economically more feasible than increasing the syngas pressure in downstream equipment (Passandideh-Fard et al., 2008). Low temperature operation results in higher selectivity (of Rh-Mn/SiO₂) to ethanol and lower methane formation (Hu et al., 2007).

Gasifiers are categorized based on the type of bed and type of flow. Bed type can be fixed-bed or fluidized bed and the flow types can be downdraft, updraft or cross-flow gasifiers. Fluidized bed gasifiers can be either bubbling bed or circulating fluidized bed. Downdraft gasifiers produce lower amounts of tar than do updraft (Kumar et al., 2009). Various bed materials (silica, alumina) and catalyst have also been used, which improve heat transfer and conversion rate of biomass in gasification processes (Acharya et al., 2009; Calvo et al., 2012). Low temperature operation results in higher selectivity (of Rh-Mn/SiO₂) to ethanol and lower methane formation (Hu et al., 2007). Increasing gasification pressure is noted to be economically more feasible than increasing the syngas pressure in downstream equipment (Passandideh-Fard et al., 2008).

Tars can deactivate catalysts/sorbents used for reforming and gas cleaning, are considered to be the major bottleneck of industrial biomass gasification (Bain et al., 2005). Tars formation is dependent on the type of gasifier, and gasification conditions. Tar concentration is reported to be 1–15, 20–100 and 0.01–1.5g/n-m³ for turbulent-bed, fixed-bed updraft and fixed-bed downdraft gasifier, respectively (Stevens, 2001). Catalytic tar cleaning process needs no additional energy input, efficiency and heating value losses are also kept at a minimum, and generates no tarry waste streams that need to be disposed of or recycled to the gasifier (Bridgwater, 1994, 1995; Simell et al., 1996). Solid oxide fuel cells (SOFCs) with Ni/GDC anodes have been successfully tested with biosyngas cleaning (Aravind & de Jong, 2012). A catalytic fluidized-bed steam reformer can be used to convert tars and hydrocarbons into syngas (Phillip, 2007).
Both the fixed-bed gasifier and fluidized-bed gasifier concepts are seen to be suitable for small to medium scale of thermal input operation (Aravind & de Jong, 2012). The fluidized bed gasifier requires a catalytic reformer at the downstream to clean the syngas (Bessou et al., 2011). Although entrained flow gasifier can produce syngas without a reformer, require energy intensive pretreatment (torrefaction/pyrolysis) of biomass in order to reach a sufficient conversion rate (Bessou et al., 2011). It is also noted that the entrained flow reactors are not easily downscaled efficiently and need much larger capacities (Aravind & de Jong, 2012).

Chemical looping gasification (CLG) process is noted to be able to produce relatively pure product gas (nearly 0% CO\textsubscript{2}) with \textit{in situ} CO\textsubscript{2} capturing in a circulating fluidized-bed (CFB) steam gasifier using CaO as the sorbent (Acharya, 2011; Acharya et al., 2009). This system consists of a bubbling fluidized bed (BFB), CFB and a cyclone (A-2-1). BFB and CFB have worked as a gasifier and regenerator, respectively. The cyclone was used to capture the solids. The regenerator is connected to the gasifier through the cyclone. The riser section of the CFB acted as a regenerator where the catalyst, CaCO\textsubscript{3} converted into CaO and CO\textsubscript{2} by the application of external heat typically at about 900°C. The product CaO and CO\textsubscript{2} is separated in the cyclone, and CaO fed to the loop-seal (gasifier) through the standpipe, and CO\textsubscript{2} is collected and supplied to the riser (regenerator) after filtration for continuous fluidization. The loop-seal acted as a BFB gasification system where biomass and steam were supplied and CaO fed from the cyclone. The loopseal is operated at 650°C where gasification with in-process CO\textsubscript{2} captured. The CaO is converted to CaCO\textsubscript{3} by absorbing CO\textsubscript{2} produced during gasification process was fed back to the regenerator to continue the cycle. Moreover, the hot CaO delivered to the gasifier/carbonator provided additional heat for the gasifier/carbonator vessel. In addition, heat releases by the exothermic carbonization reactions can supply most of the heat required by the endothermic gasification reactions (Acharya, 2011).

Thermodynamically, biosyngas can be converted into ethanol at 350°C and 30 bar (Spivey & Egbebi, 2007). The yield of ethanol depends upon the composition of biosyngas. Theoretically, one-third of the carbon from CO can be converted into ethanol in water gas shift reaction (Eq. 2.1), however two-thirds of the carbon from CO can be converted in an equimolar mixture of H\textsubscript{2} and CO (Eq. 2.3) (Munashinge & Khanal, 2010). The conversion rate of CO can be as high as 40%, yielding an alcohol mixture containing 70% ethanol (Cotter, 2007; Morrison, 2004). It is important to note that CO\textsubscript{2} can also be used by acetogens if H\textsubscript{2} is present (Eq. 2.2).
The overall stoichiometric reaction for alcohol synthesis is summarized in the following equation (Eq. 2.4). In a two-stage syngas fermentation process, stoichiometric evaluation revealed that the carbon and hydrogen recovery from the supplied carbon monoxide and hydrogen into ethanol is 28% and 74%, respectively (Richter et al., 2013) where the growth stage is operated at 5.5 pH and the production stage had lower pH than that of growth stage. Figure 2.1 depicts the stages of ethanol production process via biomass gasification and catalytic and microbial fermentation.

\[
\begin{align*}
6\text{CO} + 3\text{H}_2\text{O} & \rightarrow \text{C}_2\text{H}_5\text{OH} + 4\text{CO}_2 \\
6\text{H}_2 + 2\text{CO}_2 & \rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \\
6\text{CO} + 6\text{H}_2 & \rightarrow 2\text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2 \\
n\text{CO} + 2n\text{H}_2 & \rightarrow \text{C}_n\text{H}_{2n+1}\text{OH} + (n-1)\text{H}_2\text{O}
\end{align*}
\] (Eq. 2.1)

\[
\begin{align*}
6\text{H}_2 + 2\text{CO}_2 & \rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \\
n\text{CO} + 2n\text{H}_2 & \rightarrow \text{C}_n\text{H}_{2n+1}\text{OH} + (n-1)\text{H}_2\text{O}
\end{align*}
\] (Eq. 2.2)

\[
\begin{align*}
6\text{CO} + 6\text{H}_2 & \rightarrow 2\text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2 \\
n\text{CO} + 2n\text{H}_2 & \rightarrow \text{C}_n\text{H}_{2n+1}\text{OH} + (n-1)\text{H}_2\text{O}
\end{align*}
\] (Eq. 3)

\[
\begin{align*}
n\text{CO} + 2n\text{H}_2 & \rightarrow \text{C}_n\text{H}_{2n+1}\text{OH} + (n-1)\text{H}_2\text{O}
\end{align*}
\] (Eq. 4)

Source: Roy & Dutta, 2013

Figure 2.1 Schematic diagram of ethanol production process from syngas
2.3.2. Gas cleanup

Gas cleanup steps are crucial for preventing both catalyst fouling and poisoning in the subsequent alcohol synthesis steps (Gonzalez et al., 2012). Gas cleanup and conditioning remove the problematic tars, chars, particulate matters and other contaminants which cause slagging and downstream process inhibitions. Cyclones, adsorption columns, water or oil scrubbers and various types of filters are some of the common syngas refining units (Munasinghe & Khanal, 2010; Pereira et al., 2012). Catalytic steam reforming or thermal cracking has also been used for gas cleanup (Damartzis & Zabaniotou, 2011). Catalytic tar cleaning process needs no additional energy input, efficiency and heating value losses are also kept at a minimum, and generates no tarry waste streams that need to be disposed of or recycled to the gasifier (Bridgwater, 1994, 1995; Simell et al., 1996). Solid oxide fuel cells (SOFCs) with Ni/GDC anodes have been successfully tested with biosyngas cleaning (Aravind & de Jong, 2012).

2.3.3. Syngas synthesis into ethanol

The clean biomass syngas (biosyngas) is then converted into ethanol either by catalytic conversion or bacterial fermentation (biosynthesis).

2.3.3.1 Catalytic synthesis into ethanol

Both homogeneous and heterogeneous catalytic synthesis processes are used in the conversion of syngas into ethanol. The homogeneous catalytic synthesis process produces ethanol in large quantities, requires expensive catalysts, high operating pressure and tedious separation process (for catalyst). On the other hand, the heterogeneous catalytic processes suffer from low yield and poor selectivity (Subramani & Gangwal, 2008). The main catalyst groups are natural catalyst (dolomite and olivine), alkali (KOH, Na₂CO₃, CaCO₃, CsCO₃, ZnCl₂, NaCl etc.) and nickel-based catalysts (Mohammed et al., 2011; Acharya et al., 2009). A series of reactions take place (with syngas and catalyst) in the reactor yielding a mixture of alcohols that varies depending on the catalyst and reaction temperature and pressure. Reaction rates are noted to be quick and completed in seconds or minutes (Cotter, 2007; Morrison, 2004). The low specificity, high operating temperature and pressure, high sensitivity to toxic gases are the major setback for the chemical catalysts (Phillips et al., 1994; Vega et al., 1990; Worden et al., 1991).

2.3.3.2 Biosynthesis into ethanol

Bacterial fermentation has some advantages because microbes are less sensitive to syngas impurities like sulfur and normally produce specific alcohols instead of mixtures (Henstra et al.,
2007; Munasinghe & Khanal, 2010; Bredwell et al., 1999; Kundiyana et al., 2010), but result in poor mass transfer properties of gaseous substrates and lower ethanol yield (Munasinghe & Khanal, 2010; Wei et al., 2009). The yield is also dependent on the partial pressure of CO and the size of the fermentor (Kundiyana et al., 2010; Younesi et al., 2005; Hurst et al., 2005). In this route, mesophilic microorganisms produces short-chain fatty acids and alcohols from CO and H2, and hydrogen can be produced by carboxydotrophic hydrogenogenic bacteria which converts CO and H2O to H2 and CO2 (Henstra et al., 2007). The use of Clostridium ljungdahlii in the fermentation process of syngas improves mass transfer properties (BRI, 2008). Ethanol production with the Clostridium ljungdahlii is usually a mixture of two processes that occur at temperatures 37–39°C. The acetate production inhibits bacteria and lowers the pH that makes the bacteria shift to produce solely ethanol. The ideal pH and ethanol concentration for Clostridium ljungdahlii is noted to be 6 and 3% (greater strength is toxic for the bacteria) (Hensra et al., 2007). Other microorganisms (Clostridium autoethanogenum, Acetobacterium woodii, Clostridium carboxidivorans and Peptostreptococcus productus) are also used to ferment syngas into liquid fuel (Henstra et al., 2007; Heiskanen et al., 2007; Rajagopalan et al., 2002). Nontoxic surfactants and novel dispersion devices can enhance mass transfer (Worden et al., 1997), and resulting in higher ethanol yield in this process (Clausen & Gaddy, 1993). Some of the biological catalysts (Clostridium ljungdahlii, Clostridium autoethanogenum, Acetobacterium woodii, Clostridium carboxidivorans and Peptostreptococcus productus) are able to ferment syngas into liquid fuel more effectively than that of chemical catalysts (e.g., iron, copper or cobalt) (Heiskanen et al., 2007; Henstra et al., 2007). A brief list of different types of bacteria identified and used for biofuel production from syngas, and syngas fermentation parameters and ethanol yield are reported in the appendix (A-2-2 & A-2-3).

2.3.3.3 LCA of ethanol produced from biomass syngas (biosyngas)

The growing concern about sustainability of ethanol produced from biomass syngas prompted researchers to evaluating the LC of ethanol. The majority LCA studies on biosyngas to ethanol noted that thermochemical conversion process reduces GHG emissions (Tonini & Astrup, 2012; Mu et al., 2010; Jungmeier et al., 2007). Mu et al. (2010) studied the LC of ethanol from biosyngas (from wood chips) produced by indirectly-heated dual fluidized bed gasification technology and a modified Fischer-Tropsch catalyst molybdenum disulfide (MoS2) at atmospheric pressure. The LC material and energy required were modeled by Aspen Plus
simulation software and then the LC inventory data of material and energy have been extracted from SimaPro 7.1 and Ecoinvent 2.0 database to determine the environmental impacts of the thermochemical conversion process [gasification-synthesis combination has been modeled based on NREL report (Phillips et al., 2007) and different technological targets. The thermochemical process noted to have negative net fossil fuel consumption, consequently negative net GHG emissions (Mu et al., 2010; Grossmann & Martín, 2010) if plant is designed as energy self-sustained and no mixed alcohol separation unit installed (i.e., some syngas is diverted for heat and electricity generation). The co-product credit (mainly from electricity export) offsets the energy consumption and GHG emissions in the LC of ethanol. Otherwise thermochemical conversion process resulted in positive fossil fuel consumption and GHG emission (approximately 0.4–0.5 kg CO₂ e/L) (Mu et al., 2010).

The ethanol production processes were modeled with the mixed-integer nonlinear programming (MINLP) and implemented in the GAMS modeling system to optimize the systems (Grossmann & Martín, 2010; Martín & Grossmann, 2011). Ethanol yield was reported to be greater in low pressure gasification process than that of high pressure thus reduce production cost. Ethanol obtained from switchgrass via gasification (low pressure indirect gasification with steam: 0.26–0.75 bar; high pressure direct gasification with steam and oxygen: 2.1 bar; operating conditions are considered to be that of Phillips et al., 2007) and catalytic reaction/fermentation consumes either no energy or even produces it (Grossmann & Martín, 2010; Martín & Grossmann, 2011) because of the implementation of multieffect columns followed by heat integration (hot and cold streams) in the process. MINLP approach is also used to evaluate the LC (cradle to grave) of ethanol from wood chips considering the environmental and social criteria. The synthesis gas is cleaned, cooled and fermented by using Clostridium ljungdahlii microorganisms. This study concluded that ethanol production from forest wood waste is not sustainable because of low ethanol yield and high emissions mainly from fermentation and waste wood collection (Čuček & Kravanja, 2010).

The thermochemical conversion of forest residues into ethanol is energy self-sufficient where forest residues are assumed to be a waste product (i.e., only chipping and loading are attributed to forest residue-based E85) and no land use change is considered. The SimaPro (v.7.2) and Ecoinvent database (v.2.1) were used to evaluate the LC of ethanol and addressed the impact potentials of ethanol (E85) used in a mid-size passenger car and concluded that 43–57%
of GHG emission can be reduced compared to that of conventional gasoline if CO\textsubscript{2} sequestration is considered (i.e., approximately about 0.83 kg CO\textsubscript{2} e/L) (Hsu et al., 2010). In an updated study, ethanol produced by gasification of biomass reduced 65% of GHG emission with reference to gasoline if only the ethanol portion is considered. The GHG emission is estimated to be about 0.21 kg CO\textsubscript{2} e/L ethanol produced in that updated study (0.01 kg CO\textsubscript{2} e/MJ of ethanol; 21 MJ/L ethanol is assumed) (Hsu, 2012). Although the biorefinery system reduces CO\textsubscript{2} and CH\textsubscript{4}, releases more N\textsubscript{2}O emissions compared with a fossil fuel system thus has higher impacts in acidification and eutrophication (Cherubini & Jungmeier, 2010; Kim & Dale, 2005).

He and Zhang (2011) has designed, simulated and optimized thermochemical conversion process mainly by using Aspen Plus simulation software. The estimated energy requirement was 0.28 kWh/L ethanol. The syngas cleanup is an energy intensive process and one of the key issues in commercialization of the thermochemical conversion technology. It is noted that bioenergy system produced from forest residues (i.e., gasification and FT synthesis process) can save up to 88% GHG emission compared with a fossil fuel (Jungmeier et al., 2007). Corn stover ethanol blends (E85) offer substantial energy savings (94–95%) relative to those fueled with regular fossil gasoline and the cellulosic ethanol pathway mitigates 86–89% of GHG emissions (Wu et al., 2006). Farrell et al. (2006) also noted that cellulosic ethanol (switchgrass) reduces GHG by 88%. In contrast, energy shortage is reported in the thermochemical conversion processes (Zhang, 2008).

Tonini and Astrup (2012) evaluated the future energy systems for Denmark (fossil fuels; rapeseed based biodiesel; Fischer–Tropsch based biodiesel for 2030 and 2050) using the LCA methodology. The authors concluded that GHG emissions could be significantly reduced (from 68 to 17 Gg CO\textsubscript{2} e/PJ) by increased use of wind and residual biomass resources as well as by electrifying the transport sector. Increased share of wind power and replacement of fossil fuels with domestically available biomasses, and reduction of energy demand led to GHGs emissions savings in the future energy scenarios. It is also noted that introduction of energy crops for biofuels and the use of biofuels for heavy terrestrial transportation were responsible for most environmental impacts in the 2050 scenarios. Biodiesel production via Fischer–Tropsch is noted to be comparable with fossil diesel only for the global warming. In contrast, fossil diesel noted to be preferable over biodiesel for acidification, aquatic eutrophication and land occupation except global warming. Also, land occupation increased to a range of 600–2100×10\textsuperscript{6} m\textsuperscript{2} per PJ

31
depending on the amounts and types of energy crops introduced (Tonini & Astrup, 2012)). A comparative study of six different assessment scales and metric calculation techniques against the common biomass demand scenario revealed that assessment scale and metric calculation technique strongly influence the net GHG balance in woody biomass to energy conversion process (Galik & Abt, 2012).

Although same gasification technology is used in most of the reviewed studies a significant difference in GHG emission is observed. Table 2.3 represents a brief summary of the LCA studies concerning system boundary, conversion processes, energy consumption and GHG emissions. These studies indicate that the environmental impacts of ethanol are dependent on research targets, system boundary and assumptions, feedstock and conversion technology. It seems the environmental and social co-benefits, including land use and carbon sequestration opportunities will be drivers of future lignocellulosic ethanol, although they must also be ecologically sustainable, environmentally acceptable and economically competitive with fossil fuels.

2.4 Life cycle cost analysis (LCCA)

The production cost of ethanol is dependent on both technical and economic parameters, such as the subsidies/fit in tariff, cost of feedstocks, choice of feedstocks, energy consumption, conversion technology and efficiency, and the value of coproducts (Ballerini et al., 1994; Wyman, 1994; Aden et al., 2002; Mabee et al., 2006; Wu et al., 2006, 2008; Aden, 2008; Nechodom et al., 2008; Mark et al., 2009; Balat, 2011; Haro et al., 2012; Phillips et al., 2007; Dutta et al., 2010a; He & Zhang, 2011). The production cost of lignocellulosic ethanol is reported to be considerably higher than the market price of gasoline (Ballerini et al., 1994; Wu et al., 2008; Huang et al., 2009; Luo et al., 2010; Orikasa et al., 2009; Roy et al., 2012a,b; Roy & Dutta., 2013). It also noted that the lignocellulosic ethanol technology is not yet mature enough to be profitable on its own merits, consequently this industry is being subsidised to encourage its production achieving the GHG emission abatement targets. It is reported that biochemical conversion of biomass into ethanol requires lower investment compared to the thermochemical conversion process. Total investment for 150 MWth pant is reported to be MM$281 for biochemical conversion and MM$580 to MM$760 for thermochemical conversion process (Tunå & Hulteberg, 2014). Table 2.4 depicts the tax credit applied in Canada. The tax credit to liquid
biofuels is also prevailed in many other countries. Federal tax credit in the USA is reported to be $0.45/gallon (Murse, 2011).

Table 2.3 The LC GHG emission/energy consumption of ethanol produced by thermochemical conversion process

<table>
<thead>
<tr>
<th>Authors</th>
<th>System boundary</th>
<th>Feedstock, feed rate, cost &amp; yield</th>
<th>Gasifier type</th>
<th>Catalyst/ Bacteria</th>
<th>GHG emission kg CO₂ e/L (kWh/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He &amp; Zhang, 2011</td>
<td>Field to gate</td>
<td>Lignocellulosic biomass, 2455, 332</td>
<td>Indirect dual-bed gasifier</td>
<td>Co-Mo</td>
<td>(0.46)</td>
</tr>
<tr>
<td>Mu et al., 2010</td>
<td>Field to wheel</td>
<td>Wood chips, wheat straw, waste paper, corn stover, 2000, 270–359</td>
<td>Indirect-heating fluidized bed gasifier</td>
<td>Molybdenum disulfide (MoS₂)</td>
<td>0.4–0.5</td>
</tr>
<tr>
<td>Hsu et al., 2010</td>
<td>Field to wheel</td>
<td>Forest residues, 2000, 387–417</td>
<td>Indirect gasification</td>
<td></td>
<td>0.83^</td>
</tr>
<tr>
<td>*Hsu, 2012</td>
<td>Field to wheel</td>
<td>Forest residues, 2000, 387–417</td>
<td>Indirect gasification</td>
<td></td>
<td>0.21^^</td>
</tr>
<tr>
<td>Spath &amp; Dayton, 2003</td>
<td>Field to wheel</td>
<td>Wood chips, 2000, 0.27-0.39</td>
<td>Gasification</td>
<td>Bacteria</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Feedstock Rate, t/d</th>
<th>Yield, L/DT</th>
<th>Catalyst/ Bacteria</th>
<th>GHG emission kg CO₂ e/L (kWh/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lignocellulosic</td>
<td>2455</td>
<td></td>
<td>(0.46)</td>
</tr>
<tr>
<td>Wood chips</td>
<td>2000</td>
<td>Indirect dual-bed gasifier</td>
<td>Co-Mo</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>2000</td>
<td>Indirect-heating fluidized bed gasifier</td>
<td>Molybdenum disulfide (MoS₂)</td>
</tr>
<tr>
<td>Waste paper</td>
<td>2000</td>
<td>Indirect gasification</td>
<td>-</td>
</tr>
<tr>
<td>Corn stover</td>
<td>2000</td>
<td>Indirect gasification</td>
<td>-</td>
</tr>
<tr>
<td>Forest residues</td>
<td>2000</td>
<td>Indirect gasification</td>
<td>-</td>
</tr>
<tr>
<td>Wood chips</td>
<td>2000</td>
<td>Gasification</td>
<td>-</td>
</tr>
</tbody>
</table>

| t/d: ton/day; DT: dry ton; ^estimated based on the emission data from the graph and heating value of E85; ^^0.01 kg CO₂ eq./MJ; *ethanol portion only (Source: Roy & Dutta, 2013). |

2.4.1 Life cycle costing of ethanol produced by biochemical process

Vadas et al. (2008) noted that net energy production per hectare is greater for switchgrass than that of alfalfa-corn cropping systems, but may not return the potential income to farmers that alfalfa-corn could. The costs of cellulase and capital are the major expenses when producing lignocellulosic ethanol (Reith et al., 2002), while industrial cellulase contributes about 40–55% of the enzymatic cellulosic ethanol production cost. The estimated costs of producing ethanol from lignocellulosic residues (verge grass, wheat milling residues and woody energy crop/willow) are 0.75–0.99 €/L. The authors noted that the cellulase cost (assumed 0.51 €/L) would have to be reduced at least tenfold and the capital cost by 30% to achieve ethanol production costs comparable to those of ethanol from starch crops.
Table 2.4 Tax credits on ethanol in various provinces in Canada

<table>
<thead>
<tr>
<th>Province</th>
<th>Tax credits, ¢/L</th>
<th>Criteria for credit</th>
<th>Duration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alberta</td>
<td>9.0</td>
<td>No restriction on the source of ethanol</td>
<td>Five years from the start of an ethanol processing plant</td>
</tr>
<tr>
<td>British Columbia</td>
<td>14.5</td>
<td>Ethanol must be produced in BC; E85 to E100 and E5 to E25.</td>
<td>-</td>
</tr>
<tr>
<td>Ontario</td>
<td>14.7</td>
<td>No restriction on the source of ethanol</td>
<td>Until 2010</td>
</tr>
<tr>
<td>Saskatchewan</td>
<td>15.0</td>
<td>Ethanol must be produced in Saskatchewan</td>
<td>5 years</td>
</tr>
<tr>
<td>Quebec</td>
<td>~20</td>
<td>Ethanol must be produced in Quebec</td>
<td>1999-2012</td>
</tr>
<tr>
<td></td>
<td>20 (until August 2007)</td>
<td>Ethanol must be produced in Manitoba</td>
<td>No specific duration</td>
</tr>
<tr>
<td>Manitoba</td>
<td>15 (2007- 2010)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10 (2010- 2013)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Source: Olar et al., 2004

It is also noted that the production cost of cellulosic ethanol depends on feedstocks and their composition as well as plant capacity. The estimated production cost varies from about 0.38–0.48 US$/L (plant size: feedstocks consumption is 2000 t/day) (Huang et al., 2009; Searcy & Flynn, 2010). For the same plant capacity the production cost of ethanol from corn stover is reported to be 0.71–0.87 US$/L dependent on the assumed scenarios (Dutta et al., 2010a). The production cost is noted to be 0.56–0.77 US$/L depending on the feedstock and plant sizes (Gnansounou & Dauriat, 2010). The simulated production cost of ethanol is reported to be 0.94–1.20 US$/L which depends on the ethanol yield (Klein-Marcuschamer et al., 2010). The production cost is also noted to be dependent on the market price of fuels (Roy et al., 2012a; Zafeiriou et al., 2014).

The economic viability, GHG emission and economic performance of lignocellulosic ethanol under extreme weather conditions are also reported to be dependent on the availability of feedstock (weather condition) and the use of single or multiple feedstocks (Kou & Zhao, 2010. Wingren et al. (2003) noted that the production cost is also dependent on enzymatic processes.
The cost of ethanol produced from softwood based on simultaneous saccharification and fermentation (SSF), and separate hydrolysis and fermentation (SHF) are reported to be 0.57 and 0.63 US$/L, respectively. The main reason for SSF being lower was the lower capital cost and the overall higher ethanol yield. Major economic improvement in both SSF and SHF could be achieved by boosting income from the solid fuel coproduct, reducing energy consumption and recycling process streams. A techno-economic evaluation of the spruce-to-ethanol process, based on SO₂-catalysed steam pretreatment followed by simultaneous saccharification and fermentation with various process configurations, achieved an ethanol cost of about 0.38–0.50 €/L. Anaerobic digestion of the stillage with biogas upgrading was a demonstrably favorable option in terms of both energy efficiency and ethanol production cost (Barta et al., 2010a,b) and the contribution of enzyme is reported to be 0.04–0.05 €/L (Barta et al., 2010b).

Ballerini et al. (1994) concluded that technical and economic optimization of the pretreatment step, the total substitution of lactose by pentose hydrolysate as the main carbon source for enzyme production, and the recycling of a fraction of the enzyme, the incorporation of pentose in ethanol fermentation, and the utilization of by-products all reduce the production cost of lignocellulosic ethanol. The authors also noted that since ethanol from biomass is tax-exempted, it could compete with gasoline assuming a crude oil price of around US$50. In contrast, it is noted that with current technology, the production cost of cellulosic ethanol (0.75 $/L) is almost double compared to the market price of oil (0.48 $/L) and much of the optimism surrounding cellulosic ethanol has faded (Service, 2010). The externality (environmental and health) cost of ethanol is also reported to be dependent on the feedstock (Kusiima & Powers, 2010).

Hamelinck et al. (2005) stated that the combined effect of higher hydrolysis-fermentation efficiency (68%), lower specific capital investments, increased scale (5 times) and lignocellulosic and woody biomass feedstock costs reduced to about 67% could slash ethanol production costs to 59–40% of the current level in 10–20 years or more. The production cost is reported to be slightly higher for wood-produced ethanol compared to that of switchgrass (Pimentel & Patzek, 2005). The production costs of ethanol from energy crops vary widely due to the complex characteristics of the resource, their site specificity, national policies, labor costs and efficiency of the conversion technologies, but are expected to decline over time (Sims et al., 2006) and it is noted to have clear socioeconomic benefits (Guo et al., 2010).
The coproduct revenue and utilization of the excess solid residue for heat and power production had a considerable effect on the process economics, and improved ethanol yield and reduced energy demand resulted in significant production cost reductions (0.41–0.50 €/L) (Sassner & Zacchi, 2008; Sassner et al., 2008). Sassner et al. (2008) also concluded that the utilization of pentose fractions for ethanol production helped achieve good process economy, especially in the case of Salix or corn stover. It is also noted that ethanol produced from softwood and sold as a low percentage blend with gasoline could ultimately be cost competitive with gasoline without requiring subsidy, but that production from straw would generally be less competitive (Slade et al., 2009). Despite the environmental benefits of ethanol produced from coppice willow, its economic viability remains doubtful at present (Stephenson et al., 2010). The author argued that the production cost could be reduced significantly if the willow were altered by breeding to improve its suitability for hydrolysis and fermentation. A techno-economic assessment of lignocellulosic ethanol also revealed that commercial success of pilot plants (0.3–67 MW) remains pending, although cost-competitive ethanol can be produced with efficient equipment, optimized operation, cost-effective syngas cleaning technology, inexpensive raw material with low pretreatment cost, high performance catalysts, off-gas and methanol recycling, an optimal systematic configuration and heat integration, and a high value by-product with a plant capacity of 200 MW (He & Zhang, 2011). The estimated cost of ethanol from wood varies between 0.50–0.76 US$/L depending on the plant capacity (AEA Technology, 2003; Galbe & Zacchi, 2002; S&T2, 2004).

The reported enzyme cost of lignocellulosic ethanol varied widely, with the on-site enzyme production/purchase cost reported to date perhaps the most contentious or dubious estimation. In the USA, the costs associated with dedicated cellulase production are reported to be 0.1–0.5 US$/gal ethanol (Aden et al., 2002; Aden, 2008; Lynd et al., 2002; Wu et al., 2008). It is also predicted that in future, less cellulase will be necessary, due to increased specific enzyme activity: threefold in 2005 and tenfold in 2010 (Wu et al., 2008). The present enzyme production cost is estimated as 265 $/m³ (1 $/gal), but with recent investments and continuous research efforts, this value may drop to 130 $/m³ (0.5 $/gal) by 2010 (Bryant, 2009; Seabra et al., 2010). The most astonishing prediction seems to be of enzyme productivity: 600–2000 FPU/g glucose+Xylose between 2005 and 2010 (Wu et al., 2008), which is subject to considerable doubt. Presently, the enzyme productivity achieved is reported to be 333 FPU/g glucose (NFRI,
2010; unpublished data). Conversely, the cost of cellulase is reported to be 0.51 €/L (Reith et al., 2002). The reported enzyme cost (production/purchase) is Canadian dollar (CAD) 12/million FPU (enzyme loading: 10 FPU/g cellulose) (Gregg et al., 1989). These studies reported a wide variation of the cost of cellulase, hence the ethanol.

The enzyme production is noted to be dependent on enzyme processing plant, site of production, and the method of transportation and the protein yield. Onsite enzyme production reduces production cost compared to the off-site production. The production cost varied from $3.8–$6.8 and $4.0–$8.8/kg protein for onsite and offsite, respectively. The enzyme production cost is noted to be $0.12/L-ethanol for that ethanol processing plant capacity of 150MML/year using 11.5 mg enzyme/g substrate (Hong et al., 2013). It is also noted that despite the low cost of biomass, enzyme is a significant contributor to the production cost of ethanol (Ensinas et al., 2013). Table 2.5 shows a summary of the reported cost of cellulase and the production cost of ethanol produced from cellulosic biomass by different authors.

### 2.4.2 Life cycle costing of ethanol produced by thermochemical process

Haro et al. (2012) designed and developed the kinematic laboratory data which involves biomass pretreatment (poplar wood chips drying, size reduction to 4 cm) and gasification (atmospheric-pressure indirect circulating fluidized bed gasifier) to produce ethanol from wood chips. The estimated production cost is noted to be 0.55–0.59 $/L. The estimated production cost of ethanol produced by optimized thermochemical conversion process is reported to be 0.11–0.25$/L due to the large contribution of coproduct (hydrogen) (Grossmann & Martín, 2010; Martín & Grossmann, 2011). The production cost is reported to be greater for gasification-fermentation route compared with gasification-catalytic synthesis (Phillips, 2007). The production cost of ethanol has also been estimated for different feedstocks using the material and energy data modeled with Aspen Plus (at the NREL, USA). The forest-based feedstocks including loblolly pine, natural hardwood and eucalyptus present more attractive financial returns when compared to switchgrass and corn stover, mainly due to their composition and alcohol yield (Phillips, 2007; Gonzalez et al., 2012).
<table>
<thead>
<tr>
<th>Authors</th>
<th>Feedstock, feed rate, cost &amp; yield</th>
<th>Enzyme loading</th>
<th>Enzyme cost, $/L</th>
<th>Cost of ethanol for different cases and years, $/L</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wooley et al., 1999a</td>
<td>*CS, 2000 25</td>
<td>15-20 FPU</td>
<td>0.079</td>
<td>0.38 - - 0.248 0.217 - - - -</td>
<td>Enzyme cost need to be reduced ten-fold, dollar value in 1997</td>
</tr>
<tr>
<td>McAloon et al., 2000</td>
<td>*CS, 1050 25</td>
<td>-</td>
<td>0.05</td>
<td>0.396 - - - - - - - - - -</td>
<td>Little information is available on enzyme production, dollar value in 1999</td>
</tr>
<tr>
<td>Aden et al., 2002</td>
<td>*CS, 2000 30</td>
<td>12-17 FPU</td>
<td>0.026</td>
<td>- - 0.346 0.283</td>
<td>Buying of enzymes, dollar value in 2000</td>
</tr>
<tr>
<td>Aden et al., 2008</td>
<td>*CS, 2000 60.0-46.0 265.38</td>
<td>-</td>
<td>0.085-0.026</td>
<td>- - 1.11 0.666 0.351</td>
<td>Enzyme cost is assumed, dollar value in 2002</td>
</tr>
<tr>
<td>Dutta et al., 2010a</td>
<td>*CS, 2000 60.1</td>
<td>30-40 mg protein</td>
<td>0.085</td>
<td>- - - - - - - 0.801</td>
<td>Enzyme cost is assumed, dollar value in 2007</td>
</tr>
<tr>
<td>Eggeman et al., 2005</td>
<td>CS, 2000 35</td>
<td>15 FPU</td>
<td>0.039</td>
<td>- - - - - - - 0.262</td>
<td>Enzyme cost is assumed</td>
</tr>
<tr>
<td>Reith et al., 2002</td>
<td>VG, 2000 20 €</td>
<td>-</td>
<td>0.51 €</td>
<td>- - 0.92 € - - - - -</td>
<td>Enzyme cost is assumed</td>
</tr>
<tr>
<td>Shafiei et al., 2011</td>
<td>Spruce, 200000a 16-82 €</td>
<td>-</td>
<td>1.226 €/kg</td>
<td>- - - - - 0.44€</td>
<td>Enzyme cost is estimated</td>
</tr>
<tr>
<td>Orikasa et al., 2009</td>
<td>*RS, 200 15000^9</td>
<td>-</td>
<td>-</td>
<td>- - - - - -</td>
<td>Enzyme cost is assumed</td>
</tr>
<tr>
<td>Barta et al., 2010a</td>
<td>Spruce, 200000a 68.15</td>
<td>10 FPU</td>
<td>0.058-0.073</td>
<td>- - - - - 0.548</td>
<td>Enzyme cost is assumed</td>
</tr>
<tr>
<td>Roy et al., 2012a,b</td>
<td>RS, 150-200 150</td>
<td>9.1-12 FPU/g-straw</td>
<td>0.14-0.24</td>
<td>- - - - - 0.85-1.45</td>
<td>Enzyme cost is estimated</td>
</tr>
</tbody>
</table>

CS: corn stover; RS: rice straw; VG: verse grass; FPU: filter paper unit; *Plant life: 20 years; ^per g-cellulose; *dilute acid pretreatment; ^Lime pretreatment; ^Plant life 15 years; aPlant life: 9 years; €: cost in Euros; aAnnually (This table is partly adopted from Roy et al., 2012c).
A thermochemical process has also been designed, simulated and optimized mainly with Aspen Plus (He & Zhang, 2011) and concluded that feedstock and syngas cleaning are the major contributors in the ethanol production cost followed by the feedstock. It is also noted that cost-competitive ethanol production can be realized with efficient equipment, optimized operation, cost-effective syngas cleaning technology, inexpensive raw material with low pretreatment cost, high performance catalysts, off-gas and methanol recycling, optimal systematic configuration and heat integration, and high value byproduct with a plant capacity around 200 MW. A wide variation of production cost was also reported by several authors where the lignocellulosic ethanol production by thermochemical gasification processes were modeled (most of the studies modeled with Aspen Plus software) to estimate the production cost. The production cost varied from 0.27–1.25 $/L (Wu et al., 2006; Gonzalez et al., 2012; Haro et al., 2012; Phillips, 2007; Phillips et al., 2007; Nechodom et al., 2008; Foust et al., 2009; Mark et al., 2009; Dutta et al., 2010b; Perales et al., 2011). The feedstock and capital cost are identified to be main hotspots (Dutta et al., 2010b; Foust et al., 2009).

The ethanol production cost in an integrated process (corn and corn stover: grain 18 kg/s and stover 10.8 kg/s) is reported to be $0.32/L and noted that production cost decreased if only stover is used (Čuček et al., 2011). Although most of the theoretical studies (modeled with Aspen Plus software) noted that the thermochemical conversion of biomass to ethanol would be competitive with the fossil ethanol, in depth studies at bench/pilot plants are required for any future investment and commercial production. A summary of the reported production cost and other assumptions are reported in Table 2.6.

Moisture and ash content in preprocessed feedstock are observed to be highly sensitive to the LC GHG emission of ethanol (Daystar et al., 2013; Tan & Dutta, 2013). The GHG emission reduction is noted to be more than 13% and 7%, if moisture and ash content reduced from 50% to 30% (wt) by field drying and 7% to 1% (wt), respectively (Tan & Dutta, 2013). The authors also noted that the thermochemical pathway reduces 83% GHG emission compared with 2005 gasoline baseline. Daystar et al. (2013) reported the highest ethanol yield in the case of loblolly pine and the lowest for corn stover among hardwood, loblolly pine, eucalyptus, miscanthus, corn stover, and switchgrass. The baseline GHG emission is noted to be 2.8 kg CO$_2$ e/L from the thermochemical conversion of these feedstocks into ethanol.
Table 2.6 Summary of the reported cost of ethanol from different feedstock and energy efficiency (thermochemical conversion)

<table>
<thead>
<tr>
<th>Authors</th>
<th>Feedstock, feed rate, cost &amp; yield</th>
<th>Gasifier types</th>
<th>Catalyst/Bacteria</th>
<th>Cost, S/L</th>
<th>Energy efficiency, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Feedstock</td>
<td>Rate, t/d</td>
<td>Cost, $/t</td>
<td>Yield, L/DT</td>
<td></td>
</tr>
<tr>
<td>1Haro et al., 2012^</td>
<td>Wood chip</td>
<td>2140</td>
<td>66 DT</td>
<td>-</td>
<td>CoMo/ZnO</td>
</tr>
<tr>
<td>Nechodom et al., 2008</td>
<td>Forest waste</td>
<td>5000</td>
<td>45 DT</td>
<td>284–322</td>
<td>Iron-based catalyst</td>
</tr>
<tr>
<td>1Phillips et al., 2007</td>
<td>Wood chip</td>
<td>2000</td>
<td>35 DT</td>
<td>217–430</td>
<td>MoS₂</td>
</tr>
<tr>
<td>1Phillips, 2007</td>
<td>Wood chip</td>
<td>2000</td>
<td>39 DT</td>
<td>280</td>
<td>MoS₂</td>
</tr>
<tr>
<td>1Dutta et al., 2010b</td>
<td>Wood chip</td>
<td>2000</td>
<td>50.5 DT</td>
<td>241</td>
<td>Co-Mo</td>
</tr>
<tr>
<td>3He &amp; Zhang, 2011^</td>
<td>Lignocellulosic biomass</td>
<td>2455</td>
<td>58.66 €</td>
<td>332</td>
<td>Co-Mo</td>
</tr>
<tr>
<td>1Perales et al., 2011^</td>
<td>Wood chip</td>
<td>2140</td>
<td>66 DT</td>
<td>206</td>
<td>Rh-Mn/SiO₂, KCoMoS₂</td>
</tr>
<tr>
<td>2Piccolo &amp; Bezzo, 2009^</td>
<td>Wood</td>
<td>700000*</td>
<td>36-63 €</td>
<td>228-282</td>
<td>Clostridium ljungdahlii</td>
</tr>
<tr>
<td>2Gonzalez et al., 2012^</td>
<td>Softwood, hardwood</td>
<td>453597*</td>
<td>69.4-80.3</td>
<td>373-450</td>
<td>molybdenum disulfide</td>
</tr>
<tr>
<td>1Spath &amp; Dayton, 2003</td>
<td>Softwood</td>
<td>2204</td>
<td>25 DT</td>
<td>256-397</td>
<td>BCL/FERCO gasifer</td>
</tr>
<tr>
<td>Marti'n &amp; Grossmann, 2011</td>
<td>Switchgrass</td>
<td>22 kg/s</td>
<td>-</td>
<td>0.33-0.39</td>
<td>High/low pressure</td>
</tr>
<tr>
<td>1Foust et al., 2009</td>
<td>Wood chip</td>
<td>46 DT</td>
<td>356 L</td>
<td></td>
<td>Nickel-based catalyst</td>
</tr>
<tr>
<td>Mu et al., 2010^</td>
<td>Wood chips, wheat, straw, waste paper, corn stover</td>
<td>2000</td>
<td>270-359</td>
<td></td>
<td>Indirect-heating fluidized bed gasifier</td>
</tr>
</tbody>
</table>

1Plant life span 20 years; 2Plant life span 15 years; 3Plant life span 20 year and others 7 years; *t/year; t/d: ton/day; DT: dry ton
^Either centering the NREL studies or energy and mass balance modeled with AspenPlus
Chapter 3

Life Cycle Assessment (LCA) Methodologies

3.1 LCA Methodologies

Life cycle assessment (LCA) is a tool for evaluating environmental effects of a product, process, or activity throughout its life cycle (LC) or lifetime, which is known as a ‘from cradle to grave’ analysis. Although the concept of LCA evolved in the 1960s and there have been several efforts to develop LCA methodology since the 1970s, it has received much attention from individuals in environmental science fields since the 1990s. Since then the LCA concept was promoted, sponsored and developed by the various national and international organization (SETAC: Society of Environmental Toxicology and Chemistry, USEPA: United States Environmental Protection Agency, ISO: International Organization for Standardization, ILCAJ: Institute of Life Cycle Assessment, Japan etc.), and LCA practitioners. Consequently, consensus has been achieved on an overall LCA framework and a well-defined inventory methodology (ISO, 1997).

The LCA method is rapidly developed into an important tool for authorities, industries, and individuals in environmental sciences. The UNEP (United Nations Environment Programme)-SETAC initiative includes methods for the evaluation of environmental impacts associated with water consumption and land use (Jolliet et al., 2004). A common methodological framework (“Version Zero”) has also been developed by the Global Bioenergy Partnership (GBEP) Task Force on GHG Methodologies that could be applied to the LCA of bioenergy production and compared to the full life cycle of its fossil fuel equivalent to improve the transparency and acceptance of the results (GBEP, 2009). The LCA methodology consists of four components: Goal definition and scoping, Inventory analysis, Impact assessment and Interpretation. Figure 3.1 shows the stages of an LCA (ISO, 2006). The purpose of an LCA can be: (1) comparison of alternative products, processes or services; (2) comparison of alternative life cycles for a certain product or service; (3) identification of parts of the life cycle where the greatest improvements can be made. Accordingly, the LCA methodologies (ISO, 2006) will be used to evaluate the life cycle of ethanol from biomass.
3.1.1 Goal definition and scoping

Goal definition and scoping is perhaps the most important component of an LCA because the study is carried out according to the statements made in this phase, which defines the purpose of the study, the expected product of the study, system boundaries, functional unit (FU) and assumptions. The system boundary of a system is often illustrated by a general input and output flow diagram. All operations that contribute to the LC of the product, process, or activity fall within the system boundaries. The purpose of functional unit (FU) is to provide a reference unit to which the inventory data are normalized. The definition of FU depends on the environmental impact category and aims of the investigation. The functional unit is often based on the mass (kg) or volume (L) of the products under study; however, the distance (km), land area (ha), energy (MJ) and economic values of products are also used.

Biomass especially, agri-residues and forest residues are identified as abundant biomass resources for bioenergy. Forest residues are broadly categories into two groups: mill residues (bark, sawdust and shavings), and forest residues (tops, branches and leaves from harvest and thinning operations). Mill residue productions in various provinces of Canada are reported in Table 3.1. The price of sawdust, bark and bark piles varies from 0–22.5, 2.9–32.5 and 0–7.8 $/ODt, respectively, in 2007, Eastern Ontario, Canada (Bradley, 2010). These residues are noted to have low commercial value (Talebnia et al., 2010; sawdust), high in cellulose content, thus a suitable raw material for ethanol production (Zabihi et al., 2010; sawdust; miscanthus). The major components of different residues and the chemical compositions are presented in Table 3.2, Table 3.3 and Table 3.4. In Canada, the amount of biomass is reported to be approximately $9.4\times10^6$ MT/yr (Mabee et al., 2006). The potential sources of renewable biomass include
agricultural residues, municipal solid waste, forestry byproducts and energy crops. The technical, economic and sustainability constraints in Ontario conditions also limits their supply to ethanol industry (Kludze et al., 2010). The use of forestry wastes for liquid biofuels are also restricted due to its enormous demand by the solid biofuels industries. Miscanthus is a promising energy crop with high yield and energy content, which can be grown on low quality or marginal land, and add carbon to the soil and safeguard it against erosion (Somerville et al., 2010; Kludze et al., 2013), has an important role in sustainable energy production (Sørensen et al., 2008; Khanna et al., 2008; Bocquého & Jacquet, 2010). Therefore, the goal of this study is to evaluate the LC of ethanol produced from agri-residues/forest residues/energy crops. The FU of this study is defined as 1 L of anhydrous ethanol produced from biomass. Figure 3.2 depicts the system boundary of this study (‘cradle to gate’ scenario).

Table 3.1 Mill residues production in Canada in 2004 (ODt: Oven dry tonnes)

<table>
<thead>
<tr>
<th>Province</th>
<th>Production</th>
<th>Consumption</th>
<th>Export</th>
<th>Surplus</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alberta</td>
<td>2406</td>
<td>1924</td>
<td>0</td>
<td>481</td>
</tr>
<tr>
<td>British Columbia</td>
<td>6554</td>
<td>4338</td>
<td>350</td>
<td>1815</td>
</tr>
<tr>
<td>New Brunswick</td>
<td>1373</td>
<td>1223</td>
<td>150</td>
<td>0</td>
</tr>
<tr>
<td>Manitoba</td>
<td>225</td>
<td>212</td>
<td>0</td>
<td>13</td>
</tr>
<tr>
<td>Ontario</td>
<td>2602</td>
<td>2480</td>
<td>1</td>
<td>121</td>
</tr>
<tr>
<td>Quebec</td>
<td>6669</td>
<td>6400</td>
<td>169</td>
<td>100</td>
</tr>
<tr>
<td>Saskatchewan</td>
<td>580</td>
<td>416</td>
<td>0</td>
<td>164</td>
</tr>
</tbody>
</table>

Source: Bradley, 2010

Table 3.2 Volatile matter, fixed carbon, and ash content in selected biomass (dry basis)

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Volatile matter, %</th>
<th>Fixed carbon, %</th>
<th>Ash, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wheat straw</td>
<td>80.04</td>
<td>15.31</td>
<td>4.65</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>87.50</td>
<td>12.16</td>
<td>0.80</td>
</tr>
<tr>
<td>Sawdust</td>
<td>85.63</td>
<td>12.98</td>
<td>1.39</td>
</tr>
</tbody>
</table>

### Table 3.3 Potential feedstocks and their major components

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Components, % (w/w)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cellulose</td>
<td>Hemicellulose</td>
</tr>
<tr>
<td>Cellulose</td>
<td>48.57</td>
<td>27.7</td>
</tr>
<tr>
<td>Hemicellulose</td>
<td>39</td>
<td>32</td>
</tr>
<tr>
<td>Lignin</td>
<td>32.1</td>
<td>26.9</td>
</tr>
<tr>
<td>Ash</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Wheat straw</td>
<td>33-40</td>
<td>20-25</td>
</tr>
<tr>
<td></td>
<td>52.04</td>
<td>30.12</td>
</tr>
<tr>
<td></td>
<td>40.5</td>
<td>26.3</td>
</tr>
<tr>
<td></td>
<td>37.4</td>
<td>33.8</td>
</tr>
<tr>
<td></td>
<td>35.44</td>
<td>24.56</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td>Sawdust</td>
<td>55</td>
<td>14</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>36.96</td>
<td>22.12</td>
</tr>
<tr>
<td></td>
<td>39.21</td>
<td>23.47</td>
</tr>
<tr>
<td></td>
<td>38.2</td>
<td>24.3</td>
</tr>
<tr>
<td></td>
<td>40.0</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td>40.2</td>
<td>22.4</td>
</tr>
</tbody>
</table>

* with extractives

*Table 3.4 Chemical composition of different feedstock*

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Chemical composition, g/kg</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>N</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>420</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>455</td>
<td>8</td>
</tr>
<tr>
<td>Sawdust</td>
<td>490</td>
<td>0.1</td>
</tr>
<tr>
<td></td>
<td>562</td>
<td>10</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>453</td>
<td>2.1</td>
</tr>
<tr>
<td></td>
<td>480</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>471</td>
<td>0.44</td>
</tr>
</tbody>
</table>

44
3.1.2 Life cycle inventory (LCI) analysis

The inventory analysis involves collecting data on raw materials and energy consumption, emissions to air, water and soil, and generation of solid waste. This phase is the most work intensive and time consuming compared to other phases in an LCA, mainly because of data collection. The data collection can be less time consuming if good databases are available and if customers and suppliers are willing to help. Consequently, LCA allows the use of quality data, if that are not product specific. Nowadays, many LCA databases exist and can normally be bought together with LCA software. Data on transport, extraction of raw materials, processing of materials, production of usually used products like plastic; cardboard etc. and disposal can normally be found in an LCA-database. Data from databases can be used for processes that are not product specific, such as general data on the production of electricity, coal or packaging. For product specific data, site-specific data are required. The data should include all inputs and outputs from the processes. Inputs are energy (renewable and non-renewable), water, raw materials etc. Outputs are the products and co-products, and emission (CO₂, CH₄, SO₂, NOx, and CO) to air, water and soil (total suspended solids: TSS, biological oxygen demand: BOD, chemical oxygen demand: COD and chlorinated organic compounds: AOXs) and solid waste generation (municipal solid waste: MSW and landfills). For the simplicity of this study, available quality data are collected from the literature and different database. Rest of the required data are generated experimentally at the laboratory wherever possible or simulation technic (Aspen Plus V7.3) has been used to gather the required data. The collected and generated data are analyzed by applying LCA methodologies.

Figure 3.2 System boundary of this study
3.1.3 Impact assessment
The life cycle impact assessment (LCIA) aims to understand and evaluate environmental impacts based on the inventory analysis, within the framework of the goal and scope of the study. In this phase, the inventory results are assigned to different impact categories, based on the expected types of impacts on the environment. Impact assessment of the LCA generally consists of the following elements: classification, characterization, normalization and valuation. Classification is the process of assignment and initial aggregation of LCI data into common impact groups. Characterization is the assessment of the magnitude of potential impacts of each inventory flow into its corresponding environmental impact (e.g., modeling the potential impact of carbon dioxide and methane on global warming). Characterization provides a way to directly compare the LCI results within each category. Characterization factors are commonly referred to as equivalency factors. Normalization expresses potential impacts in ways that can be compared (e.g., comparing the global warming impact of carbon dioxide and methane for the two options). Valuation is the assessment of the relative importance of environmental burdens identified in the classification, characterization, and normalization stages by assigning them weighting which allows them to be compared or aggregated. Impact categories include global effects (global warming, ozone depletion etc.); regional effects (acidification, eutrophication, photo-oxidant formation etc.); local effects (nuisance, working conditions, effects of hazardous waste, effects of solid waste etc.).

A common framework consisting ‘midpoint’ and ‘endpoint’ approach is desirable for life cycle impact assessment (LCIA) because both approaches have their specific strengths and weakness (Heijungs et al., 2003). The Institute of Life Cycle Assessment, Japan has developed a LC impact assessment method based on endpoint modeling (LIME) to quantify the environmental impacts as accurately as possible with a high degree of transparency and to develop a single central index (Eco-index) (Fig. 3.3). The authors also concluded that a single index inevitably involves value judgment (pricing) and has a higher degree of uncertainty (Itsubo & Inaba, 2007).

3.1.4 Interpretation
The purpose of an LCA is to draw conclusions that can support a decision or can provide a readily understandable result of an LCA. The inventory and impact assessment results are discussed together in the case of an LCIA, or the inventory only in the case of LCI analysis, and
significant environmental issues are identified for conclusions and recommendations consistent with the goal and scope of the study. This is a systematic technique to identify and quantify, check and evaluate information from the results of the LCI and LCIA, and communicate them effectively. This assessment may include both quantitative and qualitative measures of improvement, such as changes in product, process, and activity design; raw material use, industrial processing, consumer use, and waste management. Cost and profit are the key indicators in decision-making on an investment, while costs are what producers or consumers understand best and an integral part of the decision-making process when identifying improvements of a product, process or activity, hence LCA results are also interpreted in the form of LC costing.

![Figure 3.3 Structure of the LCIA method based on endpoint modeling (LIME2)](image)

**Source:** Itsubo and Inaba, 2007

**3.2 Life cycle cost analysis (LCCA)**

Although an LCA is useful, always may not be sufficient basis for a sound decision making process, the LCCA can broaden the decision making process. The combination of LCA
and LCCA results can be used to guide in the biomass to biofuels strategies (Roy et al., 2007; Baldwin et al., 2012). Gerber et al. (2011) noted that the integration of environmental impacts in the optimization procedure can influence the engineering decisions related to the final process design (thermo-economic) of polygeneration systems for (renewable) energy services. The uncertainty in LCA can be managed by combining process and economic input–output approaches (Williams et al., 2009b). Nechodom et al. (2008) also noted that combination of LCA and LCCA models can be used to determine economic viability, environmental impacts, and energy efficiency of bioenergy from forest biomass. A mixed-integer linear programing (MILP) approach revealed that optimal feedstock selection, technologies, intermediate and final product flows improve economic efficiency and reduces GHG emission (ˇCuˇcek et al., 2014). Another MILP modeling framework for ethanol supply chains, where multiple decision criteria are considered in an uncertain market scenario revealed that the strategic decisions are dependent on the trade-off between environmental and economic performance and are also firmly coupled with investor’s attitude (Giarola et al., 2013).

Gerber et al. (2011) integrated the LCA indicators with an existing computer aided process engineering platform to optimize thermo-economic design of polygeneration systems for renewable energy services. The thermo-economic model has also been used to evaluate the LC of bioenergy from biomass (Gerber et al., 2011; Tock et al., 2010; Gassner & Maréchal, 2009), which can be used for analyzing both the economics and the environmental impact of bioenergy. Møller et al. (2014) has studied the environmental and economic consequences of the LC of ethanol integrating the material based LCA with welfare economic cost benefit analysis (CBA) which claimed to have broadened the perspective of advantages and disadvantages of biofuels. Therefore, the LC cost of ethanol is estimated with both fixed costs (straight line depreciation on installation, labor, maintenance and interest on investment) and variable costs (feedstock, enzyme production, utilities and waste management). The cost of a product may vary based on the base year of calculation. The consumer price index (CPI) can be used to convert costs if cost data are collected from different years. Most of the collected data are from 2010 except the processing plant construction data, which is collected from a Japanese literature published in 2007. This later data was not converted to a 2010 basis, since the Japanese CPI was not available.
Chapter 4

Life Cycle Assessment of Ethanol produced from Wheat Straw

[Published in the Journal of Biomass Materials and Bioenergy, 6(3): 276–282]

4.1 Introduction

The life cycle (LC) GHG emissions of different forms of bioenergy and their ability to reduce GHG emissions vary widely, and are dependent on land use changes, choice of feedstock, agricultural practices, refining and conversion processes with differing socioeconomic and environmental impacts (Tilman & Lehman, 2006; Luo et al., 2009; Kaufman et al., 2010). It is thus essential to evaluate the environmental impact and the economic viability of lignocellulosic ethanol. Life cycle assessment (LCA) methodology has been extensively used to evaluate the LC of lignocellulosic ethanol (Wooley et al., 1999; Sheehan et al., 2003; Kim & Dale, 2005; Adler et al., 2007; Spatari et al., 2010; Hsu et al., 2010; Seabra et al., 2010; Orikasa et al., 2009; Roy et al., 2012b). However, the LCA of ethanol from wheat straw has received only limited attention (Kaparaju et al., 2009; Hsu et al., 2010), which are mostly confined to pretreatment processes, production of alternate bioenergy, and utilization of ethanol. This study evaluated the LC of ethanol to determine if environmentally preferable and economically viable ethanol can be produced from wheat straw in Ontario, Canada.

4.2 Materials and methods

4.2.1 System boundary

Wheat is one of the most important agricultural commodities in Canada. Wheat was grown on 9638200 ha in Canada in 2009 (FAO, 2011), and regionally was grown on 475500 ha in Ontario (OMAFRA, 2011a), which may produce about 2282400 tons straw [4.8 dry-tons/ha (Evans et al., 2005)]. Wheat straw is noted to be an abundant agricultural residue with low commercial value (Talebnia et al., 2010), high in cellulose content, thus a suitable raw material for ethanol production (Zabihi et al., 2010). Cellulose, hemicellulose and lignin contents are reported to be 48.6, 27.7 and 8.2%, respectively (Saha & Cotta, 2008). An ethanol processing plant is assumed to be established in the wheat growing area (100% cropland is assumed to be under wheat crop; farmland is found to be 5.9% in Ontario) for efficient utilization of wheat straw. The ethanol processing plant capacity is considered to be 20000 kL/year. Figure 4.1 depicts the system boundary of this study (‘cradle to gate’ scenario). The roads and channels are
assumed to be 2% of rural land area in Ontario. Crop residue incorporation is important in maintaining soil organic matter, soil structure, fertility and productivity. The sustainable residue collection rate is noted to be dependent on soil type, slope, crop rotation and tillage practices. It is noted that about 50–60% crop residues can be collected without deteriorating the soil quality and productivity (Jeschke, 2011 Smith, 1986; Sheehan et al., 2002), thus the straw collection is considered to be 60% that grows in farm without the fear of soil degradation and productivity loss (Smith, 1986; Sheehan et al., 2002). The straw transportation distance from farms to the ethanol processing plant is estimated based on a published methodology (Huang et al., 2009). The baled straw is assumed to be transported to nearby collection center (5 km from the farm) and then transported to the ethanol processing plant (30 km) with 4 t- and 10 t-truck (loading capacity is assumed to be 75%), respectively. It has been reported that agricultural LCAs often exclude production processes of machines, buildings, and roads because of lack of data (Cederberg & Mattsson, 2000). The environmental impacts related to the construction of the ethanol processing plant, storage facilities and the production of transportation and other machinery are not considered.

![Schematic diagram of the life cycle of wheat straw and the system boundary of this study](image-url)

Figure 4.1 Schematic diagrams of the life cycle of wheat straw and the system boundary of this study

### 4.2.2 Biochemical conversion process

Plant biomass contains high cellulose, thus a suitable material for ethanol production. Devi et al. (2011) noted that plant biomass contains approximately 75% polysaccharides, a rich source of sugars. In the biochemical conversion process, plant cell wall breaks through the introduction of enzymes or acid in order to extract the sugars which are then converted to biofuels using microorganisms. Figure 4.2 shows the schematic diagram of ethanol production process from biomass (enzymatic hydrolysis process).
4.2.2.1 Pretreatment

Lime pretreatment is given (at 120°C for 1 h; lime 10%) (Park et al., 2010; Shiroma et al., 2011) to the crushed (size 3 mm) feedstock. Although boiler efficiencies of between 60–67% (switchgrass and corn stover; rice straw) (Wooley et al., 1999a: Orikasa et al., 2009) and 75–90% (firewood, woodchips, and straw; corn stover) (CBT, 2002; Mani et al., 2010) have been reported, a boiler efficiency of 80% was assumed for this study (Mani et al., 2010). The solid concentration during pretreatment was considered to be 30% (w/w).

4.2.2.2 Vacuum extractive fermentation and distillation

Conventional alcoholic fermentation is a typical inhibitory process, with cell growth rate affected by cellular substrate and product concentration (Rivera et al., 2006). The fermentation must be maintained between 7–10°GL (Gay-Lussac) to prevent inhibitory effects (Junqueira et al., 2009a) that reduce the yield and productivity of the process (Silva et al., 1999). Conversely, the vacuum extractive fermentation process allows the simultaneous removal of produced ethanol from the fermenter, which yields a highly concentrated wine, and as a result, reduces the amount of vinasse and energy consumption in fermentation and the subsequent distillation steps (Junqueira et al., 2009a; Silva et al., 1999). The hydrous ethanol produced in the distillation undergoes purification stages to achieve anhydrous ethanol (99.5%). Bioglycerol is reported to be a suitable agent for the separation of ethanol–water mixtures (Lee & Pahl, 1985) and be safely used to produce anhydrous ethanol for use in food or pharmaceutical industries (Dias et al., 2009). Therefore, vacuum extractive fermentation and distillation, and purification (with glycerol) processes were adopted for this study (Junqueira et al., 2009a). The enzyme loading is assumed to be 11 FPU/g straw (Talebnia et al., 2010). The enzyme cost (considering material and energy consumption) was calculated based on the literature data (Wooley et al., 1999a) and
the enzyme loading rate of this study. Ethanol yield is considered to be 0.3 L/kg dry-straw (Li et al., 2011).

4.2.2.3 Waste management

The waste stream is used to be separated into three feed streams: solids (lignin), biogas and syrup high in solids (Wooley et al., 1999a). Anaerobic digestion of the wastewater produces a biogas high in methane. Burning these byproducts streams to generate either the heat or electricity required in the processes reduces not only the waste management costs, but may also lead to profit. Therefore, it is assumed that energy consumption and cost incurred in the waste management processes would be offset by biogas and syrup generated in the process, and the lignin recovered in the waste management process can be used for process heat generation. The residual lignin is assumed to be dried by utilizing the wasted heat from the boiler. The heat generation from the residual lignin is estimated based on the heating value of lignin and efficiency of the boiler (80%; Mani et al., 2010), is assumed to be used for heat.

4.2.3 Cost analysis

The cost of ethanol is estimated with both fixed costs (straight line depreciation on installation, labor, maintenance and interest on investment) and variable costs (feedstock, enzyme production, utilities and waste management). The business capital is considered to be twice of the price of yearly feedstock demand. The yearly interest rate on investment and maintenance cost is assumed to be 3 and 2%, respectively. The economic life span of an ethanol processing plant and the yearly operating period are assumed to be 20 years and 350 days, respectively (Dutta et al., 2011; Huang et al., 2009; Wu et al., 2006). The cost of wheat straw is considered to be about 143 $/t-dry (OMAFRA, 2011b). [Note: The cost of wheat straw is even higher at present (August 2014), Approximately, $176/t at the farm gate; personal communication: Prof. B. Deen, Department of Plant Agriculture, University of Guelph, Canada)].

4.2.4 Data collection

Data collection is the most work intensive and time consuming activities in an LCA, thus allows the use of quality data, if that are not product specific. For the simplicity of this study, data have been collected from the literature and different database. Although the inventory data vary depending on the regions of the study, production process and allocation methods, the data
used are assumed to be valid for this study. A summary of the parameters/processes for which data have been collected from the literature and their sources are reported in Table 4.1.

Table 4.1 Summary of parameters for which data are collected from the literature

<table>
<thead>
<tr>
<th>Parameters/Systems</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol plant construction &amp; No. of labor</td>
<td>Asano &amp; Minowa, 2007</td>
</tr>
<tr>
<td>Straw collection</td>
<td>JA-Zenno, 2002</td>
</tr>
<tr>
<td>Enzyme</td>
<td>Wooley et al., 1999a</td>
</tr>
<tr>
<td>Yeast</td>
<td>Dutta et al., 2010a</td>
</tr>
<tr>
<td>Vacuum extractive fermentation &amp; distillation</td>
<td>Junqueira, et al., 2009a</td>
</tr>
<tr>
<td>Purification</td>
<td>Dias et al., 2009</td>
</tr>
</tbody>
</table>

4.3 Results and discussion

4.3.1 Energy consumption, CO₂ emission and production cost

The energy consumption, GHG emissions (CO₂ e) and production cost in each stage of the LC of ethanol are worked out to represent the energy-, emissions- and cost breakdown of the production steps and identify the hotspots (Fig. 4.3). The pretreatment process is observed to be the main hotspot followed by enzyme production, and others in the case of energy consumption. It is worthy to note that byproduct (residues) has a strong contribution in net energy consumption, because it offsets a part of energy consumed in the process. The estimated net energy consumption is found to be about 15 MJ/L (Fig. 4.3a). The net energy consumption for corn and cellulosic ethanol is reported to be about 10.6–17.0 and 6.0–31.0 MJ/L, respectively (Sheehan et al., 2003; Kim & Dale, 2005; Pimentel & Patzek, 2005; Luo et al., 2009a). A slight variation in net energy consumption is observed compared with some of the earlier studies, which might be because of different feedstock and processes have been used.

GHG emissions are directly related to energy and resource consumption. Therefore, main hotspot and the order of other stages are observed to be similar to those observed in the case of energy consumption. Figure 4.3(b) shows the emission breakdown of the LC of ethanol. The residues used for heat generation has a strong contribution to offsetting a part of emission of the production process. The net emission is estimated to be 0.91 kg CO₂ e/L. Emission from switch
grass and corn stover ethanol is reported to be 0.49 and 0.33 kg CO$_2$ e/L, respectively where carbon sequestration has been considered (Spatari et al., 2005). The emission is also noted to be 1.6 kg CO$_2$ e/L (Farrell et al., 2006). These results reveal that an environmental benefit can be achieved relative to gasoline (1.5 kg CO$_2$ e/L-ethanol equivalent in Canada; Environment Canada, 2010) when ethanol can be produced by using the technologies adopted in this study.

![Diagram showing energy, emission, and cost breakdowns of the life cycle of ethanol produced from wheat straw.](image)

Figure 4.3 Energy, emission and cost breakdown of the life cycle of ethanol produced from wheat straw.

The production cost of ethanol is also noted to be dependent on both technical and economic parameters, such as the cost of feedstock, choice of feedstock, energy consumption, conversion technology and efficiency, and the value of byproducts (Aden et al., 2002; Dutta et al., 2010a; Balat, 2011). Figure 4.3(c) depicts the cost breakdown of different stages of the LC of ethanol. The main hotspot is emerged to be feedstock followed by fixed cost and others. The fixed cost is calculated to be $0.26/L, which may vary, if different processing plant sizes and operating periods and life spans are considered. The enzyme cost is estimated to be $0.13/L. The net production cost is estimated to be $1.14/L. However, the net production cost would be $1.19/L, if different enzyme cost is considered ($0.18/L, i.e., 0.69/gallon ethanol; Kazi et al., 2010a,b). The use of different input data, functional units, allocation methods, reference systems
and other assumptions complicates comparison of LCA bioenergy studies (Liska & Cassman, 2008; Cherubini & Strømman, 2011), thus a direct comparison was not attempted with other studies. A wide variation was observed in the reported production cost of ethanol. The production cost of ethanol from corn stover and fescue straw is reported to be 0.71–0.87 US$/L (Dutta et al., 2010a; Kumar & Murthy, 2011). The simulated production cost of ethanol is reported to be 0.94–1.20 US$/L which depends on the ethanol yield (Klein-Marcuschamer et al., 2010). The cost is also noted to be dependent on the feedstock and plant sizes (Gnansounou & Dauriat, 2010). Table 4.2 represents a brief summary of the reported production cost, which indicates that the variation in cost among various studies might be because of different processing plant size, types of feedstock, ethanol yield and assumptions. The production cost of lignocellulosic ethanol is reported to be considerably higher than the market price of gasoline (Wooley et al., 1999a; Huang et al., 2009). This study also confirmed that despite the environmental benefits (when agri-residues is assumed to be carbon neutral) of ethanol produced from wheat straw, its economic viability remains doubtful at present, even if highly optimistic assumptions are made for the cost calculation, especially in the case of enzyme. The costs of enzyme and capital are the major expenses when producing lignocellulosic ethanol (Reith et al., 2002), thus production cost may differ when different enzyme cost is considered.

Table 4.2 Summary of the reported cost of ethanol produced from different feedstock

<table>
<thead>
<tr>
<th>Authors</th>
<th>Feedstock, feed rate, cost &amp; yield</th>
<th>²Enzyme loading</th>
<th>Enzyme cost, $/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roy et al., 2012a,b</td>
<td>RS, 150-200</td>
<td>9.1-12 FPU/g-straw</td>
<td>0.14-0.24</td>
</tr>
<tr>
<td>Wooley et al., 1999a</td>
<td>CS, 2000</td>
<td>15-20 FPU</td>
<td>0.079</td>
</tr>
<tr>
<td>Aden et al., 2002</td>
<td>CS, 2000</td>
<td>12-17 FPU</td>
<td>0.026</td>
</tr>
<tr>
<td>Dutta et al., 2010a</td>
<td>CS, 2000</td>
<td>30-40 mg protein</td>
<td>0.085</td>
</tr>
<tr>
<td>Reith et al., 2002</td>
<td>VG, 2000</td>
<td>-</td>
<td>0.51 €</td>
</tr>
<tr>
<td>Barta et al., 2010a</td>
<td>Spruce, 20000</td>
<td>254.0-270.0</td>
<td>0.058-0.073</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Authors</th>
<th>Feedstock, feed rate, cost &amp; yield</th>
<th>²Enzyme loading</th>
<th>Enzyme cost, $/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Roy et al., 2012a,b</td>
<td>RS, 150-200</td>
<td>9.1-12 FPU/g-straw</td>
<td>0.14-0.24</td>
</tr>
<tr>
<td>Wooley et al., 1999a</td>
<td>CS, 2000</td>
<td>15-20 FPU</td>
<td>0.079</td>
</tr>
<tr>
<td>Aden et al., 2002</td>
<td>CS, 2000</td>
<td>12-17 FPU</td>
<td>0.026</td>
</tr>
<tr>
<td>Dutta et al., 2010a</td>
<td>CS, 2000</td>
<td>30-40 mg protein</td>
<td>0.085</td>
</tr>
<tr>
<td>Reith et al., 2002</td>
<td>VG, 2000</td>
<td>-</td>
<td>0.51 €</td>
</tr>
<tr>
<td>Barta et al., 2010a</td>
<td>Spruce, 20000</td>
<td>254.0-270.0</td>
<td>0.058-0.073</td>
</tr>
</tbody>
</table>

CS: corn stover; VG: verse grass; FPU: filter paper unit; ¹Plant life: 20 years; ²per g-cellulose; ³dilute acid pretreatment; ⁴Lime pretreatment; ⁵Plant life 15 year; €: cost in Euro; ⁶Annually
4.3.2 Sensitivity analysis

The LCA results of lignocellulosic ethanol are noted to be more sensitive to the changes in parameters related to the biomass and ethanol yield. A wide variation in ethanol yield from wheat straw (Table 4.3) (Maas et al., 2008; Li et al., 2011; Xu et al., 2011), feedstock- and enzyme cost of lignocellulosic ethanol are also reported (Wooley et al., 1999a; Dutta et al., 2010a; Aden et al., 2002; Reith et al., 2002; Barta et al., 2010a). Therefore, the effect of ethanol yield, feedstock- and plant capacity on the emission and production cost has been determined. Carbon sequestration by the biomass also plays an important role in the LC of agri-products (Sanscartier et al., 2013). Consequently, the effect of carbon sequestration has also been evaluated.

Table 4.3 Ethanol yield from wheat straw

<table>
<thead>
<tr>
<th>Reference</th>
<th>Conversion method</th>
<th>Pretreatment</th>
<th>Yield, g/kg–wheat straw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maas et al., 2008</td>
<td>SSF; GC 220</td>
<td>Lime</td>
<td>102</td>
</tr>
<tr>
<td>Li et al., 2011</td>
<td>SSF; Cellulase 1.5 L</td>
<td>Dilute acid</td>
<td>230–240</td>
</tr>
<tr>
<td>Xu et al., 2011</td>
<td>SSF; Cellubrix L</td>
<td>NaOH</td>
<td>149</td>
</tr>
<tr>
<td>Xu et al., 2011</td>
<td>SSF; Cellubrix L</td>
<td>untreated</td>
<td>27</td>
</tr>
<tr>
<td>Panagiotou et al., 2011</td>
<td>SSF; Cellulase 1.5 L FG &amp; Novozym 188</td>
<td>Steam explosion</td>
<td>40*</td>
</tr>
</tbody>
</table>

*Pretreated wheat straw & corn cob

It is important to note that the construction- and labor cost for different plant sizes are calculated based on published methodologies (Huang et al., 2009; Asano & Minowa, 2007). The scaling factor for estimating the construction and labor cost is considered to be 0.70 and 0.27, respectively. Figures 4.4 and 4.5 depict that net energy consumption, emission and production cost dependent on the ethanol yield and feedstock cost. The lower the ethanol yield, the greater is the energy consumption, emission and production cost. Production cost is also increased with an increase in feedstock cost. Figure 4.6 confirmed that the production cost decreased when processing plant capacity is increased because of lower fixed cost in the case of greater capacity. Although the production cost reduced with the increase of processing plant capacity, emission rises because of longer transportation distance resulted from greater feedstock demand. Figure 6
also depicts that 26% of production cost can be reduced if the plant capacity rose from 5 to 200 ML/year; however, only about 4% of GHG emission would be increased. It is worthy to note that energy efficiency was assumed to be the same for different processing plant sizes i.e., energy consumption in processing steps are constant for different plant sizes. If the energy efficiency varied with the plant size the emission will be changed.

![Graph](image)

Figure 4.4 Effect of ethanol yield on net energy consumption, emission and production cost of ethanol
Figure 4.5 Effect of feedstock cost on the production cost of ethanol

Figure 4.6 Effect of plant capacity on the production cost and emission of the life cycle of ethanol
Wheat straw is considered as carbon neutral, because it is a byproduct of wheat cultivation. However, any marginal inputs and emissions are allocated to wheat straw. Emission from wheat cultivation in Ontario is reported to be 1.995 t CO$_2$e/ha (Dyer et al., 2010). Allocating this emission between wheat grains and straw (based on the economic value of grains and straw) the emission from the LC of ethanol has also been calculated. The price of wheat grains and straw is reported to be 234.4 and 143 $/t, respectively (OMAFRA, 2011b; Agriculture and Agri-food Canada; 2011). The emission is dependent on the carbon neutrality of biomass (Fig. 4.7). The emission remains constant, if biomass is considered to be carbon neutral. Conversely, the emission is increased with an increase in the feedstock cost because of greater share of emission resulted from wheat cultivation, where carbon sequestration was not considered. Emission is found to be 1.5, 1.7 and 2.0 kg CO$_2$ e/L for ethanol yield 0.30, 0.25 and 0.20 L/kg straw, respectively when feedstock cost considered to be 143$/t (Fig. 4.8). Figure 4.8 also depicts the effect of system boundary or the carbon neutrality of wheat straw. These results confirm that both environmental and economic viability of ethanol from wheat straw remains doubtful (for a ‘cradle to gate’ analysis) with present technologies. However, wheat straw based ethanol should represent lower GHG emissions for a ‘cradle to grave’ or ‘well to wheel’ LCA because CO$_2$ emissions released when using ethanol as a fuel are of biogenic origin (i.e. carbon neutral).

The impacts of soil carbon dynamics on the LC of crops noted to be minimal since most of the crop shifts are among annual crops (Dyer et al., 2010). Thus soil carbon change is not accounted, if any. However, carbon sequestration by the crop residues (harvested residues) is considered to determine its impact on the LC of ethanol derived from wheat straw. The carbon sequestration is estimated based on the carbon content (fixed carbon only) in wheat straw. Although carbon content in wheat straw is reported to be about 42%, the fixed carbon is only 15.31%. The net GHG emissions reduced to -0.24 to -0.61 kg CO$_2$ e/L if carbon sequestration (with only fixed carbon) is considered (Fig. 4.9) which is also dependent on ethanol yield,. This figure indicates that environmentally viable ethanol can be produced from wheat straw even it is considered to be carbon non-neutral i.e., emissions from the agricultural operation is shared by the harvested wheat straw. The net GHG emissions for stover is also reported to be negative (–864 kg CO$_2$ e/t) where carbon sequestration contributed about 62–66% (Roberts et al., 2010).

Moreover, it is worthy to note that this is a highly optimistic study, and all the data do not necessarily correspond to the Canadian context or to the same processing plant size. Therefore,
in-depth studies are necessary for each step of the LC of ethanol from wheat straw (especially pretreatment, enzyme and yeast production, SSF, distillation and purification) for any future investment and commercial production.

Figure 4.7 Effect of feedstock cost on the emission of the life cycle of ethanol

Figure 4.8 Effect of system boundary and the ethanol yield on life cycle GHG emission of ethanol
Figure 4.9 Effect of carbon sequestration and ethanol yield on the life cycle GHG emission

4.4 Conclusion

The net energy consumption, GHG emission and the production cost are found to be 15.0 MJ/L, 0.91 kg-CO₂ e/L and 1.14 $/L, respectively (when plant capacity considered to be 20000 kL/year) which depend on the ethanol yield, plant capacity, and system boundaries. This study also depicts that environmental benefit can be gained with present technologies if wheat straw is considered to be carbon neutral, otherwise both environmental and economic viability of ethanol from wheat straw are doubtful. It is also worthy to note that environmental viability of ethanol from carbon non-neutral wheat straw can be improved if carbon sequestration is considered.
Chapter 5

Life cycle assessment of ethanol derived from sawdust

[Published in the Bioresource Technology, 150(December): 407–411]

5.1 Introduction
The potential sources of renewable biomass in Canada include waste products from forestry and agricultural residues, municipal solid waste, and energy crops. In Canada, the amount of biomass production is reported to be approximately 9.4×10⁶ MT/year. Residual lignocellulosic feedstock could provide up to 50% of Canada’s 2006 transportation fuel demand (Mabee & Saddler, 2010). Forestry products, particularly sawdust, forest thinning and trimming are potential feedstock for ethanol production (Kadam et al., 2000; Mu et al., 2010). The life cycle (LC) GHG emissions from biofuels and their ability to reduce GHG emission are dependent on choice of feedstock, agricultural practices, and conversion technologies with differing socioeconomic and environmental impacts (Tilman et al., 2009; Luo et al., 2009; Kaufman et al., 2010). Although many researchers have evaluated the LC of lignocellulosic ethanol produced by enzymatic hydrolysis process, ethanol from sawdust received only limited attention (Slade et al., 2009; Sandilands et al., 2009), their research deals with thermochemical conversion (gasification-synthesis). This study evaluated the LC of ethanol produced by enzymatic hydrolysis and considered two scenarios to determine if environmentally preferable and economically viable ethanol can be produced from sawdust in Ontario, Canada.

5.2 Methodology
5.2.1 System boundary and assumptions
The forest products industry produces woody biomass as a byproduct, including bark, sawdust and shavings. In Canada, sawmill residue production rate is estimated to be approximately 2.3×10⁶ dry-tons/year (Ackom et al., 2010). The forest area in Ontario is reported to be 71,067,769 ha in 2008 (MNR, 2011), which produces a considerable amount of residues. Sawdust is reported to be high in cellulose content, thus a suitable raw material for ethanol production. Cellulose, hemicellulose and lignin contents are reported to be 55, 14 and 21%, respectively (Olsson & Hahn-Hägerdal, 1996). Ethanol yield is assumed to be 0.305 L/kg of dry sawdust (Olsson & Hahn-Hägerdal, 1996). Two scenarios are considered to evaluate the LC of ethanol from sawdust (Table 5.1). Sawdust from sawmills (base case: S₁) and sawdust produced...
from forest residues (thinning, pruning, shaving etc.: \( S_2 \)) are considered as carbon neutral, because these are byproducts of timber industry (sawmill) and forest, respectively. However, any marginal inputs (energy consumption in collection and transportation of sawdust, and preparation of sawdust from forest residues) and emissions are allocated to sawdust from sawmills or sawdust produced from forest residues (thinning, pruning, shaving etc.). GHG emission has been calculated in terms of CO\(_2\) e (i.e., GWP for a time span of 100 year; IPCC, 2001).

Table 5.1 Scenarios of this study.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Feedstock source</th>
<th>Transport distance, km</th>
<th>^Cost, $/t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenario-1 (base case)</td>
<td>Sawdust (sawmill byproduct)</td>
<td>15*</td>
<td>80</td>
</tr>
<tr>
<td>Scenario-2</td>
<td>Sawdust (produced from forest residues: thinning, pruning, and the logging residues)</td>
<td>20</td>
<td>60</td>
</tr>
</tbody>
</table>

*Distance estimated based on the Mani et al., 2006; 6 m (20 feet) trailer truck is used for transportation; ^plant gate price.

An ethanol processing plant is assumed to be established nearby the forest/sawmill area for efficient utilization of forest and sawmill residues. The ethanol processing plant capacity is considered to be 20000 kL/year. Biomass is noted to have a low bulk density and higher moisture content ranging from 10–70%. The moisture content in raw material (sawdust/forest residues) is considered to be 40% (wb). The transportation distance is assumed to be 15 km (base case: sawdust transportation distance is estimated based on feedstock demands and the transportation distance reported by Mani et al., 2006). The bagged sawdust assumed to be transported by 6 m (20 feet) trailer truck. The transportation capacity is calculated based on the density of sawdust (417 kg/m\(^3\)) and volume of the trailers. The loading capacity is assumed to be 75% of the volume of the trailer. Cradle to gate scenario [system boundary of LC of ethanol from sawdust: sawdust either from sawmills (transportation) or sawdust prepared from forest residues (collection and transportation) followed by pretreatment, saccharification and fermentation, distillation and purification, and waste management] has been adopted for this study (Fig. 5.1). The environmental impacts related to the construction of the ethanol processing plant, storage facilities and the production of transportation and other machines, building and roads are not considered. It is also worthy to note that energy input in the form of labor and energy content in
the feedstock are not taken into account. Net energy consumption is defined as the difference between the sum of the energy consumption in each process and the amount of energy recovered from the lignin byproduct (hereafter referred to byproduct).

Figure 5.1 Schematic diagrams of the LC of sawdust and the system boundary of this study

5.2.2 Ethanol production

5.2.2.1 Pretreatment

Lime pretreatment (calcium capturing by carbonation, i.e., CaCCO process at 120°C for 1 h; lime 10%) is considered for this study (Park et al., 2010; Shiroma et al., 2011). The solid concentration during pretreatment is considered to be 30% (w/w).

5.2.2.2 Fermentation and distillation

The pretreated sawdust slurry (solid content 10% wt) is then allowed for simultaneous saccharification and fermentation (SSF) at 33°C for 72 h. The enzyme loading is considered to be 14 FPU (filter paper unit)/g-cellulose (McMillan et al., 1999). Vacuum extractive fermentation and distillation, and purification (using glycerol) processes are adopted (Dias et al., 2009; Junqueira et al., 2009a). The ethanol concentration in the vacuum extractive fermentation is assumed to be more than 7.5% (wt).

5.2.2.3 Enzyme (cellulase) and yeast production

Energy consumption in enzyme production process is calculated based on the enzyme production cost (enzyme loading: 15 FPU/g-cellulose i.e. 19263 FPU/L) and retail electricity price in the USA in 1997 (Wooley et al., 1999a; EIA, 2010). Then, enzyme cost of this study is worked out (based on the 2012 electricity price in Ontario). The cost of yeast ($0.01/gallon) is collected from the literature (Dutta et al., 2010a).

5.2.2.4 Waste management

The waste stream is assumed to be separated into centrifuged solids (lignin) and liquid streams (waste water). The lignin is assumed to be dried by utilizing the wasted heat from the
boiler. Anaerobic digestion of the wastewater produces biogas (Cardona & Sa´nchez, 2006). It is assumed that energy consumption and cost incurred in waste management processes would be offset by biogas, and the byproduct recovered in the waste management processes can be used for process heat generation. Based on the heating value of lignin and the boiler efficiency (80%; Mani et al., 2010) heat generation from the byproduct is estimated and used to offset some of the heat supplied by LNG (liquid natural gas). The emission and cost that credited to lignin is determined with the emission factor and cost of LNG.

5.2.3 Cost analysis

The economic life of the ethanol processing plant and the yearly operating period are assumed to be 20 years and 350 operation days, respectively (Dutta et al., 2011; Huang et al., 2009; Wu et al., 2006). The business capital is assumed to be equivalent to twice of the price of yearly feedstock demand. Both fixed costs (straight line depreciation on installation, labor, maintenance and interest on investment: $0.3/L) and variable costs (feedstock, enzyme production, utilities and waste management: $0.78/L) are taken into account to estimate the production cost of ethanol. The yearly interest rate on investment is assumed to be 3% and maintenance cost is 2% of processing plant cost. Sawmill residues, particularly sawdust, are noted to be abundant with low commercial value (about $20/t at processing plant gate; Mani et al., 2006). However, higher cost of sawdust ($100) has also been reported (Millman, 2008). The cost of sawdust is considered to be about 80 $/t-wet. The cost of forest residues is assumed to be 75% of the price of sawdust.

5.2.4 Data collection

Both the estimated and literature data are used to evaluate the LC of ethanol. Although the inventory data vary depending on the regions of the study and technologies used, the data used are assumed to be valid for this study. A summary of the parameters/processes for which data have been collected from literature are reported in the Supporting Information (Table 5.2).
Table 5.2 Summary of parameters for which data are collected from literature

<table>
<thead>
<tr>
<th>Parameters/Systems</th>
<th>Actual data</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol plant construction</td>
<td>$38 million</td>
<td>Asano &amp; Minowa, 2007</td>
</tr>
<tr>
<td>No. of labor (persons)</td>
<td>23</td>
<td>Asano &amp; Minowa, 2007</td>
</tr>
<tr>
<td>*Forest residue collection (L/t)</td>
<td>1.95</td>
<td>JA-Zenno, 2002</td>
</tr>
<tr>
<td>Sawdust production from forest residues (kWh/t)</td>
<td>20.56</td>
<td>TianYuan, 2013</td>
</tr>
</tbody>
</table>

Enzyme:

- Energy consumption kWh/L: 0.802
  - Wooley et al., 1999a
- Material cost ($/L): 0.014
  - Wooley et al., 1999a
- Yeast ($/gallon): 0.01
  - Dutta et al., 2010a
- Vacuum extractive fermentation & distillation
  - (MJ/kg hydrous ethanol): 7.525
    - Junqueira, et al., 2009a
- Purification (MJ/kg ethanol): 1.085
  - Dias et al., 2009
- Ethanol yield (L/kg-dry sawdust): 0.305
  - Olsson et al., 1996

Note: Plant capacity is 20000 kL/year; labor cost $46000/person/year; *assumed to be same that of straw collection; boiler efficiency 80% (Mani et al., 2010).

5.3 Results and discussion

5.3.1 Net energy consumption and CO₂ emission

The energy consumption (fossil fuel and electricity) in each stage of the LC of ethanol and the energy output from byproduct are calculated to estimate the net energy consumption (Fig. 5.2). Utilization of byproduct offsets some of the energy consumption and has a strong contribution to the net energy consumption. Energy consumption remains the same for different stages of the LC of ethanol for both scenarios except collection, transportation and pretreatment. Energy consumption in collection, transportation and sawdust preparation are estimated to be 0.41, 0.15 and 0.64 MJ/L for scenario-2. On the other hand, for scenario-1 energy consumption in transportation is estimated to be 0.11 MJ/L and no energy is consumed for collection and preparation, because sawdust is assumed to be readily available at the sawmill gate. Depending on the scenarios of the study, the estimated net energy consumption varied from 12.29–13.37 MJ/L. A slight variation in net energy consumption is observed because of the difference in assumed transportation distance, and energy consumption in collection and sawdust preparation.
when forest residues are used (scenario-2). The pretreatment process is observed to be the main hotspot followed by distillation, and others in the case of energy consumption. Net energy consumption is found to be within the range of reported net energy consumption of cellulosic ethanol (Kim & Dale, 2005; Roy & Dutta, 2012). The variation in net energy consumption might be because of different assumptions and feedstock (for example, earlier authors has used corn stover as a feedstock and byproduct is used for electricity generation; however the latter has used wheat straw as a feed stock and byproduct is used for heat generation) have been used.

Figure 5.2 Energy breakdown of the life cycle of ethanol

Figure 5.3 depicts emission breakdown of the LC of ethanol. The GHG released from different stages are directly related to energy and resource consumption. The main hotspot is observed to be the pretreatment followed by distillation and other stages. The byproduct (lignin) recovered and used for heat generation have a strong contribution to offsetting some of the emission from different stages. The net emission is estimated to be 0.75–0.92 kg CO₂ e/L. Wang et al., (2012) noted that energy recovery is dependent on the waste management scenarios, thus the net emission may vary, if different waste management scenarios are considered. A slight variation in net GHG emission is also observed mainly because of the difference in energy consumption for collection (forest residues) and pretreatment (includes sawdust preparation from forest residues) resulting from the assumptions for different scenarios. It seems environmental
benefit can be gained from sawdust ethanol relative to gasoline (1.5 kg CO₂ e/L-ethanol equivalent in Canada; Environment Canada, 2011), if the ethanol can be produced by using the technologies considered for this study, which seems to be supported by the findings of other researcher (Schmer et al., 2008). However, the environmental benefit drastically improved if carbon sequestration is considered (Fig. 5.4). The estimated net emission varied from -0.54 to -0.72 kg-CO₂ e/L. Figure 5.4 also depicts that significant environmental benefit (GHG) can be achieved compared with the gasoline. It is also worthy to note that natural forest is considered to be the source of sawdust for both scenarios. The environmental benefit from the LC of ethanol derived from sawdust may change if source is considered to be the purpose grown forest. The net GHG emissions reported to be -885 kg-CO₂ e/t in the case of yardwaste and carbon sequestration contributed about about 62–66% to net GHG emissions reduction (Roberts et al., 2010), which also support the findings of this study.

![Figure 5.3 Emission breakdown of the life cycle of ethanol](image)

**5.3.2 Production cost**

Figure 5.5 represents the cost breakdown of different stages of the LC of ethanol. The main hotspot has emerged to be the feedstock, followed by fixed cost and others. The feedstock cost is estimated to be $0.33–0.44/L depending on the source of feedstock. The fixed cost is calculated to be $0.25–$0.26/L for a plant capacity of 20000 kL/y, which may vary, if different processing plant sizes, operating periods and life spans are considered. Although little variation
is observed in feedstock and fixed cost due to different assumptions. The net production cost is estimated to be about $0.98–$1.04/L because of the variation in feedstock-, fixed-, collection-, transportation- and pretreatment cost. The estimated production cost indicates that ethanol from sawdust will have a steep competition with its counterpart (i.e., fossil gasoline). The production cost of ethanol is noted to be dependent on assumption, feedstock cost, allocation methods and reference systems (Cherubini & Strømman, 2011). Consequently, a direct comparison was not attempted with other studies. However, the production cost of this study is observed to be within the range of reported production cost (0.55–1.45 US$/L) of lignocellulosic ethanol (Barta et al., 2010a; Dutta et al., 2010a; Roy et al., 2012b). The variation in production cost among different studies might be because of differences in ethanol yield, feedstock cost, processing plant size, system boundary and assumptions (Gnansounou & Dauriat, 2010; Cherubini and Strømman, 2011). It is worthy to note that this study has been conducted based on the estimated and literature data, and all the data do not necessarily correspond to the Canadian context or to the same processing plant size. Consequently, in-depth studies are needed for any future investment and commercial production from sawdust/forest residues in Canada.

Figure 5.4 Effect of carbon sequestration on the net emission of the life cycle of ethanol
Results of an LCA are dependent on the energy and resource input at each stage of the LC of ethanol. It is also noted that LCA results are more sensitive to the changes in parameters related to the biomass and ethanol yield. Consequently, sensitivity of the variation in energy consumption at each stage (transportation, pretreatment, SSF, distillation) and ethanol yield is investigated. The variation of each parameter is assumed to be ±20% compared to the base case. It is observed that a change in the parameters also resulted in a change in net energy consumption, emission and production cost are changed (Figs. 5.6–5.8). The net energy consumption is observed to be dependent on the variation in energy consumption at each stage; however, the effect of ethanol yield is confirmed to be more sensitive compared to others. Any increase in considered parameters, net energy consumption, emission and production cost are also increased except the ethanol yield. The net energy consumption, emission and production cost decreased with an increase in ethanol yield. Moreover, this study revealed that feedstock and fixed cost are the main contributors to the production cost of ethanol followed by pretreatment. Therefore, it is imperative that feedstock and fixed cost need to be mitigated to diminish production cost of ethanol. At present this can only be achieved with implementing modified agro-industrial and environmental policy (it may be in the form of FiT program).
Figure 5.6 Effect of the change in energy consumption at different stages on net energy consumption (MJ/L).

Figure 5.7 Effect of the change in energy consumption at different stages on net emission (kg-CO₂ e/L)
Figure 5.8 Effect of the change in energy consumption at different stages on net cost ($/L)

Figure 5.9 Effect of the changes in feedstock- and fixed cost on the production cost of ethanol
The Government of Ontario has launched a Feed-in-Tariff (FiT) program to encourage people and organizations to develop renewable energy projects, especially producing electricity from renewable sources (OPA, 2013; Sanscartier et al., 2009). The FiT is varied depending on the source of renewable energy ($0.1–$0.55/kWh). The price of produced electricity is guaranteed for 20 years (40 years for waterpower). In Canada, the renewable energy sector is not only subsidized but also fossil fuel (Milan, 2010). A similar FiT program in renewable liquid biofuels sector of Ontario would reduce their production costs. Therefore, we assumed that fixed and feedstock cost can be reduced to 25–75% of the base case with the introduction of FiT program. The production cost of ethanol significantly reduced with the introduction of FiT program (Fig. 5.9), which confirmed that economically viable ethanol can be produced from sawdust if FiT program for liquid biofuels is implemented in Ontario. The production cost is estimated to be 0.51 $/L (in reference to the base case at plant gate) if $0.025/MJ FiT is considered. If fossil gasoline can be replaced by this amount of incentive to ethanol industry, the estimated emission abatement cost would become about $400/t CO₂ e. However, any reduction in this incentive to replace fossil gasoline emission abatement cost will also be reduced. It seems that ethanol industry will emerge as an economically viable/profitable rural agro-industry for the producers/investors, if a similar FiT program that of electricity from renewable sources is implemented. It may also help in achieving the GHG emission reduction target set by Canada, improving energy security and combating global warming potential, simultaneously creating rural employment opportunity and enhance rural economy in Ontario. Finally, FiT program would help Ontario become a leader in the ethanol market.

5.4 Conclusion
This study reveals that despite estimated environmental benefit of ethanol that produced from sawdust with adopted technologies, its economic viability remains doubtful unless FiT program is considered. A modified agro-industrial and renewable energy policy that allows FiT to the lignocellulosic ethanol industry in Ontario not only reduces production cost but also may encourage future investment and create more green jobs as well as help in achieving committed GHG emission reduction targets in Canada.
6.1 Introduction

The rising cost of fossil fuels and the geo-political uncertainty associated with their supply chains, and growing concerns about climate change led to recognize liquid biofuels as an alternative to fossil fuels for transportation. In 2010, secondary transportation fuel consumption is reported to be 2595 PJ in Canada, a growth of 38.2% from 1990 level (Natural Resource Canada, 2013). However, in 2010, ethanol contributed only 1.7% and 3.2% to total transportation energy and motor gasoline, respectively (Natural Resource Canada, 2013) (Fig. 6.1), which depicts the substantial demand of ethanol in Canada. Renewable energy not only provides significant environmental benefits but also enhances rural economies (Kim & Dale, 2003; Spatari et al., 2005; Farrell et al., 2006). Production of biofuels from biomass (agricultural and forest residues, and energy crops) has been emphasized, because it does not compete with food or feed (Zaldivar et al., 2001; Gray et al., 2006; Hahn-Hägerdal et al., 2006; Sánchez & Cardona, 2008).

Although ethanol production from biomass has been emphasized, concern about soil fertility and structural stability and restricts the collection of agricultural residues (Sheehan et al., 2002; Blanco-Canqui & Lal, 2009). Farmers are also reluctant to the removal of crop residues from their farms (Tyndall et al., 2010). In Canada, the potential sources of renewable biomass include agricultural residues, municipal solid waste, forestry byproducts and energy crops. The technical, economic and sustainability constraints in Ontario conditions also limits their supply to ethanol industry (Klundze et al., 2010). The use of forestry wastes for liquid biofuels are also restricted due to its enormous demand by the solid biofuels industries. Miscanthus is a promising energy crop with high yield and energy content, which can be grown on low quality or marginal land, and add carbon to the soil and safeguard it against erosion (Somerville et al., 2010; Kludze et al., 2013), has an important role in sustainable energy production (Sørensen et al., 2008; Khanna et al., 2008; Bocquêho & Jacquet, 2010).

Klundze et al (2013) noted that Ontario has an adequate land base for producing miscanthus to meeting/surpassing numerous viable uses of biomass without significantly affecting food
crops supply. Although life cycle assessment (LCA) methodology has been extensively used to evaluate the life cycle (LC) of lignocellulosic ethanol, the LCA of ethanol from miscanthus has received limited attention (Fazio & Monti, 2011; Scown et al., 2012; ), which are mostly deal with biorefinery, crop location and agricultural practices. This study evaluates the LC of ethanol produced by enzymatic hydrolysis considering three scenarios to determine if environmentally preferable and economically viable ethanol can be derived from miscanthus in Ontario, Canada.

6.2 Methodology

6.2.1 Study area, system boundary and assumptions

Ontario is located in east-central region (48°N to 83°W) of Canada (60°N to 95°W) and consists of two major regions (southern and northern). The southern region is further divided into four sub-regions, namely southern-, western-, central-, and eastern Ontario (Fig. 6.2). The land area in Ontario is 91.8 million ha with 4.4 million ha of tillable land, and only about 3.6 million ha is arable for growing conventional crops. The land classes are scattered throughout various regions (Fig. 6.3) and the area under different land classes varies from region to region (Table 6.1).

Figure 6.1 Transportation fuel consumption and contribution of ethanol in Canada
Figure 6.2 Different regions in Ontario, Canada

Figure 6.3 Different regions and land classes in Ontario, Canada
Table 6.1 Land areas in Ontario, ha

<table>
<thead>
<tr>
<th>Regions</th>
<th>Land class and tillable land area, ha</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Class 1</td>
</tr>
<tr>
<td>Southern Ontario</td>
<td>238102</td>
</tr>
<tr>
<td>Western Ontario</td>
<td>724831</td>
</tr>
<tr>
<td>Central Ontario</td>
<td>165830</td>
</tr>
<tr>
<td>Eastern Ontario</td>
<td>32005</td>
</tr>
</tbody>
</table>

Source: Kludze et al., 2013

Availability of crop residues are reported to be limited because of technical, economic and sustainability constraints in Ontario conditions (Kludze et al. 2010). On the other hand, Ontario has adequate land base for producing energy crops, especially miscanthus to meet/surpass diverse uses (Kludze et al., 2013). The land area in Ontario is 91.8 million ha with 4.4 million ha of tillable land, and only about 3.6 million ha is arable for growing conventional crops (Statistics Canada 2008; OMF, 2013). The land in Ontario has been classified into seven classes (A-6-1). It is also grouped as the prime- (classes 1, 2 & 3) and marginal lands (classes 4 & 5). The productivity of miscanthus is dependent on the type of land (land classes) (Table 6.2).

Table 6.2 Land classes, soil types and miscanthus yield

<table>
<thead>
<tr>
<th>Land class</th>
<th>Description</th>
<th>Soil type</th>
<th>Yield, dry-t/ha</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class 1</td>
<td>Suitable for field crops</td>
<td>Silt loam-clay loam</td>
<td>11.14</td>
</tr>
<tr>
<td>Class 2</td>
<td>Suitable for field crops with moderate limitations</td>
<td>Silt loam-clay loam</td>
<td>11.14</td>
</tr>
<tr>
<td>Class 3</td>
<td>Suitable for field crops with moderately severe limitations</td>
<td>Sandy-clay</td>
<td>10.03</td>
</tr>
<tr>
<td>Class 4</td>
<td>Has severe limitations for field crops</td>
<td>Sandy-loam</td>
<td>8.9</td>
</tr>
<tr>
<td>Class 5</td>
<td>Very severe limitations for field crops</td>
<td>Loam</td>
<td>7.8</td>
</tr>
</tbody>
</table>

Prime land: classes 1, 2 & 3; Marginal land: classes 4 & 5 (Source: Kludze et al., 2013)
Three scenarios are established to evaluate the LC of ethanol derived from miscanthus (Table 6.3). Miscanthus yield, net emission from cultivation and feedstock cost for various scenarios are assumed to be the average yield, emission and cost of corresponding land classes, respectively. Cradle to gate scenarios is adopted to outline the system boundary of this study (Fig. 6.4). Both the estimated and literature data are used to evaluate the LC of ethanol (Table 6.4). Infrastructure construction, production of transportation and other machineries, and energy input in the forms of labor and feedstock are not considered. Emission has been estimated in terms of CO\textsubscript{2} e (i.e., GWP for a time span of 100 year; IPCC, 2001). Net energy consumption is determined based on the difference between the sum of the energy consumption in each process and the amount of energy recovered from the lignin (hereafter referred to byproduct). Net emission is the difference between the emission from input energy and the sum of carbon sequestration and the amount of emission offset by the byproducts recovered from the system.

Table 6.3 Scenarios of this study.

<table>
<thead>
<tr>
<th>Scenarios</th>
<th>Descriptions</th>
<th>Yield, tDM/ha</th>
<th>Feedstock cost, $/tDM</th>
<th>On farm emission, kg CO\textsubscript{2}e/tDM</th>
</tr>
</thead>
<tbody>
<tr>
<td>S\textsubscript{1}</td>
<td>All classes of land are used for miscanthus cultivation</td>
<td>10.02</td>
<td>66.19</td>
<td>54.62</td>
</tr>
<tr>
<td></td>
<td>Only prime land is used for miscanthus cultivation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S\textsubscript{2}</td>
<td>Miscanthus cultivation</td>
<td>10.86</td>
<td>64.56</td>
<td>16.94</td>
</tr>
<tr>
<td></td>
<td>Only marginal land is used for miscanthus cultivation</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S\textsubscript{3}</td>
<td>Miscanthus cultivation</td>
<td>8.35</td>
<td>71.50</td>
<td>167.67</td>
</tr>
</tbody>
</table>

Prime land: Classes 1, 2 & 3; Marginal land: Class 4 & 5 (Source: Kludze et al., 2013; Sanscartier et al., 2013).

6.2.2 Miscanthus cultivation

Miscanthus has received increasing attention as a source of renewable energy because of its high productivity, and its proven economics as an energy crop in Europe and USA (Khanna et al., 2008; Bocqueho & Jacquet, 2010; Sherrington & Moran, 2010; Kludze et al., 2013). After planting, miscanthus can stands for fifteen to twenty years on the farm, and has a very low agrochemical requirement (DEFRA, 2007). Miscanthus grows in tropical, subtropical and temperate regions; however does not grow at a temperature below 6°C (AEBIOM, 2010). Thus, miscanthus can be grown in all the regions of Ontario and its cultivation is noted to be economically viable.
in Ontario (Vyn et al., 2012; Kludze et al., 2013). Miscanthus stands persist for fifteen to twenty years. Miscanthus yield increases for the first 3 years and then remains constant for the remaining years. Yield varies from region to region. Miscanthus has very low agro-chemical requirement (DEFRA, 2007). The hybrid species yield more compared to others.

Table 6.4 Summary of parameters for which data are collected from literature

<table>
<thead>
<tr>
<th>Parameters/Systems</th>
<th>Actual data</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>Miscanthus cultivation (kg CO₂e/tDM)</td>
<td>16.94 to 167.67</td>
<td>Sanscartier et al., 2013</td>
</tr>
<tr>
<td>Feedstock cost ($/tDM)</td>
<td>64.56 to 71.5</td>
<td>Kludze et al., 2013</td>
</tr>
<tr>
<td>*Crushing (size 3 mm) (kWh/kg)</td>
<td>0.06095</td>
<td>Roy et al., 2012a; b</td>
</tr>
<tr>
<td>Ethanol processing plant construction</td>
<td>$38 million</td>
<td>Asano &amp; Minowa, 2007</td>
</tr>
<tr>
<td>No. of labor (persons)</td>
<td>23</td>
<td>Asano &amp; Minowa, 2007</td>
</tr>
<tr>
<td>Enzyme:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Energy consumption kWh/L</td>
<td>0.802</td>
<td>Wooley et al., 1999</td>
</tr>
<tr>
<td>Material cost ($/L)</td>
<td>0.014</td>
<td>Wooley et al., 1999</td>
</tr>
<tr>
<td>Yeast ($/gallon)</td>
<td>0.01</td>
<td>Dutta et al., 2010a</td>
</tr>
<tr>
<td>Vacuum extractive fermentation &amp; distillation (MJ/kg hydrous ethanol)</td>
<td>7.525</td>
<td>Junqueira, et al., 2009</td>
</tr>
<tr>
<td>Purification (MJ/kg ethanol)</td>
<td>1.085</td>
<td>Dias et al., 2009</td>
</tr>
<tr>
<td>Ethanol yield (L/kg-dry miscanthus)</td>
<td>0.305</td>
<td>Nilsson et al., 2008; Li et al., 2013; Zhang et al., 2012; DOE, 2006</td>
</tr>
</tbody>
</table>

Note: Plant capacity is 20000 kL/year; labor cost $46000/person/year; *assumed to be same that of straw; boiler efficiency 80% (Mani et al., 2009); $: Canadian dollar.

Inputs in miscanthus cultivation and harvesting stage are reported in supporting information (A-6-2 & A-6-3). Typically, miscanthus is harvested in late winter or early spring; thus, contains low moisture at harvest (15–20%) (DEFRA, 2007; Kludze et al., 2013; Sanscartier et al., 2013). A portion of agricultural land in northern Ontario has been excluded in this study because of its short growing periods (100–145 frost free days). The net emission from agriculture
(hereafter referred to feedstock) is estimated based on energy inputs in agriculture and the carbon dynamics i.e., carbon storage in all pools (A-6-4).

Figure 6.4 Schematic diagrams of the life cycle of sawdust and the system boundary of this study

6.2.3 Transportation

Harvested and baled miscanthus is transported to the ethanol processing plant by 6 m (20 feet) tailor trucks (loading capacity is assumed to be 75%). The moisture content in harvested miscanthus is considered to be 15% and the bulk density of baled miscanthus is 218 kg/m$^3$ (Vyn et al., 2012). Fuel consumption in the transportation process is calculated based on the loading capacity, feedstock moisture content and specific volume of baled miscanthus. The ethanol processing plant capacity is assumed to be 2000 kL/year. Miscanthus transportation distance from farms to the ethanol processing plant is estimated based on following equations (Eqs. 1 & 2) (Huang et al., 2009). Roads and channels are assumed to be 2% of tillable land at the rural area. The transportation distance depends on the scenarios and it varies from is 17.7–48.0 km.

Radius of the area, $R_{km} = \{F/(\pi faflcY)\}^{1/2}$ . . . . . . .  (Eq.6. 1)

where, $F =$ Annual feedstock demand, t

$\pi =$ constant

$fa =$ fraction of total farmland from which feedstock can be collected or produced

$flc =$ fraction of surrounding farmland containing crops

$Y =$ biomass yield per unit area (dry), t/km$^2$

Transportation distance (collection center–processing plant), $D_{km} = 2Rf_w/3$ .  (Eq. 6. 2)

where, $f_w =$ road winding factor (assumed to be 1.3; Sokhansanj & Turhollow, 2002)

6.2.4 Ethanol production

6.2.4.1 Pretreatment

Pretreatment, either physicochemical or chemical or biological is a prerequisite to improve components digestibility and improve the ethanol yield from miscanthus (Brosse et al., 2009).
Although different pretreatments are employed to miscanthus [ammonia fiber expansion, acid hydrolysis, NaOH pretreatment, wet explosion etc. and liquid hot water (LHW)] pretreatment (Sørensen et al., 2008; Murnen et al., 2008; Han et al., 2011; Vanderghem et al., 2012; Khullar et al., 2013; Li et al., 2013), the LHW pretreatment with lime is given to the crushed miscanthus (3 mm) in this study (Shiroma et al., 2011). The solid concentration during pretreatment is considered to be 30% (w/w).

6.2.4.2 Fermentation and distillation
Vacuum extractive fermentation and distillation, and purification (using glycerol as an additive) processes are employed (Dias et al., 2009; Junqueira et al., 2009a). The pretreated miscanthus slurry (solid content 10% wt) is allowed for simultaneous saccharification and fermentation (SSF) at 33°C for 72 h. Although the reported enzyme loading for ethanol production varies from 10–20 FPU/g-cellulose (Gregg et al., 1996; Brosse et al., 2009), the enzyme loading is assumed to be 8.04 FPU/g miscanthus. Similarly, the ethanol yield also varies from 0.189–0.427 L/kg (DOE, 2006; Nilsson, 2008; Zhang et al., 2012; Li et al., 2013). The ethanol yield is considered to be 0.305 L/kg-dry feedstock.

6.2.4.3 Energy consumption in enzyme and yeast production
Energy consumption in enzyme production process is estimated based on the reported enzyme production cost (Wooley et al., 1999a). Then, the enzyme cost of this study is estimated (based on the 2012 electricity price in Ontario) (A-6-5); however, the production cost of yeast ($0.01/gallon) is derived from the literature (Dutta et al., 2010a).

6.2.4.4 Waste management
The waste stream of lignocellulosic ethanol consists of solids (lignin) and liquid (wastewater). The waste stream is centrifuged into lignin and liquid streams. Anaerobic digestion of the wastewater produces biogas (Cardona & Sa´nchez, 2006) and the dried lignin (dried by utilizing wasted heat from boiler) is combusted in boiler for heat recovery (boiler efficiency is considered to be 80%; Mani et al., 2010). It is assumed that biogas offsets the energy consumption in waste management processes and heat recovered from lignin offsets some of the process heat supplied by liquid natural gas (LNG). The emission and cost that credited to recovered heat is ascertained with the emission factor and cost of LNG.
6.2.5 Cost analysis

The production cost of ethanol is estimated based on both fixed costs (straight line depreciation on installation, labor, maintenance and interest on investment) and variable costs (feedstock, enzyme production, utilities and waste management). The economic life span of the processing plant and the yearly operating period are assumed to be 20 years and 350 operation days, respectively (Dutta et al., 2011; Huang et al., 2009; Wu et al., 2006). The business capital is assumed to be equivalent to twice of the price of yearly feedstock demand. The yearly interest rate on investment is assumed to be 3% and maintenance cost is 2% of processing plant cost. The cost of miscanthus is considered to be about 63–74 $/tDM depending on the scenarios (Kludze et al., 2013).

6.3 Results and discussion

6.3.1 Net energy consumption

The energy consumption in each stage of the LC of ethanol and the energy recovery from byproducts are estimated to represent energy breakdown of ethanol production process (Fig. 6.5). Feedstock cultivation is emerged to be the main hotspot followed by pretreatment, distillation, enzyme, SSF, yeast, and transportation for each scenario. A slight variation in transportation energy consumption is observed because of the difference in transportation distance among the scenarios. The transportation distance is found to be shortest and longest for scenario-1 (S1) and scenario-3 (S3), respectively, because of the difference among the corresponding land area. The net energy consumption varies from 13.02–13.34 MJ/L. The byproduct offsets a part of energy consumed in the process, which has a strong contribution to net energy consumption for all scenarios. The net energy consumption is noted to be sensitive to coproduct allocations and assumptions of the study (Pimentel & Patzek, 2005; Roy & Dutta, 2012). Thus, the net energy consumption varied from other studies because of different feedstock is used and various assumptions are made in those studies (Sheehan et al., 2003; Kim & Dale, 2005; Roy et al., 2012a,b; Roy & Dutta, 2012). However, the net energy consumption may vary, if different pretreatment methods are adopted.
6.3.2 Greenhouse gas emission (CO$_2$e)

Figure 6.6 shows the emission breakdown of the LC of ethanol for different scenarios. The emissions are directly related to energy and resource consumption (fossil energy and electricity) at different stages except feedstock because carbon dynamics offsets a major part in this step. The pretreatment process is emerged to be the main hotspot followed by distillation, enzyme, SSF, yeast, and transportation except $S_3$ where feedstock is emerged as the main hotspot because of the positive carbon dynamics (i.e., carbon released to the atmosphere). Consequently, emission from feedstock is found to be 0.18, 0.06 and 0.55 kg/L for $S_1$, $S_2$ and $S_3$, respectively. A slight variation in CO$_2$ emission is observed in the case of transportation, caused by the difference in transportation distance among different scenarios. The carbon dynamics is noted to be dependent on the land classes, crop replacement/rotation and biomass yield (Klundze et al., 2013; Sanscartier et al., 2013). The emission from the feedstock is the highest in the case of marginal land ($S_3$) and the lowest for prime land ($S_2$). These variations might not only because of land type but also region and crop rotation, because various crop rotations are considered for different scenarios (A-6-4).
The net emissions from the LC of ethanol are estimated to be 0.92, 0.79 and 1.31 kg/L for scenarios S1, S2, and S3, respectively which are seem to be dependent on the carbon dynamics. It is worthy to mention that the byproduct used for heat recovery, and the carbon dynamics has a robust contribution to offsetting a part of emission of the LC of ethanol. The estimated net emissions from the LC of ethanol reveal that environmental benefit can be achieved even miscanthus is grown on the marginal in Ontario and ethanol produced by adopting the technologies considered in this study.

### 6.3.3 Net production cost

The production cost breakdown depicts that fixed cost is the main hotspot followed by the feedstock, pretreatment, distillation, enzyme, SSF, yeast and transportation (Fig. 6.7). There is a slight variation in fixed-, feedstock-, and transportation cost which is yielded by the difference in feedstock production cost and the transportation distance among the scenarios. The fixed-feedstock-, and transportation cost varied from 0.246–0.247, 0.212–0.235, and 0.006–0.017 $/L, in the case of scenarios S1, S2, and S3, respectively. The net production cost for S1, S2, and S3 are estimated to be 0.80, 0.79, and 0.83$/L, respectively. It is important to note that the breakeven
feedstock cost is considered for the production cost estimation, which may vary depending on the biomass logistics and farmers profit margins.

Although a wide variation in production cost of lignocellulosic ethanol is reported, the estimated production cost of this study is observed to be reasonable and comparable with those studies (Barta et al., 2010a; Dutta et al., 2010a; Klein-Marcuschamer et al., 2010; Kumar & Murthy, 2011; Roy et al., 2012a,b; Roy & Dutta, 2012, 2013). The enzymes cost for converting biomass into ethanol in enzymatic hydrolysis process is also noted to be a major hindrance to the development of an economically viable lignocellulosic ethanol industry (Roy et al., 2012b; Banerjee et al., 2010b; Merino et al., 2007). The production cost of ethanol is also noted to be dependent on the conversion technology, enzyme loading, feedstock, allocation methods and plant sizes (Gnansounou & Dauriat, 2010; Roy et al., 2012a,b; Roy & Dutta, 2012); consequently, production cost may vary, if different conversion methods, allocation, and plant sizes are considered. This study indicates that miscanthus is a promising feedstock for ethanol in Ontario, Canada.
6.3.4 Sensitivity analysis

LCA methodology identifies the potential hotspots of product, production system and activity. The potential hotspot of this study is identified to be the feedstock in case of energy consumption and emission; however, fixed cost is emerged to be the main hotspot in the case of production cost. A wide variation is also observed in the case of transportation distance (10–49 km) and carbon dynamics (-0.5 to 0.03 dry t C/ha year; Sanscartier et al., 2013) among the scenarios. Liquid biofuels production is rapidly increasing, and affecting land allocation among crops (Roy & Shiina, 2010), thus, commercial biofuel production may target higher-quality lands, due to better profit margins and push the cereals and subsistence crops to the low-quality land. Although the carbon dynamics of scenario S3 is greater than that of others (S1 and S2), miscanthus can be grown on marginal lands which are not suitable for food crops (Kludze et al., 2013; Sanscartier et al., 2013) and environmental benefit can be achieved compared to fossil gasoline.

Carbon sequestration is the process of capture and long-term storage of atmospheric carbon i.e., CO₂. Carbon can be captured from the atmosphere through biological, chemical or physical processes and depositing it in a reservoir. Carbon sequestration rate in soil depends on soil types, farming system, soil management, weather, crop displacement, and biomass yield (aboveground and belowground). Removal of crop residues or harvesting of biomass affect the soil nutrient balance and depletes soil fertility, and crop productivity (Henao & Baanante, 2006; Haskins et al., 2006). Lal (2009) also noted that harvesting of crop residues for biofuels feedstock jeopardize soil and water resources which are already under great stress.

Aboveground minimum source carbon (MSC) requirement is noted to be 1.8±0.44 to 2.5±1.0 t/ha/year depending on the tillage systems (Johnson, 2006). Blanco-Canqui and Lal (2009) suggested crop residues removal rate as low as 25%, beyond which soil fertility and structural stability would be negatively affected. In contrast, it is also noted that about 50–60% crop residues can be collected without deteriorating the soil quality and productivity (Smith, 1986; Sheehan et al., 2002; Jeschke, 2011). Beale & Long (1995) noted that at the end of the growing season 39% of the biomass is partitioned to roots and rhizomes in the case of miscanthus. This information indicates that miscanthus can be harvested for biofuels without deteriorating the soil quality and productivity. Moreover, miscanthus can be economically cultivated all over Ontario (Kludze et al., 2013; Kludze et al., 2010). The breakeven feedstock
cost has also been used for cost estimation, which may vary depending on the profit margin of stakeholders and biomass logistics. Consequently, sensitivity of the variation in transportation distance, pretreatment energy consumption, feedstock and fixed cost are investigated (based on the third scenario: S₃).

Figures 6.8 & 6.9 represent the effect of variation in transportation distance and pretreatment energy consumption (variation are considered to be ±20 to ±60% for both case) on the net energy consumption, emission and production cost, respectively. The net energy consumption, emission and production cost varies from 10.7–17.3 MJ/L, 1.1–1.6 kg-CO₂ e/L and 0.7–0.9 $/L, respectively, depending on the severity of the variation of different parameters. The effect of the change in pretreatment energy consumption seems to be severe than that of transportation distance.

Figure 6.8 Effect of the variation in transportation distance and pretreatment energy consumption on the net energy consumption (MJ/L)

Figure 6.10 represents the effect of the variation (±10 to ±30%) of feedstock cost on the net production cost. The net production cost varies from 0.75–0.90 $/L depending on the severity of the variation. The production cost can be reduced if agri-industrial and environmental policies are enacted to support the miscanthus based ethanol industry, especially miscanthus grows on the marginal land.
Figure 6.9 Effect of the variation in transportation distance and pretreatment energy consumption on the net emission and production cost

Figure 6.10 Effect of feedstock and fixed cost (S/L)
The carbon dynamics is dependent on the land classes, biomass yield, crop rotation/replacement (Kludze et al., 2013; Sanscartier et al., 2013). Consequently, carbon dynamics may vary if different crop rotation/replacement or variety of miscanthus is adopted. The net emission from the LC of ethanol is found to be directly related with the carbon dynamics (Fig. 6.11). Negative carbon dynamics (carbon stored from the atmosphere)) reduces the net emission from the LC of ethanol. In contrast positive carbon dynamics (carbon released to the atmosphere) increases the net emission from the LC of ethanol. Therefore, careful attention should be in place in selecting miscanthus variety, crop rotation which not only help in reducing net emission from the LC of ethanol, but may also improve farm economy and attract more investment in the rural ethanol industry.

![Graph](image.png)

Figure 6.11 Effect of carbon dynamics on the net emission of the life cycle of ethanol

This study reveals that miscanthus grows on the marginal land in Ontario could be a potential feedstock for lignocellulosic ethanol industries and avoid any competition with food crops for prime land help Ontario improves her food and energy security, and enhance rural economy. It is also noted that genetically modified (GM) crops can serve various purposes, such as improving yield and increasing the share of useful components or decreasing the need for chemical fertilizers or water, and improves farm income (Bennett et al., 2004; ScienceDaily, 2005). Consequently, GM miscanthus may further improve farm income, reduce net emission.
from the LC of ethanol and help Canada achieve renewable energy and emission reduction target.

6.4 Conclusion

Ethanol derived from miscanthus is found to be environmentally preferable and economically viable in Ontario. Although a slight variation is observed in the case of net energy consumption and production cost among the scenarios, the variation is robust in the case of net emission where carbon sequestration plays an important role. It is worthy to mention that both the environment and economic benefit can be gained, even miscanthus is grown on the marginal land ($S_3$) in Ontario for ethanol. Thus, miscanthus grown on marginal land is emerged as a promising feedstock for ethanol industry in Ontario, which may avoid any sort of competition with food crops for better quality land, improve farm income and rural economy, and help meeting the ethanol demand and achieving GHG emission target of Canada.
Identification of suitable plant location for ethanol industry in Ontario, Canada

7.1 Introduction

Evaluation of the life cycle (LC) of ethanol derived from miscanthus revealed that miscanthus is a promising feedstock for environmentally and economically viable ethanol in Ontario, Canada (Chapter 6). The emission and production cost are also noted to be dependent on the feedstock, location, conversion technologies, plant sizes and biomass logistics (Wooley et al., 1999; McAloon, et al., 2000; Gnansounou & Dauriat, 2010; Roy et al., 2012a,b; Roy & Dutta, 2012). Consequently, this study attempts to identify the potential locations for the miscanthus based ethanol plant in Ontario, Canada not only to abate emission but also to minimize the production cost.

7.2 Materials and methods

7.2.1 Study area

The land area in Ontario is 91.8 million ha with 4.4 million ha of tillable land. The land has been grouped into seven land classes (A-6-1) (AAFC, 2008; OMAF, 2013). Land in Ontario is also classified as prime- (classes 1, 2 and 3) and marginal (classes 4 and 5) land, suitable for cultivation and other classes are not suitable for cultivation (class 6 and class 7). Ontario has two major regions: northern and southern. Agricultural land in northern region has short growing period (100–145 frost free days), thus not suitable for miscanthus cultivation. The southern region consist of four sub-regions: Central-, Southern-, Western- and Eastern Ontario which are suitable for miscanthus cultivation (Vyn et al., 2012; Kludze et al., 2013; Sanscartier et al., 2013) and assumed to be the area for this study. The area under different land classes varies from region to region and scattered throughout the regions (Fig. 6.1). Table 7.1 shows the area under different land classes and the total area of various regions.

7.2.2 System boundary

The cradle to gate scenario is adopted to outline the system boundary of this study (Fig. 6.2). Although all classes of cultivable lands are suitable for miscanthus, yield, production cost and net emission from cultivation are varied depending on the land classes, crop rotation and regions (Klundze et al., 2013; Sanscartier et al., 2013). Consequently, four scenarios have been
established for various regions (central-, southern-, western- and eastern Ontario) to evaluate the LC of ethanol derived from miscanthus (Table 7.2). A summary of parameters/process for which data have been collected from the literature and their sources are reported in the previous chapter (Table 6.4), except emission from miscanthus cultivation and cost of feedstock (which are reported on table 7.2). The procedure of net energy consumption calculation and other assumptions are also reported in the previous chapter (section 6.2.1).

Table 7.1 Land area under different tillable land classes and various regions in Ontario, ha

<table>
<thead>
<tr>
<th>Regions</th>
<th>*Land class and tillable land area, ha</th>
<th>^Regional area, ha</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Class 1</td>
<td>Class 2</td>
</tr>
<tr>
<td>Southern Ontario</td>
<td>238102</td>
<td>876664</td>
</tr>
<tr>
<td>Western Ontario</td>
<td>724831</td>
<td>254067</td>
</tr>
<tr>
<td>Central Ontario</td>
<td>165830</td>
<td>113526</td>
</tr>
<tr>
<td>Eastern Ontario</td>
<td>32005</td>
<td>312567</td>
</tr>
</tbody>
</table>

*Kludge et al., 2013; ^Wikipedia

Table 7.2 Scenarios of this study

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Land class</th>
<th>Soil type</th>
<th>Crop rotation</th>
<th>Yield, tDM/ha</th>
<th>Cost, $/tDM</th>
<th>*Emission, kg-CO₂e/tDM</th>
</tr>
</thead>
<tbody>
<tr>
<td>S₂</td>
<td>3</td>
<td>Sandy-clay</td>
<td>Continuous soybean rotation</td>
<td>10.03</td>
<td>65.67</td>
<td>-88.77</td>
</tr>
<tr>
<td>S₃</td>
<td>3</td>
<td>Sandy-clay</td>
<td>Corn-corn-forage-forage rotation</td>
<td>10.03</td>
<td>65.67</td>
<td>167.47</td>
</tr>
<tr>
<td>S₄</td>
<td>4 &amp; 5</td>
<td>Sandy loam</td>
<td>Long term pasture</td>
<td>8.35</td>
<td>71.50</td>
<td>167.67</td>
</tr>
</tbody>
</table>

Sources: Kludge et al., 2013; Sanscartier et al., 2013; *net emission from miscanthus cultivation is estimated considering the carbon dynamics.

7.2.3 Transportation, ethanol production and cost analysis

Transportation, ethanol production, and cost analysis processes are described in the previous chapter (section 6.2.3 to 6.2.5).
7.3 Results and discussion

7.3.1 Net energy consumption

The net energy consumption in the LC of ethanol was dependent on the energy consumption in each stage that considered in the system boundary of the study. A slight variation in transportation energy consumption was observed because of the difference in transportation distance among the scenarios. The transportation distance varied from 12.0–71.5 km depending on the location and scenarios (S₁ to S₄). It was found to be the shortest for Eastern Ontario and the longest for Western Ontario for each scenario compared with other locations. The transportation distance was found to be the shortest and the longest for scenario S₁ and S₄, respectively, for each location except Central Ontario where transportation distance for S₄ was found to be lower than that of S₂ and S₃ (Fig. 7.1). Feedstock cultivation has emerged as the main hotspot followed by pretreatment, distillation, enzyme, SSF, yeast, feedstock, and transportation for each scenario (Fig. 7.2). This figure also indicates that energy recovery from byproducts plays an important role in net energy consumption in the LC of ethanol.

![Figure 7.1 Feedstock transportation distance at different location in Ontario](image-url)
The byproduct offsets a part of energy consumed in the process, which has a robust contribution to the net energy consumption for all scenarios. The net energy consumption varied from 13.0–13.4 MJ/L. The net energy consumption was noted to be sensitive to coproduct allocations and assumptions of the study (Pimentel & Patzek, 2005; Roy & Dutta, 2012). Thus, the net energy consumption varied from other studies because of different feedstock has been used and various assumptions were made in those studies (Kim & Dale, 2005; Roy et al., 2012a,b; Roy & Dutta, 2012). The net energy consumption may vary, if different miscanthus variety, cultivation and pretreatment methods are adopted. Similar to the transportation distance, the energy consumption was found to be the lowest for S₁ and highest for S₄ among the scenarios; however a slight variation was observed among the processing plant locations (Fig. 7.3).

7.3.2 Greenhouse gas emission (CO₂ e)

The emissions were directly related to energy and resource consumption at different stages except feedstock because carbon dynamics offsets a major part in the case of feedstock. The pretreatment process has emerged as the main hotspot followed by distillation, enzyme, SSF, yeast, and transportation, except S₃ and S₄ where feedstock has emerged as the main hotspot because of the positive carbon dynamics (i.e., carbon released to the atmosphere) of feedstock (Fig. 7.4). On the other hand, negative carbon dynamics were observed in the case of S₁ and S₃.
Consequently, emissions from feedstock were found to be -0.09, -0.29, 0.55 and 0.55 kg/L for S1, S2, S3 and S4 (marginal land), respectively. A slight variation in CO₂ emission was observed in the case of transportation, which caused by the difference in transportation distance among the scenarios and locations. The carbon dynamics was noted to be dependent on the land classes, crop replacement/rotation and biomass yield (Kludze et al., 2013; Sanscartier et al., 2013). Consequently, the net emission would be varied if different crop displacement or crop rotation were considered.

The emission from feedstock was the highest in the case of S4 and the lowest for S1. These variations indicate that carbon dynamics dependent not only on the land type and region but also on the crop rotation. Although, same land class was considered for S2 and S3, the carbon dynamics varied, might be because of different crop displacements were assumed. The net emission from the LC of ethanol was estimated to be 0.45–1.32 kg/L depending on the scenarios and processing plant locations, which seems to be mainly dependent on the carbon dynamics and the emission offsets by the byproduct. The results also confirmed that these variations might not only because of land type but also region and crop rotation, because various crop rotations were considered for different scenarios. The net emission was found to be the lowest in the case of S2 for a plant location at Eastern Ontario and the highest in the case of S4 at Western Ontario (Fig. 7.5). These values indicate that environmental benefit can be achieved from miscanthus based
ethanol at all locations that considered in this study, even if miscanthus was cultivated on marginal land. It is important to mention that the net emission may vary if different crop displacement is considered.

Figure 7.4 Emission breakdown of the life cycle of ethanol (Southern Ontario)

Figure 7.5 Net emissions at different location in Ontario
7.3.3 Production cost

The production cost breakdown depicts that the fixed-, feedstock-, and transportation cost were varied from 0.246–0.247, 0.205–0.235, and 0.005–0.020 $/L, respectively depending on the scenarios and the location of processing plant. A slight variation in fixed- and feedstock cost was resulted by the difference in feedstock production cost among the scenarios. Similarly, the difference in transportation distance caused the variation in transportation cost. However, cost of other stages of the LC of ethanol remained the same because of the same technologies were applied for various scenarios. Although, there was a slight variation in fixed-, feedstock- and transportation cost among the scenarios, the fixed cost has emerged as the main hotspot followed by feedstock, pretreatment, distillation, SSF, yeast and transportation for all locations (Fig. 7.6).

![Figure 7.6 Cost breakdown of the life cycle of ethanol (Southern Ontario)](image)

The estimated net production cost varied from 0.79–0.84 $/L depending on the scenarios and location of the processing plant. Although a slight variation was observed among the scenarios and locations, the net production cost was found to be the lowest for S2 and the plant location at Eastern Ontario, and the highest for S4 and the plant location at Western Ontario because of the variation in fixed-, feedstock-, and transportation cost among the scenarios (Fig. 7.7). The breakeven feedstock cost was considered for the production cost estimation, which may vary depending on the biomass logistics and farmers profit margins, consequently the net production cost may also vary, if the feedstock cost is varied. The production cost of ethanol was
also noted to be dependent on the conversion technology, enzyme loading, feedstock, allocation methods and plant sizes (Gnansounou & Dauriat, 2010; Roy & Dutta, 2012); consequently, production cost may vary, if different conversion methods, allocation, and plant sizes are considered. Although a wide variation in production cost of lignocellulosic ethanol was reported, the estimated production cost of this study was observed to be reasonable and comparable with other studies (Dutta et al., 2010a; Klein-Marcuschamer et al., 2010; Kumar & Murthy, 2011; Roy et al., 2012a; Roy & Dutta, 2012, 2013).

Figure 7.7 Net production cost at different locations in Ontario.

7.3.4 Sensitivity analysis

The LCA results of lignocellulosic ethanol are reported to be more sensitive to the changes in parameters related to the biomass and ethanol yield (Roy & Dutta, 2013; Roy et al., 2012b). A wide variation in ethanol yield from miscanthus (DOE, 2006; Nilsson, 2008; Zhang et al., 2012; Li et al., 2013), feedstock- and enzyme cost of lignocellulosic ethanol are also reported (Dutta et al., 2010a; Barta et al., 2010a; Aden et al., 2002). The LCA methodology identifies the potential hotspots of product, production system or activity depending on the goal of the study. The potential hotspots were identified to be the feedstock, pretreatment and fixed cost in case of energy consumption, emission and production cost, respectively. This study also indicates that byproducts have a robust contribution in the LC of lignocellulosic ethanol. The breakeven
feedstock cost was used to estimate the production cost, which may depend on the biomass logistics, farmers profit margin and renewable energy policy. Therefore, the effect of plant capacity (which is mainly sensitive to fixed cost), ethanol yield and feedstock cost on the production cost have been determined. Then the effect of the variation (±20%) of different parameters on energy consumption, emission and production has also been worked out for $S_4$.

It seems that the ethanol plant capacity affects the production cost and emission (Fig. 7.8). The production cost decreased with an increase in plant capacity; however, emission increases because of the higher feedstock demand resulted in longer transportation distance. The production cost was found to be reduced from 1.0–0.67 $/L and emission increased from 1.29–1.37 kg CO$_2$e/L for the increase of plant capacity from 5 to 300 ML/y. Increasing biomass and ethanol yield may help in reducing biomass demand consequently the transportation distance.

Figure 7.9 depicts that the production cost of ethanol not only dependent on the feedstock cost but also on the ethanol yield. Although there was a slight variation in the case of fixed cost because of different feedstock demand, it seems that the higher the ethanol yield the lower the production cost. Higher ethanol yield not only reduces the feedstock demand, consequently transportation distance, but also has a positive impact on each stages of the LC of lignocellulosic ethanol.

![Figure 7.8 Effect of ethanol plant capacity on production cost and emission](image-url)
Figure 7.9 Effect of ethanol plant capacity on production cost and emission

Figure 7.10 shows the severity of the effect of the variation in different parameters on the net energy consumption. The net energy consumption varied from 12.1–14.8 MJ/L and it seems that pretreatment has the most robust effect on net energy consumption. Energy recovered from byproduct contributes to offset part of total energy. The net emission and production cost varied from about 1.2–1.5 kg-CO$_2$ e/L and 0.8–1.0 $/L, respectively, depending on the severity of the variation (Figs. 7.11). These figures also depict that ethanol yield has more robust impact on both net emission and production cost than others. It is worthy to mention that although higher ethanol yield reduced energy recovery from the byproduct, consequently lesser opportunities for emission and cost offsetting because of lower amount of byproduct (lignin) recovery from the system, the net emission and production cost observed to be reduced. It is also important to note that the production cost can further be reduced if agri-industrial and environmental policies are enacted to support the miscanthus based ethanol industry, especially for miscanthus grows on the marginal land and used for ethanol.

This study also support our earlier findings (chapter 6) that miscanthus grows on the marginal land in Ontario could be a potential feedstock for lignocellulosic ethanol industries and avoid any competition with food crops for prime land help Ontario improves her food and energy security, and enhance rural economy. It is important to note that net emission from the LC not...
only dependent on the land classes but also on the crop displacement ($S_2$ & $S_3$ where same land classes are used).

Figure 7.10 Effect of the variation of different parameters on net energy consumption (MJ/L)

Figure 7.11 Effect of the variation of different parameters on net emission

101
The Eastern Ontario has emerged to be the best location for miscanthus based ethanol industry among the locations studied in Ontario which seems to be environmentally and economically viable. Bennett et al. (2004) reported that genetically modified (GM) crops can serve various purposes, such as improving yield, increasing the share of useful components or decreasing the need for chemical fertilizers or water, and improves farm income. Therefore, net emission and production cost of ethanol from miscanthus may further be reduced, if GM miscanthus is considered and promoted for ethanol industry, improve farm income and rural economy, and future energy security.

7.4 Conclusion
This study identifies the potential locations for miscanthus based ethanol industry in Ontario, Canada and determines the environmental and economic viability of the miscanthus based ethanol. A slight variation was observed in the case of net energy consumption, and production cost; however, the variation was emerged to be robust in the case of net emission where carbon dynamics plays a key role. The scenario S2 was found to be the best option to abate GHG emissions, which indicates that GHG emissions were dependent not only on the land classes but also on the crop displacement. The results indicate that the miscanthus based ethanol industries are economically and environmentally viable for all scenarios and locations in Ontario, even if miscanthus was grown on marginal land; consequently, miscanthus arose to be a promising feedstock for ethanol industry in Ontario. However, Eastern Ontario was appeared as the best option for miscanthus based ethanol industry in Ontario. The miscanthus based ethanol industry might need to be regulated to avoid any sort of competition with food crops for higher quality land; improve farm income and rural economy. The information generated in this study is emerged to be novel, may help the stakeholders in their decision making processes, and help meeting the ethanol demand, and help achieving GHG emissions target of Canada.
Chapter 8

Development of a Continuous Stirred Tank Bioreactor for Syngas Fermentation

8.1 Introduction

Although both the biochemical and thermochemical conversion technologies are used for ethanol production from biomass, biochemical dominates over thermochemical process (Subramani & Gangwal, 2008). Most of the biomass contains a large amount of non-carbohydrate materials (lignin) that cannot be converted into ethanol by microorganisms in the biochemical conversion process (Henstra et al., 2007). Several challenges have also been reported in biochemical routes such as high pretreatment and enzyme cost, low fermentability of mixed sugar stream (C₅) and the generation of inhibitory soluble compounds (Munasinghe and Khanal, 2010). Conversely, gasification is very effective at converting non-carbohydrate biomass fractions and all other components of biomass into syngas with nearly equal efficiency and effectiveness (Pereira et al., 2012; Weber et al., 2010; Wang & Yan, 2008; Phillips et al., 2007; Brown, 2007; Henstra et al., 2007; Aden et al., 2002), eliminates the complex pretreatment steps and requirement of costly enzymes (Munasinghe & Khanal, 2010). Some of the biological catalysts (Clostridium ljungdahlii, Clostridium autoethanogenum, Acetobacterium woodii, Clostridium carboxidivorans and Peptostreptococcus products) are able to ferment syngas into liquid fuel more effectively than that of chemical catalysts (iron, copper or cobalt) (Heiskanen et al., 2007; Henstra et al., 2007).

Till date various types (batch and continuous stirred tank; two stages continuous stirred tank; trickle-bed, microbubble dispersion, monolithic biofilm, bubble column, membrane-based system) of reactors have been developed and used for syngas fermentation (Richter et al., 2013; Mohammadi et al., 2012; Datar et al., 2004). The continuous culture was noted to be advantageous compared to a batch culture in a fermentation system (Richter et al., 2013). The mass transfer between substrate and microbes was also dependent on the level syngas mixing with the fermentation media. Higher agitation speed tend to produce finer bubbles thus slow rising velocity in fermentation media, improves microbes accessibility to syngas and improves mass transfer rates (Munasinghe & Khanal, 2010). This study attempts to develop a reactor employing an innovative gas supply and effluent extraction systems with continuous stirred tank for ethanol production and evaluate the developed reactor.
8.2 Materials and Methods

8.2.1 Reactor development

Bioreactor is a device that supports biologically active aerobic or anaerobic environment in which biochemical conversion can be taken place involving microbes. The environmental conditions in a bioreactor such as syngas and media flow rates, temperature, pH and agitation speed were not only monitor but also controlled. Consequently, a laboratory scale bioreactor (3L) has been developed with transparent polyvinylchloride (PVC) pipe (Fig. 8.1), which was coupled with pH meter (PHE-1411, Omega Environmental, Inc., Laval, QC, Canada) and a pressure gauge (PHH-222, Omega Environmental, Inc., Laval, QC, Canada) to monitor working temperature, pH and pressure, respectively. The pH meter was equipped with a temperature probe (TP-07). Membrane separator (PVDF, GE: 0.02 µm) was also put in place to extract the effluent free of microbes (A-8-1). A membrane support has also been developed to facilitate the effluent extraction from the top layers (A-8-2). A list of materials and accessories for the reactor are appended in the appendix (A-8-3). The gas chamber has also been developed and fabricated at the University of Guelph, Ontario, Canada. The materials used for the gas chamber are listed in the appendix (A-8-4).

Figure 8.1 Photograph of the developed reactor
Figure 8.2 Schematic diagram of the gas chamber (not to scale)

Figure 8.3 Photograph of the developed gas chamber
Syngas fermentation into ethanol was noted to be dependent on the gas-liquid mass transfer (Devarapalli et al., 2013; Lee, 2010). The gas-liquid mass transfer can be improved by increasing the residence time of gas in the aqueous media (Lee, 2010). The bubbling technology helps in improving the gas retention time in the aqueous media. Although the size of bubble affects the retention time, a bubbling tube was incorporated in the bioreactor to improve the gas retention time in the aqueous media of the reactor, which can easily be replaced with other bubbling systems. The reactor can be used for both anaerobic and aerobic condition. The media and effluent (ethanol) were supplied and extracted from the reactor with a micro-pump (GF-F155001, Gilson Inc., USA), respectively. The tubing (F117938) was selected based on the desired flow rates. It is noteworthy to mention that the following parameters were considered for the development of the bioreactor: Innovative, purpose, usefulness, flexibility, easy monitoring, durability, safety, easy assemble and disassemble, easy cleaning, and inexpensive.

8.2.2 Microorganism and media
American Type Culture Collection (ATCC#55380; Clostridium ljungdhalii) was purchased from Cedarlane, Burlington, Ontario, Canada and used in this study. The recommended broth media for ATCC#55380 has been prepared at the laboratory based on the preparation manual supplied by Cedarlane. The components of broth media and the production procedure are reported in the appendix (A-8-5). Clostridium ljungdahlil in the fermentation process of syngas not only improves mass transfer properties, but also capable of producing only ethanol (BRI, 2008). Aseptically the microorganism was transferred into the produced broth media in the test tubes and cultured. Cells were anaerobically propagated in the prepared broth media at 37°C in an incubator (Heratherm IGS60, Thermo Electron LED GmbH, Germany) (A-8-6). The propagated cells were then used in the syngas fermentation process.

8.2.3 Syngas fermentation
In a gasification process all feedstock components are decomposed into syngas (H2, CO, CO2, CH4) with few residues (tar and ash) and trace amount of other gases (He & Zhang, 2011; Wei et al., 2009). Usually, the composition and quality of syngas from biomass are dependent on the type of feedstock and gasification parameters (He & Zhang, 2011; Carpenter et al., 2010; Wei et al., 2009). A wide range of syngas composition has been used by the researchers (Richter et al., 2013; Kundiyana et al., 2011; Sim et al., 2007; Younesi et al., 2006). The composition of syngas most recently reported was 60% CO; 35% H2 and 5% CO2 (Ricter et al., 2013). However,
only the CO has been used in the fermentation process to prove the concept of the developed reactor (Chang et al., 1998). The working volume of the reactor and planned operating temperature were 2 L and 37°C, respectively. The reactor was operated under continuous condition, after the initial two days batch condition. A bypass tube was used to connect the reactor and the media-jar. Another tube from the media-jar was connected to the exhaust tube to release the excess gas if any.

The syngas, fresh media and effluent extraction flow rates were 5.0–15.0, 0.25–0.75 and 0.25–0.75 mL/min, respectively. For this purpose the pump was calibrated against different operating speed (A-8-7). The fresh media and effluent extraction rate was controlled to maintain the working volume in the reactor. The working pH, temperature, gas and ethanol concentration were also monitored. Lee (2010) reported the highest growth rate of Clostridium ljungdahlii on PETC 1754 with 5 g/L fructose and 1 g/L yeast extract and pH 6.5–7.5. The working pH was reported to be 5.5–6.5 for optimal growth of the cells (Richter et al., 2013; Mohammadi et al., 2012, Abubackar et al., 2012; Lee, 2010). The optimum microorganism growth was reported at pH 4.4–6.2 (Richter et al., 2013; Liou et al., 2005). On the other hand the highest ethanol yield was observed at pH 4.75 (Abubackar et al., 2012); however in the second stage i.e., ethanol production stage pH was maintained to 4.4–4.8 (Richter et al., 2013). Consequently, the working pH was controlled to 4.5–5.0 by adding 1N NaOH in the reactor with a syringe, if required. The agitation speed was also controlled to 300–500 rpm. Figure 8.4 shows the photograph of the experimental setup (details in A-8-8). Figure 8.5 shows the schematic diagram of the experimental setup of this study.
Figure 8.4 Photograph of the experimental setup

Figure 8.5 Schematic diagram of the experimental setup of this study
8.2.4 Analytical method

The effluent has been collected periodically for each experimental condition to determine their effect on fermentation activities and ethanol productivity. The effluent has been analyzed by using a Bruker Scion 436 Gas Chromatograph coupled with a quadruple mass analyzer. The volatiles are separated using a 5% phenyl-methyl silicone bonded-phase fused silica capillary column (DB-5MS, 30 m × 0.25 mm i.d., film thickness 0.25 mm), operating at 41.4 kPa of column head pressure, resulting in a flow of 1.0 mL/min at 35°C. The solid phase microextraction (SPME) fiber is desorbed and maintained in the injection port at 280°C for the first 5 min of the chromatographic analysis. The injection port was in a splitless mode. The temperature program was isothermal for 5 min at 35°C, raised to 200°C at a rate of 10°C/min, and then raised to 250°C at a rate of 15°C/min, and held for 5 min. The transfer line to the mass spectrometer was maintained at 280°C. The ions were obtained by electronic impact ionization at positive ion mode at 70 eV, the data collection rate was 1 scan/s over the m/z (mass to charge ratio) range of 10 to 150. Compounds were tentatively identified by comparing their mass spectra with those contained in the NIST/EPA/NIH and Wiley libraries.

8.3 Results and discussion

8.3.1 pH and temperature profile during syngas fermentation

The bioreactor was placed in an incubator at 37°C to maintain the fermentation temperature for optimum growth. However, the temperature found to be risen upto 46°C might be because of exothermic reaction during syngas fermentation. Once the temperature was found to be risen above 37.5°C the door of the incubator kept open, which caused the temperature fluctuation (Fig. 8.6).
Figure 8.6 pH and temperature profile of the fermentation broth

The pH value in the fermentation broth was also found to be varied with time, syngas flow rate and media flow rate. Initially the pH decreased with the fermentation period might be because of the microbial activities, ethanol, propanol and formaldehyde production (Fig. 8.6). Many researchers observed higher ethanol yield at lower pH environment, because microorganism produces less acid which prevents a further pH drop, consequently yielded higher ethanol (Datar et al., 2004). In contrast, 110% higher ethanol yield was reported at pH 6.8 compared to that of pH 5.5 (Cotter et al., 2009), however, higher cell densities has been reported at pH 6.8 compared with pH 5.5. A drastic improvement in the ethanol yield with C. ljungdahlii has also been reported when the pH dropped to 4.0–4.5 (Klasson et al., 1993), which seems to be supporting the findings of this study.

8.3.2 Ethanol and other alcoholic compounds

The qualitative analysis of the effluent revealed that ethanol and some other alcoholic compounds (propanol, formaldehyde, isopropyl alcohol etc.) have been produced from syngas (CO) fermentation process. Figure 8.7 represents the GC-MS results, while syngas and media flow rate were maintained to 5 mL/min and 0.25 mL/min, respectively after two days of batch phase. The qualitative analysis confirmed that ethanol was produced during the fermentation process. Gas-liquid mass transfer was noted to be the main constrain in ethanol production from syngas fermentation because of low CO and H₂ solubility in the fermentation broth (Devarapalli
et al., 2013). However, in this study only CO has been used in the fermentation process. The mass transfer can be improved by the reactor configuration, agitation speed, syngas and media flow rates (Devarapalli et al., 2013; van Kasteren et al., 2005). The agitation speed helps break the bubble and enhance gas retention time and increasing the interfacial area available for the mass transfer (van Kasteren et al., 2005). The samples were also collected to determine the effect of agitation, syngas and media flow rate. The results of this study revealed that ethanol can be produced by using the developed bioreactor, and it seems gas-liquid mass transfer has been improved. Alternate syngas supply (bubbling) and bioreactor design may further improve gas-liquid mass transfer, thus the ethanol yield. In this purpose, different gas supply/bubbling system can be used to improve the bubbling process which may produce smaller bubble, consequently improve gas retention time in the media and increase mass transfer.

![Mass spectra of the effluent](image)

**Figure 8.7** Mass spectra of the effluent

### 8.4 Conclusion

The developed bioreactor was found to be able to produce ethanol form syngas fermentation process. The ethanol yield appears to be dependent on the experimental parameters.
Chapter 9

Evaluation of the Life Cycle of Ethanol derived from Biosyngas Fermentation

9.1 Introduction

The evaluation of the life cycle (LC) of ethanol derived from miscanthus by enzymatic hydrolysis process revealed that miscanthus is a promising feedstock for environmentally and economically viable ethanol in Ontario, Canada (Chapter 6 & 7). Ethanol has been produced by either biochemical processes (hydrolysis) or thermochemical processes (gasification /pyrolysis of biomass to syngas followed by biosynthesis or chemical synthesis). Each process has its strengths and weaknesses. The cost of cellulase is the major expense when producing lignocellulosic ethanol with conventional technology (Singh & Kumar, 2010) and contributes about 40–55% of the enzymatic ethanol production cost. Distillation, enzyme production and pretreatment were also reported to be the main contributors to the LC of ethanol produced by conventional technology (Roy et al., 2012; Orikasa et al., 2009). Thus, a wide variation was reported on GHG emissions and production cost. The use of the cost effective and innovative fermentation strategies integrated in the technology chain of gasification and gas cleaning, combined with syngas fermentation or catalytic synthesis could significantly improve the overall economics of ethanol from biomass.

Biosynthesis of syngas results in poor mass transfer properties of gaseous substrates and low ethanol yield (Munasinghe & Khanal, 2010). Conversely, higher ethanol yield was also reported in this process (Clausen & Gaddy, 1993). Although the thermochemical process produces ethanol in large quantities, it requires expensive catalysts and high operating pressure (Subramani & Gangwal, 2008). Ethanol production from syngas either by biosynthesis or catalytic synthesis process have been studied by many researchers (Ruth, 2005; Martchamadol, 2007; Clausen & Gaddy, 2008; Munasinghe & Khanal, 2010) except for few examples (Foust et al., 2009; Mu et al., 2010) where comparative studies between biosynthesis and catalytic synthesis have been conducted. This study attempts to evaluate the LC of ethanol produced by biosynthesis of syngas from pretreated (torrefied) and untreated (non-torrefied) miscanthus with or without chemical looping gasification (CLG).
9.2 Materials and methods

9.2.1 System boundary and assumptions

Lignocellulosic biofuels were noted to be environmentally sustainable products (González-García et al., 2012; He & Zhang, 2011; Hsu et al., 2010). Production cost and emissions from thermochemical conversion of biomass into ethanol were also reported to be dependent on the feedstock, processing conditions, plant capacity, byproduct utilization etc. (Chapter 2; Tables 2.3 & 2.6). Moreover, production cost of ethanol from syngas fermentation has also widely varied among the reported studies (Piccolo & Bezzo, 2009; Martín & Grossmann, 2011). Consequently, this study attempts to evaluate the LC of ethanol produced by syngas (derived from treated and untreated biomass: miscanthus) fermentation (Fig. 9.1) to determine if environmentally friendly and economically viable ethanol can be produced by biosynthesis process in Ontario, Canada. The raw biomass was assumed to be transported to the integrated processing plant. Although the processing plant cost may vary depending on the type of processing, it was assumed to be the same for all scenarios of this study.

![Figure 9.1 Schematic diagram of the system boundary of this study.](image)

9.2.2 Pretreatment (torrefaction)

Torrefaction is a mild heat treatment process given to biomass (typically from 200–300°C in an inert atmosphere) that improves thermochemical properties of biomass, producing a more stable, denser, hydrophobic material with higher energy values and thus reduces the biomass handling cost. It was also reported that torrefied biomass can be easily transported and fed to the gasifier (Bessou et al., 2011). The optimum torrefaction temperature was reported to be 275°C (Acharya, 2013). Consequently, torrefied biomass was produced with a Quartz Wool Matrix (QWM) reactor at 275°C for 45 min in an inert condition (Acharya, 2013). The experimental setup is shown in the appendix (A-9-1). Although experiments have been conducted to measure the energy consumption during the torrefaction process of biomass and flue gas properties were monitored (A-9-2), the estimated energy consumption (A-9-3) was used for the LC analysis because the QWM reactor is yet to be optimized. Biomass yield in the torrefaction process was
reported to be about 70% (Tumuluru et al., 2011; Acharya, 2013); however, biomass yield was assumed to be about 85% for this study (Kambo, 2014).

9.2.3 Ultimate analysis
The biomass samples were analyzed with CHNS-O analyzer (Flash 200 CHNS-O, Organic Elemental Analyzer, Thermo Fisher Scientific, The Netherlands) based on ASTM D5373-08 to determine the components in biomass (A-9-4). Samples were dried at 105°C for 24 hours prior to ultimate analysis. Then samples were combusted at 925°C in Helium atmosphere, while reduction was carried at 650°C. The components of various biomasses are reported in Table 9.1. Based on the elemental analysis, the air requirement in the gasification process was calculated.

Table 9.1 Components of different feedstock

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>S</th>
<th>O</th>
<th>Ash</th>
<th>HHV, MJ/kg</th>
</tr>
</thead>
<tbody>
<tr>
<td>Miscanthus</td>
<td>46.66</td>
<td>6.00</td>
<td>0.21</td>
<td>0.00</td>
<td>45.34</td>
<td>1.80</td>
<td>18.47</td>
</tr>
<tr>
<td>T-miscanthus</td>
<td>49.55</td>
<td>5.71</td>
<td>1.16</td>
<td>0.00</td>
<td>42.24</td>
<td>1.34</td>
<td>20.18</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>46.33</td>
<td>5.59</td>
<td>0.00</td>
<td>0.00</td>
<td>43.72</td>
<td>4.36</td>
<td>18.87</td>
</tr>
<tr>
<td>Willow</td>
<td>47.81</td>
<td>6.07</td>
<td>0.52</td>
<td>0.00</td>
<td>44.55</td>
<td>1.05</td>
<td>20.01</td>
</tr>
</tbody>
</table>

T: torrefied, Mass yield of torrefied biomass: 85% (Kambo, 2014)

9.2.4 Gasification and syngas cleaning
Although different sorbents have been used in the gasification process, calcium oxide was noted to be cheaper and effective for capturing CO₂ at very high temperatures, resulting in a small fraction of CO₂ in the flue gas and minimizing auxiliary power consumption (Acharya, 2011). The author also reported that in a CLG system, heat releases by the exothermic carbonization reactions can supply most of the heat required by the endothermic gasification reactions. Therefore, CaO was used as absorbent for this study. Treated and untreated biomass was thermally degraded with or without CaO in a micro gasifier (TGA-FTIR; TGA: SDT-Q600, TA Instruments-Waters LLC, New Castle, USA; FT-IR: Thermo Scientific Nicolet 6700, TA Instruments-Waters LLC, New Castle, USA) (A-9-5 & A-9-6) at 900°C. The air supply was controlled from 13.0–14.0 mL/min based on the components of biomass to ensure the sub-stoichiometric oxygen supply. The TGA experimental parameters are also reported in the appendix (A-9-7). The solid particles in the product gas can be separated in the cyclone.
The product gas can be cleaned with water scrubber or water wash process (Spath & Dayton, 2003; van Kasteren et al., 2005). The water scrubber is assumed to be used to remove any tars from the syngas (Han & Kim, 2008; van Kasteren et al., 2005). The thermal degradation experiment indicates that syngas composition may also be dependent on the feedstock (A-9-8 to A-9-12).

The syngas compositions were noted to be dependent on the feedstock and gasification conditions (Wei et al., 2009; He & Zhang, 2011; Kuo et al., 2014; Dutta & Stefan, 2014). The syngas quality was also reported to be improved in the CLG (i.e., chemical looping gasification) process (Acharya et al., 2009). Consequently, the lesser efforts are required in the syngas cleaning process in the case of torrefied biomass and CLG processes. The benefit achieved in syngas cleaning process was assumed to be offset by the efforts required in the torrefaction and CLG gasification process. Although thermal degradation experiments have been conducted, the simulated (with Aspen Plus V7.3) data have been used to estimate cold gas efficiency and the ethanol yield. The CGE calculation procedure is reported in the appendix (A-9-13). The simulation block diagram, simulation flowsheet and other parameters are reported in the appendix (A-9-14 to A-9-16). The simulated syngas composition also confirmed that gas quality were not only dependent on the feedstock but also on the gasification conditions. The simulated syngas composition, heating value and cold gas efficiency are reported in the appendix (A-9-17).

9.2.5 Syngas fermentation

Syngas fermentation process adopted in this study was assumed to be same that reported in the previous chapter (section 8.2.3). Low pressure and temperature fermentation of syngas reduces the operating costs, however requires large amount of energy because ethanol need to be separated from water (Martín & Grossmann, 2011). Several authors reported that the ethanol yield from syngas fermentation was dependent on the syngas compositions and, CO and H₂ conversion efficiency. The ethanol yield of this study was estimated based on the following procedure (Eq. 9.1) (Spath & Dayton, 2003). The estimated ethanol yield was found to be varied from 0.36–0.39 L/kg-miscanthus depending on the cold gas efficiency and gas to ethanol conversion efficiency (80%) (Table 9.2). However, ethanol yields were normalized to untreated feedstock while evaluating the LC of ethanol, and energy, emission and cost breakdown were worked out. Although mixed alcohol production has been reported by several authors,
*Clostridium Ljungdhalii* can produce only ethanol from syngas. Consequently, ethanol is assumed to be the only final product in the syngas fermentation process.

\[
Y = \frac{F \times HHV_F \times \eta_{\text{gas+cond}} \times X_{(CO+H_2)/\text{EtOH}}}{1.5 \times 10^5}.
\]  
(Eq. 9.1)

where,  
\(Y\) = Ethanol yield, million gal/year  
\(F\) = Feed rate, tons/day (dry basis)  
\(HHV_F\) = Higher heating value of the feedstock, Btu/lb (dry)  
\(\eta_{\text{gas+cond}}\) = Cold gas efficiency of gasifier + conditioning  
\(X_{(CO+H_2)/\text{EtOH}}\) = Average conversion of CO and H\(_2\) into ethanol

<table>
<thead>
<tr>
<th>Authors</th>
<th>Biomass</th>
<th>Gasification condition</th>
<th>CGE, %</th>
<th>Yield, L/kg-FS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Martín &amp; Grossmann, 2011</td>
<td>Switchgrass</td>
<td>Low pressure</td>
<td>-</td>
<td>0.32–0.33</td>
</tr>
<tr>
<td>Martín &amp; Grossmann, 2011</td>
<td>Switchgrass</td>
<td>High pressure</td>
<td>-</td>
<td>0.26</td>
</tr>
<tr>
<td>van Kasteren et al., 2005</td>
<td>Wood chips</td>
<td></td>
<td>-</td>
<td>0.36</td>
</tr>
<tr>
<td>Spath &amp; Dayton, 2003</td>
<td>Wood chips</td>
<td></td>
<td>70.00</td>
<td>0.26–0.33</td>
</tr>
<tr>
<td></td>
<td>Miscanthus (S(_1))</td>
<td></td>
<td>78.83</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>T-miscanthus (S(_2))</td>
<td></td>
<td>78.65</td>
<td>0.39</td>
</tr>
<tr>
<td>This study</td>
<td>Miscanthus (S(_3))</td>
<td>CLG</td>
<td>79.06</td>
<td>0.36</td>
</tr>
<tr>
<td></td>
<td>T-miscanthus (S(_4))</td>
<td>CLG</td>
<td>78.67</td>
<td>0.39</td>
</tr>
</tbody>
</table>

FS: Feedstock; T: Torrefied; CLG: chemical looping gasification

**9.2.6 Separation (distillation & purification)**

Ethanol concentration in the fermentation broth affects the microbial activities and in reducing concentration, microorganism can produce more ethanol (Nielsen & Prather, 2009). The ethanol concentration in the broth was considered to be 5% (Martín & Grossmann, 2011; van Kasteren et al., 2005). Ethanol was assumed to be separated by using membrane-assisted vapor stripping (MAVS) distillation system (Vane & Alvarez, 2008) and then purified by using glycerol as an additives (Dias et al., 2009).
9.2.7 Waste management

Ethanol production from biosyngas (fermentation route) results in two waste streams: solid (char, tar etc.) and liquid (waste water) (Martián & Grossmann, 2011; van Kasteren et al., 2005). Char, tar and other solid particles were assumed to be feedback to the gasifier. The good quality ash can be used, either as fertilizer or raw materials of cement or other construction industries (Pérez-Villarejo et al., 2012; Chatveera & Lertwattanaruk, 2011; Salas et al., 2009). The revenue generated from ash was assumed to be used to offset wastewater treatment cost. Although energy was consumed in the gasification process, a considerable amount of heat was also recovered from the cooler (van Kasteren et al., 2005). The emission and cost that credited to the recovered heat in the gasification process was determined with the emission factor and cost of LNG.

9.2.8 Cost analysis

Cost analysis methods were discussed in the previous chapter (section 6.2.5). Ethanol processing plant cost was workout based on the ratio of construction cost of biochemical and thermochemical ethanol plant reported by Foust et al. (2009), and the construction cost reported by Asano & Minowa (2007).

9.2.9 Data collection

In this study, we tried to use site-specific or country specific data wherever possible and remaining were collected from the literature. Although data for different processes (torrefaction, gasification, ethanol productivity etc.) were collected from the lab scale experiments, both the estimated (pretreatment) and the literature data were used in this study, because the equipment are yet to be optimized or too small to get valued data. A summary of parameters/processes for which data have been collected from the literature and their sources were reported in Table 9.3.

9.3 Results and discussion
9.3.1 Net energy consumption

Energy consumption at all stages and energy recovery were examined to denote the net energy consumption in the LC of ethanol (Fig. 9.2). The assessment revealed that there was a wide variation among the stages, and the gasification process was found to be the main hotspot followed by the distillation, fermentation, feedstock production and others. Energy consumption was greater in the case of torrefied feedstock (S2) compared with untreated feedstock (S1). However, CLG process reduced the energy consumption in the gasification process. Energy
content in torrefied feedstock was greater than that of untreated feedstock, thus noted to be favorable to reduce transportation energy. In contrast, the transportation energy was observed to be greater when it was normalized to untreated biomass. It was also important to note that an integrated ethanol processing plant was considered where torrefied feedstock was produced and fed into the gasifier. Thus, energy consumption in all stages was also found to be slightly greater except the gasification compared with untreated feedstock because of the difference in ethanol yield (adjusted).

Table 9.3 Summary of parameters for which data are collected from literature or estimated

<table>
<thead>
<tr>
<th>Parameters/Systems</th>
<th>Actual data</th>
<th>Sources</th>
</tr>
</thead>
<tbody>
<tr>
<td>^Miscanthus cultivation (kg CO₂e/tDM)</td>
<td>167.67</td>
<td>Sanscartier et al., 2013</td>
</tr>
<tr>
<td>Feedstock cost ($/tDM)</td>
<td>71.50</td>
<td>Kludge et al., 2013</td>
</tr>
<tr>
<td>*Crushing (size 3 mm) (kWh/kg)</td>
<td>0.06</td>
<td>Roy et al., 2012a; b</td>
</tr>
<tr>
<td>*Ethanol processing plant construction</td>
<td>$45 million</td>
<td>Estimated</td>
</tr>
<tr>
<td>No. of labor (persons)</td>
<td>23</td>
<td>Asano &amp; Minowa, 2007</td>
</tr>
<tr>
<td>Pre-treatment (torrefaction, MJ/kg)</td>
<td>0.41</td>
<td>Estimated</td>
</tr>
</tbody>
</table>

Gasification

| Energy consumption (MJ/kg-ethanol)          | 1.53        | van Kasteren et al., 2005                    |
| Heat recovery (MJ/kg-feedstock)            | 1.92        | van Kasteren et al., 2005                    |
| Fermentation (MJ/kg-ethanol)               | 3.28        | van Kasteren et al., 2005                    |
| Distillation (MJ/kg-hydrous ethanol)       | 2.80        | Vane & Alvarez, 2008                         |
| Purification (MJ/kg-ethanol)               | 1.09        | Dias et al., 2009                            |
| Ethanol yield (L/kg-dry miscanthus)        | 0.36-0.39   | Estimated                                    |

Note: Plant capacity is 20000 kL/year; labor cost $46000/person/year; ^Miscanthus grown on marginal land; *assumed to be same that of straw; #Calculated based on the ratio of construction cost of biochemical and thermochemical ethanol plant reported by Foust et al. (2009), and construction cost reported by Asano & Minowa (2007); $: Canadian dollar.

Although no external energy was required in the case of scenarios S₂ & S₄ to gasify the feedstock, energy was required only for steam production for the systems. Consequently, energy consumption in the gasification process (S₂ & S₄) was observed to be lower compared with
steam gasification process ($S_1$ & $S_3$). The energy consumed in the steam generation process was found to be the main contributor in the gasification process. Biomass to steam (400°C) ratio was considered to be one. The net energy consumption was found to be varied from 13.19–14.81 MJ/L. The heat recovered from the gasification process offset a part of energy consumes in the LC of ethanol and has a significant contribution to the net energy consumption.

![Figure 9.2 Energy consumption at various stages of the LC of ethanol](image)

### 9.3.2 GHG emission (CO$_2$e)

GHG emissions at different stages were also varied among the scenarios and the stages of the LC of ethanol. Similar to the net energy consumption, the main hotspot was also found to the gasification; however, in the case of GHG emissions it was followed by feedstock, distillation, fermentation and others (Fig. 9.3). The net GHG emissions were found to be 1.27, 1.32, 1.19 and 1.24 kg-CO$_2$e/L for scenarios, $S_1$, $S_2$, $S_3$ and $S_4$, respectively. It is important to note that although $S_1$ performed better compared with the $S_2$; however, CLG option improved this performance (i.e., $S_1>S_3$ and $S_2>S_4$). It is also noteworthy to mention that heat recovered in the gasification process offset a portion of GHG emissions of the LC of ethanol. These results indicate that an environmental benefit can be achieved relative to gasoline if ethanol can be produced by using the technologies and scenarios adopted in this study. GHG emissions from the LC of the ethanol reported to be varied from 0.27–0.83 kg-CO$_2$e/L (Hsu et al., 2010; Tan & Dutta, 2013) which
might be because of the assumptions, plant capacities and feedstock. It seems that the results of this study were a bit greater than those reported data because of different feedstock and assumptions were made. In contrast, GHG emissions for the hybrid poplar was reported to 2.8 kg-CO$_2$/e/L (Daystar et al., 2013), which indicates that the results of this study is reasonable.

Figure 9.3 Emission at different stages of the LC of ethanol

9.3.3 Production cost

The production cost of ethanol was slightly varied among the production pathways ($S_1$, $S_2$, $S_3$ and $S_4$) of this study. Figure 9.4 depicts the GHG emissions from different stages of the LC of ethanol. Figure 9.4 also shows that the hotspot was the fixed cost followed by either gasification or feedstock cost depending on the production path. Production costs were found to be 0.78, 0.81, 0.90 and 0.88$/L for $S_1$, $S_2$, $S_3$ and $S_4$, respectively. It is worthy to note that heat recovery process has robust contribution to the net production cost of ethanol. This study also confirmed that production cost of ethanol is dependent on the feedstock, conversion technologies, and assumptions (Martí’n & Grossmann, 2011; Gonzalez et al., 2012). The feedstock cost and the production rate of hydrogen reported to be played an important role in the production cost of ethanol from syngas (Martí’n & Grossmann, 2011). A wide variation was observed in the literature, which was dependent on the feedstock, conversion technologies, allocation methods and plant sizes. The production cost of this study seems to be comparable with other studies (Perales et al., 2011; Piccolo & Bezzo, 2009). This study revealed that both the environmentally preferable and economically viable ethanol can be produced from miscanthus
grown on the marginal land and produced by gasification-biosynthesis process. It is also noteworthy to mention that this was an optimistic study, and all the data are neither to Canadian context nor from the same plant size, consequently, a full LC evaluation is required before any future investment and commercial production.

Figure 9.4 Production cost at different stages of the LC of ethanol

9.3.4 Sensitivity analysis

It was reported that ethanol produced from syngas can be cost-competitive with efficient equipment, optimized operation, cost-effective syngas cleaning technology, low feedstock and pretreatment cost, optimal configuration, heat integration, and high value byproduct (He & Zhang, 2011). CaO based sorbent can capture CO$_2$ at a relatively high temperature, eases the gas cleaning process compared with the convectional techniques. The syngas compositions were also noted to be dependent on the feedstock and gasification conditions (Wei et al., 2009; He & Zhang, 2011; Kuo et al., 2014; Dutta & Stefan, 2014). The gas quality was reported to be improved if torrefied biomass is used (Kuo et al., 2014). The syngas quality was also improved in the case of CLG (Acharya et al., 2009). Ethanol yield from syngas was dependent on the gas quality, cold gas efficiency (CGE) and gas to ethanol conversion efficiency. The investment in the ethanol industry may also depend on the processes integrated at the processing plant. The H$_2$ enriched syngas production was dependent on the type of biomass, biomass to steam and Ca/C ratio, and the type of gasifier and gasification temperature (Guoxin & Hao, 2009; Grasa &
Consequently, the effect of the variation (±20 to ±60%) at each stage of the LC of ethanol (transportation, pre-treatment, gasification, fermentation, distillation, heat recovery processes), and feedstock and fixed cost on the LC of ethanol were evaluated.

The net energy consumption, GHG emissions and production cost slightly varied, even variation was considered to be ±20 to ±60% for transportation and pretreatment because of their little contribution in the LC of ethanol (Figs. 9.5–9.6). Figures 9.7–9.8 show the effect of the variation in gasification and heat recovery on the LC of ethanol. The net energy consumption, GHG emissions and production cost were varied from 7.44–21.67 MJ/L, 0.85–1.70 kg-CO$_2$ e/L and 0.65–0.92 $/L, respectively. It seems that the effect of the variation in gasification was more robust compared with heat recovery, because contribution of gasification process was greater than that of heat recovery.

![Figure 9.5 Effect of transportation and pretreatment on net energy consumption](image-url)
Figure 9.6 Effect of transportation and pretreatment on emission and cost

Figure 9.7 Effect of the variation of gasification and heat recovery on net energy consumption (MJ/L)
Figure 9.8 Effect of the variation of gasification and heat recovery on emission and cost

Figures 9.9–9.10 represent the effect of the variation of fermentation and distillation on the net energy consumption, GHG emissions and production cost. The estimated net energy consumption, GHG emissions and production cost were found to be varied from 12.88–16.22 MJ/L, 1.17–1.38 kg-CO$_2$e/L and 0.72–0.85 $/L, respectively. The effect of distillation on the net energy consumption seems to be robust compared to that of fermentation, because of the variation between distillation and fermentation (Fig. 9.9). The variation in GHG emissions and production cost dependent on the severity of variation (Fig. 9.10). The net production cost was also observed to be varied from 0.70–0.84 $/L depending on the severity of the variation of fixed and feedstock cost (Fig. 9.11). It seems that the variation of fixed cost has more impact on the production cost than that of feedstock cost, because fixed has greater contribution. The LC GHG emissions and production cost were also found to be dependent on the CGE (Fig. 9.12). GHG emissions and production cost were found to be about 0.95–1.46 kg-CO$_2$e/L and 0.64–0.86 $/L, respectively depending on the CGE. This variation was resulted because of the variation in ethanol yield which was dependent on the CGE.
Figure 9.9 Effect of the variation of fermentation and distillation on net energy consumption (MJ/L)

Figure 9.10 Effect of variation of fermentation and distillation on emission and cost
Figure 9.11 Effect of variation of fixed and feedstock cost on production cost ($/L)

Figure 9.12 Effect of CGE on GHG emissions and production cost

This study also supports the earlier findings (chapter 6 & 7) that environmentally and economically viable ethanol can be produced from miscanthus by gasification-biosynthesis process with or without CLG, even if miscanthus is grown on the marginal land. The
environmental and economic benefit from miscanthus based ethanol may lead the stakeholders target the quality land (prime land) for better profit margin. Consequently, miscanthus production for ethanol industry needs to be regulated to avoid any sort of competition with food crops.

9.4 Conclusion
This study reveals that both the environmental and cost benefit can be achieved from ethanol that produced from miscanthus with adopted technologies. Although a slight variation was observed among the scenarios of this study, the untreated (non-torrefied) miscanthus is emerged to be a better option in terms of energy consumption, GHG emissions and production cost compared with torrefied miscanthus. The CLG process reduced net energy consumption and GHG emissions for both the untreated and treated miscanthus but production cost was increased compared with the non-CLG process. Untreated miscanthus used in CLG and non-CLG process was found to be the best option interns of GHG esmissions and production cost, respectively.
Chapter 10

Conclusions and Recommendations

10.1 Conclusions

This study is a new approach for the development and determination of a novel and adoptable renewable energy technology. The techno-economic and environmental evaluation of the life cycle (LC) of ethanol produced from various biomasses (agri-residue: wheat straw; forest residue: sawdust; energy crop: miscanthus) is performed by adopting different technological approaches. Life cycle assessment (LCA) methodologies have been used in the evaluation processes. The potential plant locations for the miscanthus based ethanol plant in Ontario, Canada have also been identified to abate greenhouse gas (GHG) emissions and minimize the production cost. Net energy consumption, GHG emissions and production cost are found to be dependent on the feedstock, plant location, conversion technology, processing plant size, system boundaries, biomass logistics and assumptions. This study makes it possible to draw a comparison among the selected technologies and feedstock, determine the most suitable pathways, and generate useful and novel information to facilitate the stakeholders involved in bioenergy sectors. It is worthy to note that although the LCA is a powerful tool for the evaluation of the environmental effects of a product/process/activities, results are dependent on the data quality system boundary, process modeling, time horizon and geographical location.

10.1.1 Evaluation of the LC of ethanol produced by enzymatic hydrolysis process

The LCA study depicts that environmental benefit can be gained with present technologies if wheat straw is considered to be carbon neutral, otherwise both environmental and economic viabilities of ethanol from wheat straw are doubtful while carbon sequestration is not considered. The environmental viability of ethanol from wheat straw can be improved if carbon sequestration is considered (resulted in negative GHG emissions).

The evaluation of the LC of ethanol from sawdust reveals that despite estimated environmental benefit, its economic viability remains doubtful unless the FiT program is considered. A modified agro-industrial and renewable energy policy that allows FiT to the lignocellulosic ethanol industry in Ontario not only reduces production cost but may also encourage future investment and create more green jobs as well as help in achieving committed GHG emissions reduction targets in Canada.
Ethanol derived from miscanthus is found to be environmentally preferable and economically viable at all locations in Ontario; however, Eastern Ontario has appeared as the best option for the miscanthus based ethanol industry, if miscanthus is grown on marginal land. Although a slight variation is observed in the case of net energy consumption and production cost among the scenarios, the variation is robust in the case of GHG emissions where carbon dynamics plays a key role. This study also revealed that GHG emissions are dependent not only on the land classes but also on the crop displacement. It is worthy to mention that both the environment and economic benefits can be gained, even if miscanthus is grown on the marginal land in Ontario for ethanol. Consequently, miscanthus grown on marginal land has emerged as a promising feedstock for the ethanol industry in Ontario, which may avoid any sort of competition over food crops for better quality land.

10.1.2 Evaluation of the LC of ethanol produced by gasification-biosynthesis process

This study also confirmed that both the environmental and cost benefit can be gained from ethanol that is produced from miscanthus with adopted technologies. The untreated (non-torrefied) miscanthus is emerged to be a better option in terms of energy consumption, GHG emissions and production cost compared with torrefied miscanthus. The CLG process reduced net energy consumption and GHG emissions for both the untreated and treated (torrefied) miscanthus; however, production cost has increased. The miscanthus based ethanol industry might need to be regulated to avoid any sort of competition for higher quality land. Also a careful consideration needs to be given to crop rotation/replacement to improve soil carbon dynamics, to abate any productivity loss, and may improve farm income and rural economy.

This study revealed that GHG emissions and the production cost of ethanol are dependent on feedstock, conversion technologies, system boundaries, allocation methods, and the utilization of byproducts. The LCA study also confirmed that both technological pathways are environmentally and economically viable. Although, the results of this study indicate that similar benefits can be gained, they seem to be inclined towards the gasification-biosynthesis pathway. Biotechnological advances, especially in enzyme production would improve the viability of enzymatic hydrolysis process. The novel information generated in this study may help the stakeholders in their decision making processes, attract more investment in this sector, help meet the ethanol demand, and help achieve GHG emission target of Canada.
10.1.3 Continuous stirred tank bioreactor

This is a new approach for the development of a continuous stir tank bioreactor. It seems that the developed bioreactor can be used to generate ethanol from syngas. However, this study needs to be continued for further evaluation and development.

10.2 Recommendations

10.2.1 Life cycle assessment

The LC of ethanol is evaluated based on both the literature, and estimated and simulated data. All the literature data are not from the same plant size and specific site. Some optimistic assumptions are made to evaluate the LC of ethanol, especially for the enzyme production. The results of this study advocate for a full LCA model based on the bench or pilot scale plant (for onsite data) that can facilitate an effective decision making process for the lignocellulosic ethanol industry. Consequently, the following recommendations can be made for further study on the LC of lignocellulosic ethanol:

i. Site specific or country specific data from the same plant size needs to be collected, if available for further evaluation.

ii. A bench scale or pilot scale lignocellulosic ethanol plant needs to be built for in-depth evaluation purposes before any future investment and commercial production.

iii. Integrated and innovative bio-refinery approaches need to be taken into account for future study.

iv. Alternate use of byproducts or coproducts, especially in the case of CLG where $H_2$ enriched syngas is produced, needs to be considered.

v. The variations of agricultural land price and miscanthus yield and processing plant capacity also needs to be considered for further study.

vi. The LCA study on LC of ethanol can also be extended to other environmental parameters, such as eutrofication, acidification, water consumption, and human toxicity.

10.2.2 Improvement of bioreactor

To improve the gas-liquid mass transfer, thus the ethanol yield the following recommendations are made:

i. An innovative gas supply system needs to be developed to improve gas retention time in the liquid.
ii. Micro-bubble technology can be used to improve gas retention time in the liquid, thus the mass transfer.

iii. Alternative/innovative reactor design can also be considered.

iv. Various gas and media flow rates, and stirrer speed can be used to evaluate the mass transfer and the ethanol yield.

v. The effect of cell density also needs to be evaluated.

Finally, it seems that long term national or international support on research and development process would help to develop innovative technologies, consequently improve the viability of the lignocellulosic ethanol.
Chapter 11

References


Acharya, B. (2013). Torrefaction and pelletization of different forms of biomass of Ontario (Master Thesis), University of Guelph, Canada.


production using vacuum extractive fermentation process. Chemical Engineering Transaction, 17, 1627–1632.


Lee, P. H. (2010). Syngas fermentation to ethanol using innovative hollow fiber membrane. Graduate Theses and Dissertations, Paper 12377, Iowa State University, USA.

biorefinery using wheat straw feedstock (No. 23500). North Dakota State University, Department of Agribusiness and Applied Economics.


thermochemical fuels, power, and/or animal feed protein. Biofuels, Bioproducts and Biorefining, 3(2), 231–246.


gasification of biomass materials. The 7th High Temperature Air Combustion and

Crop Science, 45(3), 812–819.

assessment of ethanol production via thermochemical conversion of biomass by entrained

Sustainable energy: A review of gasification technologies. Renewable and Sustainable
Energy Reviews, 16(7), 4753–4762.

Pérez-Villarejo, L., Eliche-Quesada, D., Iglesias-Godino, F. J., Martínez-García, C., & Corpas-
Iglesias, F. A. (2012). Recycling of ash from biomass incinerator in clay matrix to produce

gasification process to make ethanol via mixed alcohols synthesis. Industrial &
Engineering Chemistry Research, 46(26), 8887–8897.

gasification and mixed alcohol synthesis of lignocellulosic biomass. National Renewable


London, UK.

leaching after wood ash fertilization from drained peatland. In Regular Recycling of Wood


Appendices

A-2-1 The schematic diagram of chemical looping gasification (CLG) system

Source: Acharya, 2011
### A-2-2 Brief summary of microorganisms identified and used for syngas fermentation

<table>
<thead>
<tr>
<th>Species</th>
<th>Optimum Temp. C</th>
<th>pH</th>
<th>Time, h</th>
<th>Products</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mesophilic bacteria</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clostridium ljungdahlii</td>
<td>37</td>
<td>6.0</td>
<td>3.8</td>
<td>Acetate, ethanol</td>
<td>Tanner et al., 1993</td>
</tr>
<tr>
<td>Clostridium autoethanogenum</td>
<td>37</td>
<td>5.8-6.0</td>
<td>-</td>
<td>Acetate, ethanol</td>
<td>Abrini et al., 1994</td>
</tr>
<tr>
<td>Clostridium carboxidivorans</td>
<td>38</td>
<td>6.2</td>
<td>6.2</td>
<td>Acetate, ethanol, butyrate, butanol</td>
<td>Liou et al., 2005</td>
</tr>
<tr>
<td>Oxobacter pfennigii</td>
<td>36–38</td>
<td>7.3</td>
<td>13.9</td>
<td>Acetate, n-butyrate</td>
<td>Krumholz et al., 1985</td>
</tr>
<tr>
<td>Acetobacterium woodii</td>
<td>30</td>
<td>6.8</td>
<td>13</td>
<td>Acetate</td>
<td>Sharak et al., 1987</td>
</tr>
<tr>
<td>Eubacterium limosum</td>
<td>38–39</td>
<td>7.0–7.2</td>
<td>7</td>
<td>Acetate</td>
<td>Sharak et al., 1982, 1987</td>
</tr>
<tr>
<td>Rhodospirillum rubrum</td>
<td>30</td>
<td>6.0</td>
<td>8.84</td>
<td>H₂</td>
<td>Kerby et al., 1995</td>
</tr>
<tr>
<td>Rubrivivax gelatinosus</td>
<td>34</td>
<td>6.7–6.9</td>
<td>6.7</td>
<td>H₂</td>
<td>Dashekvicz &amp; Uffen, 1979; Uffen, 1976</td>
</tr>
<tr>
<td>Rhodopseudomonas palustris P4</td>
<td>30</td>
<td>nr</td>
<td>23</td>
<td>H₂</td>
<td>Jung et al., 1999</td>
</tr>
<tr>
<td><strong>Mesophilic archaea</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanosarcina barkeri</td>
<td>37</td>
<td>7.4</td>
<td>65</td>
<td>CH₄</td>
<td>O’Brien et al., 1984</td>
</tr>
<tr>
<td>Methanosarcina acetivorans strain C2A</td>
<td>37</td>
<td>7</td>
<td>24</td>
<td>Acetate, formate, CH₄</td>
<td>Rother &amp; Metcalf, 2004</td>
</tr>
<tr>
<td><strong>Thermophilic bacteria</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Moorella thermoacetica</td>
<td>55</td>
<td>6.5–6.8</td>
<td>10</td>
<td>Acetate</td>
<td>Daniel et al., 1990</td>
</tr>
<tr>
<td>Moorella thermoautotrophica</td>
<td>58</td>
<td>6.1</td>
<td>7</td>
<td>Acetate</td>
<td>Savage et al., 1987</td>
</tr>
<tr>
<td>Species</td>
<td>pH Range</td>
<td>T (°C)</td>
<td>Method</td>
<td>Product</td>
<td>Source</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>----------</td>
<td>--------</td>
<td>--------</td>
<td>---------</td>
<td>---------------------------------</td>
</tr>
<tr>
<td>Moorella strain AMP</td>
<td>60–65</td>
<td>6.9</td>
<td>-</td>
<td>H₂</td>
<td>Jiang, 2006</td>
</tr>
<tr>
<td>Carboxydothermus hydrogenoformans</td>
<td>70–72</td>
<td>6.8–7.0</td>
<td>2</td>
<td>H₂</td>
<td>Svetlitchnyi et al., 2001</td>
</tr>
<tr>
<td>Carboxydibrachium pacificus</td>
<td>70</td>
<td>6.8–7.1</td>
<td>7.1</td>
<td>H₂</td>
<td>Sokolova et al., 2001</td>
</tr>
<tr>
<td>Carboxydocella sporoproducens</td>
<td>60</td>
<td>6.8</td>
<td>1</td>
<td>H₂</td>
<td>Slepova et al., 2006</td>
</tr>
<tr>
<td>Carboxydocella thermoautotrophica</td>
<td>58</td>
<td>7</td>
<td>1.1</td>
<td>H₂</td>
<td>Sokolova et al., 2002</td>
</tr>
<tr>
<td>Thermincola carboxydiphila</td>
<td>55</td>
<td>8</td>
<td>1.3</td>
<td>H₂</td>
<td>Sokolova et al., 2005</td>
</tr>
<tr>
<td>Thermosinus carboxydivorans</td>
<td>60</td>
<td>6.8–7.0</td>
<td>1.2</td>
<td>H₂</td>
<td>Sokolova et al., 2004</td>
</tr>
<tr>
<td><strong>Thermophilic archaea</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methanothermobacter thermoautotrophicus</td>
<td>65</td>
<td>7.4</td>
<td>140</td>
<td>CH₄</td>
<td>Daniels et al., 1977</td>
</tr>
<tr>
<td>Thermococcus strain AM4</td>
<td>82</td>
<td>6.8</td>
<td>-</td>
<td>H₂</td>
<td>Sokolova et al., 2004</td>
</tr>
</tbody>
</table>

**Source:** Henstra et al., 2007.


### A-2-3 Syngas fermentation parameters and ethanol yield

<table>
<thead>
<tr>
<th>Microorganism</th>
<th>Cell density</th>
<th>Media</th>
<th>Reactor</th>
<th>Feedstock</th>
<th>Temp. °C</th>
<th>pH</th>
<th>Agitation, rpm</th>
<th>Yield</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>C. Ljungdahlii, ATCC#55383</td>
<td>10 g/L</td>
<td>ATCC1754 PETC</td>
<td>Two stage: 1L CSTR &amp; 4-L bubble column</td>
<td>60% CO, 35% H&lt;sub&gt;2&lt;/sub&gt;, &amp; 5% CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>37</td>
<td>5.5</td>
<td>200</td>
<td>0.37 g/(L·h.</td>
<td>Richter et al., 2013</td>
</tr>
<tr>
<td>Clostridium ragsdalei</td>
<td>0.95 g/L</td>
<td>Batch</td>
<td>20%CO, 5%/H&lt;sub&gt;2&lt;/sub&gt;, 15%/CO&lt;sub&gt;2&lt;/sub&gt;, &amp; 60% /N&lt;sub&gt;2&lt;/sub&gt;</td>
<td>32</td>
<td>6</td>
<td>-</td>
<td>1.89 g/L ethanol, 1.45 g/L acetate</td>
<td>Kundiyana et al., 2011</td>
<td></td>
</tr>
<tr>
<td>C. Ljungdahlii, ATCC#55383</td>
<td>0.95 g/L</td>
<td>Batch</td>
<td>50% CO, 30% H&lt;sub&gt;2&lt;/sub&gt;, and 20% CO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>35</td>
<td>-</td>
<td>-</td>
<td>6 g/L ethanol to acetate ratio 2.6</td>
<td>Lee, 2010</td>
<td></td>
</tr>
<tr>
<td>C. Ljungdahlii (growth phase)</td>
<td>Modified nitrogen limitation media</td>
<td>Batch (80 ml)</td>
<td>-</td>
<td>37</td>
<td>6.8</td>
<td>-</td>
<td>0.02 g/L ethanol &gt; 0.06 g/L acetate</td>
<td>Cotter et al., 2009</td>
<td></td>
</tr>
<tr>
<td>C. Ljungdahlii (resting phase)</td>
<td>Modified nitrogen limitation media</td>
<td>Batch (80 ml)</td>
<td>-</td>
<td>37</td>
<td>4.5</td>
<td>-</td>
<td>0.02 g/L ethanol &gt; 0.06 g/L acetate</td>
<td>Cotter et al., 2009</td>
<td></td>
</tr>
<tr>
<td>C. autoethanogenum</td>
<td>DSMZ 640</td>
<td>Batch (250 ml)</td>
<td>20% CO, 10% H&lt;sub&gt;2&lt;/sub&gt;, 20% CO&lt;sub&gt;2&lt;/sub&gt;, and 50% N&lt;sub&gt;2&lt;/sub&gt; (flow rate: 10 mL/min)</td>
<td>37</td>
<td>6.0</td>
<td>-</td>
<td>0.66 g/L ethanol 1.40 g/L acetate</td>
<td>Cotter et al., 2008</td>
<td></td>
</tr>
<tr>
<td>C. Ljungdahlii (growth phase)</td>
<td>Modified reinforced Clostridial</td>
<td>Batch (250 ml)</td>
<td>20% CO, 10% H&lt;sub&gt;2&lt;/sub&gt;, 20% CO&lt;sub&gt;2&lt;/sub&gt;, and 50% N&lt;sub&gt;2&lt;/sub&gt; (flow rate: 7.5 mL/min)</td>
<td>37</td>
<td>6.8</td>
<td>-</td>
<td>0.23 g/L ethanol 2.10 g/L acetate</td>
<td>Cotter et al., 2008</td>
<td></td>
</tr>
<tr>
<td>Clostridium aceticum</td>
<td>0.8 g/L</td>
<td>Batch</td>
<td>78% CO, 4% H&lt;sub&gt;2&lt;/sub&gt;, 18% Ar</td>
<td>30</td>
<td>8.5</td>
<td>-</td>
<td>2.27 g/L acetate</td>
<td>Sim et al., 2007</td>
<td></td>
</tr>
<tr>
<td>C. Ljungdahlii</td>
<td>1.2 g/L</td>
<td>ATCC1754 PET</td>
<td>Batch (125 ml)</td>
<td>55% CO, 20% H&lt;sub&gt;2&lt;/sub&gt;, 10% CO&lt;sub&gt;2&lt;/sub&gt;, and 15% Ar</td>
<td>37</td>
<td>4.5</td>
<td>-</td>
<td>0.60 g/L ethanol 1.11 g/L acetate</td>
<td>Younesi et al., 2005</td>
</tr>
<tr>
<td>Organism</td>
<td>Media Details</td>
<td>Culture Details</td>
<td>Reactor Type</td>
<td>Volume</td>
<td>pH</td>
<td>Ethanol (g/L)</td>
<td>Acetate (g/L)</td>
<td>Reference</td>
<td></td>
</tr>
<tr>
<td>------------------------</td>
<td>-----------------------------------</td>
<td>-----------------</td>
<td>--------------</td>
<td>--------</td>
<td>----</td>
<td>--------------</td>
<td>---------------</td>
<td>----------------</td>
<td></td>
</tr>
<tr>
<td>C. ljungdahlii</td>
<td>ATCC1754 PETCH</td>
<td>Batch (125 mL)</td>
<td>55% CO, 20% H₂, 10% CO₂, and 15% Ar</td>
<td>37</td>
<td>-</td>
<td>-</td>
<td>0.012</td>
<td>0.024</td>
<td>Najafpour &amp; Younesi, 2006</td>
</tr>
<tr>
<td>C. ljungdahlii</td>
<td>ATCC1754 PETCH</td>
<td>CSTR (20L)</td>
<td>55% CO, 20% H₂, 10% CO₂, and 15% Ar</td>
<td>37</td>
<td>4.5</td>
<td>-</td>
<td>11 g/L ethanol and acetate</td>
<td>Younesi et al., 2006</td>
<td></td>
</tr>
<tr>
<td>Eubacterium limosum</td>
<td>0.75 g/L</td>
<td>Gas lift reactor</td>
<td>100% CO</td>
<td>37</td>
<td>6.8</td>
<td>-</td>
<td>Butyrate, acetate, &amp; 38 mmol ethanol</td>
<td>Chang et al., 1998</td>
<td></td>
</tr>
<tr>
<td>C. ljungdahlii</td>
<td>ATCC1754 PETCH</td>
<td>STR, with cell recycle (13.5 L)</td>
<td>55% CO, 20% H₂, 10% CO₂, and 15% Ar</td>
<td>37</td>
<td>4.5</td>
<td>300-500</td>
<td>1.5 g/L ethanol</td>
<td>Phillips et al., 1994</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Designed media based on E. Coli</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.5 g/L acetate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C. ljungdahlii</td>
<td>4 g/L</td>
<td>Cell recycled</td>
<td>55% CO, 20% H₂, 10% CO₂, and 15% Ar</td>
<td>36</td>
<td>4.5</td>
<td>300-500</td>
<td>48 g/L ethanol</td>
<td>Phillips et al., 1993</td>
<td></td>
</tr>
</tbody>
</table>


A-6-1 Land classification in Ontario

<table>
<thead>
<tr>
<th>Classification</th>
<th>Descriptions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Class 1</td>
<td>Well developed and has no significant limitations in use for crops.</td>
</tr>
<tr>
<td>Class 2</td>
<td>Has moderate limitations that restrict the range of crops or requires moderate conservation practices.</td>
</tr>
<tr>
<td>Class 3</td>
<td>Has moderately severe limitations that restrict the range of crops or requires special conservation practices.</td>
</tr>
<tr>
<td></td>
<td>Has severe limitations that restrict the choices of crops or requires special conservation and management practices, or both.</td>
</tr>
<tr>
<td>Class 4</td>
<td>Has very severe limitations that restrict their capability in producing perennial forage crops, and improvement practices are feasible.</td>
</tr>
<tr>
<td>Class 5</td>
<td>Unsuitable for cultivation, and can be used for unimproved permanent pasture.</td>
</tr>
<tr>
<td>Class 6</td>
<td>Has no capacity of arable culture or permanent pasture.</td>
</tr>
</tbody>
</table>

*Source: AAFC, 2008; OMAF, 2013*
## A-6-2 On-farm inputs for miscanthus cultivation in different regions

<table>
<thead>
<tr>
<th>Items/Parameter</th>
<th>Other input values</th>
<th>Western Ontario</th>
<th>Southern Ontario</th>
<th>Eastern Ontario</th>
<th>Central Ontario</th>
</tr>
</thead>
<tbody>
<tr>
<td>Land class</td>
<td>1-2</td>
<td>3</td>
<td>3</td>
<td>4-5</td>
<td></td>
</tr>
<tr>
<td>Soil type</td>
<td>Silt Loam-Clay Loam</td>
<td>Clay</td>
<td>Clay</td>
<td>Loam</td>
<td></td>
</tr>
<tr>
<td>Displace crop rotation</td>
<td>Corn-soy rotation</td>
<td>Continuous soybean rotation</td>
<td>Corn-Corn-Forage-Forage rotation</td>
<td>Long term pasture</td>
<td></td>
</tr>
<tr>
<td>Rhizome yield (production) (tonne/ha)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>20</td>
</tr>
<tr>
<td>Rhizome required (tonne/ha)</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Distance rhizome producer to farm (km)</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>Moisture content at harvest (%)</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Miscanthus crop lifespan (years)</td>
<td>20</td>
<td>20</td>
<td>20</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Crop residue left on soil at harvest (% of peak biomass produced)</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>Below ground biomass contribution to total mass (%)</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>35</td>
<td>35</td>
</tr>
<tr>
<td>Spring yield years 3 to 20 (dry tonne/ha)</td>
<td>11.10</td>
<td>11.10</td>
<td>11.10</td>
<td>10.03</td>
<td>8.90</td>
</tr>
<tr>
<td>Stand failure year 2 (% of area)</td>
<td>10</td>
<td>10</td>
<td>20</td>
<td>40</td>
<td>40</td>
</tr>
<tr>
<td>N application rate year 2-20 (kg/ha)</td>
<td>60</td>
<td>60</td>
<td>80</td>
<td>80</td>
<td>60</td>
</tr>
<tr>
<td>P application rate year 2-20 (kg/ha)</td>
<td>12</td>
<td>12</td>
<td>11</td>
<td>11</td>
<td>9</td>
</tr>
<tr>
<td>K application rate year 2-20 (kg/ha)</td>
<td>105</td>
<td>105</td>
<td>105</td>
<td>95</td>
<td>79</td>
</tr>
<tr>
<td>Percent of N requirements fulfilled with urea</td>
<td>100%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total herbicide application Year 1 (kg active ingredient /ha)</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>11.8</td>
</tr>
<tr>
<td>Herbicide/pesticide application rate Year 2-20 (kg active ingredient /ha)</td>
<td>4.00</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>4.00</td>
<td>4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>------</td>
<td>----</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Herbicide application rate at termination (kg active ingredient /ha)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fuel use for Miscanthus planting (L/ha)</td>
<td>69.06</td>
<td>69.06</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Production efficiency</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0.85</td>
</tr>
<tr>
<td>Displaced crop C pools</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Harvested material yield (dry t/ha)</td>
<td>2.3</td>
<td>2.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residues yield (dry t/ha)</td>
<td>2.3</td>
<td>2.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total above ground biomass (dry t/ha)</td>
<td>4.7</td>
<td>4.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Belowground biomass (dry t/ha)</td>
<td>2.2</td>
<td>2.2</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soil C (dry t/ha)</td>
<td>80.9</td>
<td>80.9</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total C (dry t C/ha)</td>
<td>87.8</td>
<td>87.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Miscanthus C pools (average of life expectancy of stand)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Harvested material yield (dry t C/ha)</td>
<td>5.2</td>
<td>5.19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Residues yield (dry t C/ha)</td>
<td>2.2</td>
<td>2.23</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total above ground biomass (dry C t/ha)</td>
<td>7.4</td>
<td>7.42</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Belowground biomass (dry t C/ha)</td>
<td>4.0</td>
<td>4.00</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Loss soil C at conversion (%)</td>
<td>2.5</td>
<td>0.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Initial soil C after conversion (dry t C/ha) - assume loss at conversion</td>
<td>78.9</td>
<td>78.90</td>
<td>66.14</td>
<td>74.27</td>
<td>86.89</td>
</tr>
<tr>
<td>Total C returned to land (dry t C/ha)-above only</td>
<td>2.30</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total C returned to land (dry t C/ha) - above and below</td>
<td>6.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ICBM output - final soil C (dry t C/ha)</td>
<td>85.3</td>
<td>85.27</td>
<td>85.27</td>
<td>84.95</td>
<td>84.95</td>
</tr>
<tr>
<td>Total final C (dry t C/ha)</td>
<td>96.7</td>
<td>96.7</td>
<td>96.7</td>
<td>95.2</td>
<td>94.0</td>
</tr>
<tr>
<td>Total average C (dry t C/ha)</td>
<td>93.5</td>
<td>93.5</td>
<td>87.1</td>
<td>89.8</td>
<td>95.0</td>
</tr>
<tr>
<td>Annual system C capture (t C/ha*yr)</td>
<td>0.45</td>
<td>0.45</td>
<td>1.21</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>Annual system C capture (t CO2/ha*yr)</td>
<td>1.63</td>
<td>1.63</td>
<td>4.42</td>
<td>1.17</td>
<td>-1.46</td>
</tr>
</tbody>
</table>

Source: Sanscartier et al., 2013
### A-6-3 On-farm energy and other inputs for miscanthus cultivation

<table>
<thead>
<tr>
<th>Items/Parameters</th>
<th>Inputs and other values</th>
<th>Energy use (diesel)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Diesel use (L/ha)</td>
</tr>
<tr>
<td><strong>Year one - Stand establishment</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rhizome production</td>
<td>12.23</td>
<td>1.18</td>
</tr>
<tr>
<td>Rhizome required (tonne/ha)</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>Rhizome delivery</td>
<td>3.29</td>
<td>0.32</td>
</tr>
<tr>
<td>Rhizome planting</td>
<td>69.06</td>
<td>6.65</td>
</tr>
<tr>
<td>Pesticide production and distribution (input = application rate in kg/ha)</td>
<td>10.00</td>
<td>1.28</td>
</tr>
<tr>
<td>Pesticides application</td>
<td>0.88</td>
<td>0.08</td>
</tr>
<tr>
<td>Mowing</td>
<td>6.39</td>
<td>0.62</td>
</tr>
<tr>
<td><strong>Crop residue contribution to total biomass produced</strong></td>
<td>0.30</td>
<td></td>
</tr>
<tr>
<td><strong>Total crop residue (above ground and below ground) returned to soil (dry tonne/ha)</strong></td>
<td>6.56</td>
<td></td>
</tr>
<tr>
<td><strong>Year two</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stand failure (%)</td>
<td>10%</td>
<td></td>
</tr>
<tr>
<td>Rhizome production and delivery</td>
<td>1.55</td>
<td>0.15</td>
</tr>
<tr>
<td>Rhizome planting (by hand, assumption: 5% of energy required for machine planting)</td>
<td>0.35</td>
<td>0.03</td>
</tr>
<tr>
<td>Fertilizer production and distribution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N (input = application rate in kg/ha)</td>
<td>60.00</td>
<td>0.08</td>
</tr>
<tr>
<td>P (input = application rate in kg/ha)</td>
<td>12.00</td>
<td>0.20</td>
</tr>
<tr>
<td>K (input = application rate in kg/ha)</td>
<td>105.00</td>
<td>0.07</td>
</tr>
<tr>
<td>Application of fertilizers</td>
<td>2.26</td>
<td>0.22</td>
</tr>
<tr>
<td>Pesticide production and distribution (input = application rate in kg/ha)</td>
<td>4.00</td>
<td>0.51</td>
</tr>
</tbody>
</table>
Pesticides application  |  0.88  |  0.08  
Harvest  |  40.25  |  3.88  
Transport to on-farm storage  |  1.61  
Crop residue contribution to total biomass produced  |  0.30  
Total crop residue (above ground and below ground) returned to soil (dry tonne/ha)  |  13.13  

**Year 3 to 20**

Harvest  |  40.25  |  3.88  
Transport to on-farm storage  |  1.61  
Fertilizer production and distribution  
- N (input = application rate in kg/ha)  |  60.00  |  0.08  
- P (input = application rate in kg/ha)  |  12.00  |  0.20  
- K (input = application rate in kg/ha)  |  105.00  |  0.07  
Fertilizer application  |  2.26  |  0.22  
Pesticide production and distribution (input = application rate in kg/ha)  |  4.00  |  0.51  
Application of pesticides  |  0.88  |  0.08  
Crop residue contribution to total biomass  |  0.30  
Total crop residue (above ground and below ground) returned to soil (dry tonne/ha)  |  13.13  

**Termination**

Herbicide production and distribution (input = application rate in kg/ha)  |  4.00  |  0.51  
Application of pesticides  |  0.88  |  0.08  
Ploughing  |  11.61  |  1.12  

**Total on-farm per year (allocating Years 1 and 2 to 18 years after establishment of crop)**  |  51.69  |  7.68  

**Source:** Sanscartier et al., 2013
### A-6-4 Estimated emission from farm input and carbon sequestration

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Western Ontario</th>
<th>Southern Ontario</th>
<th>Eastern Ontario</th>
<th>Central Ontario</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Location</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Land class</td>
<td>1-2</td>
<td>3</td>
<td>3</td>
<td>4-5</td>
</tr>
<tr>
<td>Soil type</td>
<td>Silt loam - clay loam</td>
<td>Clay</td>
<td>Clay</td>
<td>Loam</td>
</tr>
<tr>
<td>Displace crop rotation</td>
<td>Corn-soy rotation</td>
<td>Continuous soybean rotation</td>
<td>Corn-corn-forage-forage rotation</td>
<td>Long term pasture</td>
</tr>
<tr>
<td>Emission from farm input</td>
<td>128858.17</td>
<td>149714.94</td>
<td>166284.58</td>
<td>155710.04</td>
</tr>
<tr>
<td>Change in C content in all pools</td>
<td>-157434.66</td>
<td>-237784.33</td>
<td>1185.43</td>
<td>11957.97</td>
</tr>
<tr>
<td>Net emission</td>
<td>-28576.49</td>
<td>-88069.39</td>
<td>167470.01</td>
<td>167668.00</td>
</tr>
</tbody>
</table>

Raw data source: Sanscartier et al., 2013
**A-6-5 Calculation of energy consumption and material cost of enzyme production**

Energy consumption and material cost were calculated based on the enzyme production cost reported by Wooley et al., 1999 (enzyme loading: 15 FPU/g-cellulose≈19263 FPU/L). Electricity price was 4.2¢/kWh in 1997 in USA (EIA, 2010). Based on these information, and enzyme loading rate of this study material and energy cost (based on the electricity price in Canada in 2012) for enzyme were estimated.

**Reference**


A-8-1 Membrane separator

A-8-2 Membrane support
**A-8-3 List of materials/accessories for the developed bioreactor**

<table>
<thead>
<tr>
<th>Name of items</th>
<th>Quantity</th>
<th>Material type</th>
<th>Model No.</th>
<th>Manufacturer</th>
<th>Cost, $</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bioreactor</td>
<td>1</td>
<td>Plexiglass(R) VH-100 Acrylic Resin, &amp; PVC-9002-86-2</td>
<td>-</td>
<td>Developed</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Swagelok</td>
<td>12</td>
<td>Stainless steel</td>
<td>316Z77</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Swagelok</td>
<td>1</td>
<td>Stainless steel</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Swagelok</td>
<td>1</td>
<td>Plastic</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>pH meter</td>
<td>1</td>
<td>MV-RS232</td>
<td>Omega</td>
<td>148.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>pH probe</td>
<td>1</td>
<td>HHWT-SD1-ATC</td>
<td>Omega</td>
<td>63.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Temperature probe</td>
<td>1</td>
<td>PHE-1411</td>
<td>Omega</td>
<td>40.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pressure gauge</td>
<td>1</td>
<td>DPG110/120</td>
<td>Omega</td>
<td>-</td>
<td>Digital</td>
<td>-</td>
</tr>
<tr>
<td>Aeration tube</td>
<td>1</td>
<td>DPG110/120</td>
<td>Omega</td>
<td>-</td>
<td>Rubber</td>
<td>-</td>
</tr>
<tr>
<td>Support for aeration tube</td>
<td>1</td>
<td>Stainless steel</td>
<td>-</td>
<td>Developed</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Micro pump</td>
<td>1</td>
<td>GF-F155001</td>
<td>Gilson</td>
<td>1295.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pump head</td>
<td>1</td>
<td>GF-F117800</td>
<td>Gilson</td>
<td>550.8</td>
<td>Two channel head</td>
<td>-</td>
</tr>
<tr>
<td>Peristatic Tubing</td>
<td>10</td>
<td>Polypropylene</td>
<td>GF-F1825121</td>
<td>92.65</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Connection tube</td>
<td>1</td>
<td>PVC</td>
<td>06422-05</td>
<td>Cole-Parmer</td>
<td>35.0</td>
<td>25 feet</td>
</tr>
<tr>
<td>Connector</td>
<td>1</td>
<td>Plastic</td>
<td>F1179931</td>
<td>Mandel</td>
<td>-</td>
<td>Set of 10</td>
</tr>
<tr>
<td>Membrane separator</td>
<td>1</td>
<td>-</td>
<td>Developed</td>
<td>-</td>
<td>Materials from Dr. Sheng</td>
<td></td>
</tr>
<tr>
<td>Membrane support</td>
<td>1</td>
<td>Stainless steel</td>
<td>-</td>
<td>Developed</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Jars (for media &amp; effluent)</td>
<td>6</td>
<td>Glass</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Reactor lead opener</td>
<td>2</td>
<td>Steel</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Teflon ferrule</td>
<td>1</td>
<td>Teflon</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>Set of 10</td>
</tr>
</tbody>
</table>
A-8-4 List of materials/accessories for anaerobic gas chamber

<table>
<thead>
<tr>
<th>Name of items</th>
<th>Quantity</th>
<th>Material type</th>
<th>Model No.</th>
<th>Manufacturer</th>
<th>Cost, $</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anaerobic gas chamber</td>
<td>1</td>
<td>PVC, 58092421, Bayer Material Science LLC</td>
<td>-</td>
<td>Developed</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Valve</td>
<td>2</td>
<td>PVC</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Glove (pair)</td>
<td>1</td>
<td>Rubber</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pipe fittings</td>
<td>2</td>
<td>PVC 9002-86-2</td>
<td>USA</td>
<td>National Pipe &amp; Plastics, Inc.</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hinge</td>
<td>2</td>
<td>Steel</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Handle</td>
<td>3</td>
<td>Steel</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

A-8-5 List of chemicals and their amount used for broth media

Peptone..............................................10.0 g
Beef Extract........................................10.0 g
Yeast Extract.......................................3.0 g
Dextrose............................................5.0 g
NaCl.................................................5.0 g
Soluble Starch.................................1.0 g
L-Cysteine HCl.................................0.5 g
Sodium Acetate.................................3.0 g
Resazurin (0.025%).........................4 ml
DI Water...........................................1000 ml

Add all ingredients except L-Cysteine HCl. Bring media to boil to drive off oxygen. Cool down media while bubbling with oxygen free gas. Add L-Cysteine HCl and adjust pH to 6.8. Dispense under same gas phase and autoclave at 121ºC.
A-8-6 Photograph of the incubator

![Heratherm IGS60]

A-8-7 Calibration curve of the pump

\[ y_{\text{in}} = 0.08044x - 0.01799 \quad (R^2 = 0.9989; n=36) \]

\[ y_{\text{out}} = 0.08044x - 0.01470 \quad (R^2 = 0.9987; n=36) \]
A-8-8 Photographs of overall experimental setup
A-9-1 Experimental setup of torrefaction process adopted in this study

![Diagram of torrefaction setup]

Source: Acharya, 2013

A-9-2 Composition of flue gas from biomass torrefaction process

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Torrefaction time, min</th>
<th>Composition of flue gas, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CO₂</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>0</td>
<td>19.85</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>19.88</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>19.89</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>19.88</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>0</td>
<td>16.15</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>15.60</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>15.66</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>15.68</td>
</tr>
<tr>
<td>Sawdust (pine)</td>
<td>0</td>
<td>18.11</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>18.87</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>18.85</td>
</tr>
<tr>
<td></td>
<td>45</td>
<td>19.17</td>
</tr>
</tbody>
</table>
Energy consumption in the torrefaction of biomass (for 45 min)
Specific heat of biomass has been calculated based on the following formula (Ravi et al., 2004):

\[
\begin{align*}
C_p^{(dry\ wood)} & = 0.1031 + 0.003867T \text{ kJ/kg-K} \\
C_p^{(wet\ wood)} & = \frac{C_p^{(dry\ wood)} + 4.187M}{1+M} + (0.02355T - 1.32M - 6.191)M \text{ kJ/kg-K}
\end{align*}
\]  

(Eq. A-1)  
(Eq. A-2)

where, \( T \) = absolute temperature, K
\( M \) = the mass fraction of moisture in wood

The estimated specific heat (\( C_p \)) of wood = 1.522 kJ/kg-k (moisture is assumed to be 15%).

Energy consumption in torrefaction process = \( mC_p t=0.41 \text{ MJ/kg} \).

A-9-5 Photograph of thermo gravimetric analyzer (TGA)

SDT-Q600

A-9-6 Photograph of Fourier transform infrared spectroscopy (FT-IR)

Thermo Scientific Nicolet 6700
A-9-7 TGA/FT-IR experimental parameters

<table>
<thead>
<tr>
<th>Pretreatment</th>
<th>Feedstock</th>
<th>Sample size, mg</th>
<th>Air flow rate, mL/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw</td>
<td>Miscanthus</td>
<td>10.18</td>
<td>13.00</td>
</tr>
<tr>
<td></td>
<td>Wheat straw</td>
<td>8.00</td>
<td>10.00</td>
</tr>
<tr>
<td></td>
<td>Sawdust (pine)</td>
<td>10.13</td>
<td>14.00</td>
</tr>
<tr>
<td>PT</td>
<td>Miscanthus</td>
<td>8.83</td>
<td>13.00</td>
</tr>
<tr>
<td></td>
<td>Wheat straw</td>
<td>9.52</td>
<td>13.00</td>
</tr>
<tr>
<td></td>
<td>Sawdust (pine)</td>
<td>9.51</td>
<td>14.00</td>
</tr>
<tr>
<td>Raw-CaO</td>
<td>Miscanthus</td>
<td>19.86</td>
<td>13.00</td>
</tr>
<tr>
<td></td>
<td>Wheat straw</td>
<td>19.98</td>
<td>13.00</td>
</tr>
<tr>
<td></td>
<td>Sawdust (pine)</td>
<td>20.30</td>
<td>14.00</td>
</tr>
<tr>
<td>PT-CaO</td>
<td>Miscanthus</td>
<td>18.00</td>
<td>13.00</td>
</tr>
<tr>
<td></td>
<td>Wheat straw</td>
<td>18.00</td>
<td>13.00</td>
</tr>
<tr>
<td></td>
<td>Sawdust (pine)</td>
<td>19.15</td>
<td>14.00</td>
</tr>
</tbody>
</table>

Note: Thermal degradation temperature: 900 °C; Heating rate: 20 °C/min; Pretreatment (PT): 275 °C@45 min, ER: 0.3; Ratio of CaO and biomass is 1.

A-9-8 Comparison among various raw biomasses

(MS: miscanthus; SD: sawdust; WS: wheat straw; Wt: weight loss; HF: heat flow)
A- 9-9 Comparison among various torrefied biomasses

![Graph showing comparison among various torrefied biomasses.](image)

(MS: miscanthus; SD: sawdust; WS: wheat straw; Wt: weight loss; HF: heat flow)

A- 9-10 Comparison among various raw biomasses degraded with CaO

![Graph showing comparison among various raw biomasses degraded with CaO.](image)

(MS: miscanthus; SD: sawdust; WS: wheat straw; Wt: weight loss; HF: heat flow)
A-9-11 Comparison among various torrefied biomasses degraded with CaO

A-9-12 Comparison among raw and torrefied with or without CaO (miscanthus)
A-9-13 Cold gas efficiency (CGE) calculation for steam gasification (Gai & Dong, 2012).

\[ CGE \% = \frac{G_{p} LHV_{\text{product gas}}}{HHV_{\text{fuel+Steam}}} \times 100 \]  

(Eq. A-3)

where, \( G_{p} \) = volume of product gas from the gasification (Nm\(^3\)/kg-fuel)

The lower heating value (LHV) product gas is calculated from the following equation (Alamo et al., 2009).

\[ LHV (\text{MJ/Nm}^3) = \sum_{i} LHV_{i} \times X_{i} \]  

(Eq. A-4)

where, \( X \) = mole fraction of the corresponding gas

\( LHV_{i} \) = lower heating value of corresponding gas

Reference:


A-9-14 Summary of ASPEN simulation parameters (Feed stream input conditions for CLG simulation)

<table>
<thead>
<tr>
<th>Feed Stream</th>
<th>Temperature (°C)</th>
<th>Pressure (atm)</th>
<th>Flowrate (kmol h(^{-1}))</th>
<th>Component</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIOMASS</td>
<td>25</td>
<td>1</td>
<td>1(^a)</td>
<td>Biomass</td>
</tr>
<tr>
<td>H2O-FEED</td>
<td>25</td>
<td>1</td>
<td>1</td>
<td>H(_2)O (Conventional)</td>
</tr>
<tr>
<td>CAO-FEED</td>
<td>25</td>
<td>1</td>
<td>6(^b)</td>
<td>CaO (Conventional Solid)</td>
</tr>
<tr>
<td>STEAM</td>
<td>400</td>
<td>1</td>
<td>85(^b)</td>
<td>H(_2)O (Conventional)</td>
</tr>
</tbody>
</table>

\(^a\) Input as mass flowrate (kg h\(^{-1}\)) using biomass molecular weight.

\(^b\) Fed in excess of required stoichiometric amount.
Summary of ASPEN simulation parameters and CLG block diagram.

Fig. CLG block diagram (Stefan, 2014)
A-9-16 CLG simulation flowsheet (Stefan, 2014)
### A-9-17 Product gas compositions (simulated) and CGE

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Conditions</th>
<th>Gas composition, %</th>
<th>( \text{Nm}^3/\text{kg-FS} )</th>
<th>LHV, MJ/N m(^3)</th>
<th>CGE, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CO</td>
<td>H(_2)</td>
<td>CO(_2)</td>
<td>CH(_4)</td>
</tr>
<tr>
<td>Miscanthus</td>
<td>Raw</td>
<td>40.76</td>
<td>51.44</td>
<td>6.04</td>
<td>1.76</td>
</tr>
<tr>
<td></td>
<td>Torrefied</td>
<td>40.57</td>
<td>51.67</td>
<td>5.99</td>
<td>1.78</td>
</tr>
<tr>
<td></td>
<td>Raw, CLG</td>
<td>8.24</td>
<td>89.52</td>
<td>1.05</td>
<td>1.19</td>
</tr>
<tr>
<td></td>
<td>Torrefied, CLG</td>
<td>8.21</td>
<td>89.56</td>
<td>1.04</td>
<td>1.19</td>
</tr>
<tr>
<td>Wheat straw</td>
<td>Raw</td>
<td>41.28</td>
<td>50.81</td>
<td>6.20</td>
<td>1.72</td>
</tr>
<tr>
<td></td>
<td>Raw, CLG</td>
<td>8.33</td>
<td>89.42</td>
<td>1.07</td>
<td>1.18</td>
</tr>
<tr>
<td>Sawdust</td>
<td>Raw</td>
<td>40.36</td>
<td>51.92</td>
<td>5.93</td>
<td>1.79</td>
</tr>
<tr>
<td></td>
<td>Raw, CLG</td>
<td>8.33</td>
<td>89.42</td>
<td>1.07</td>
<td>1.18</td>
</tr>
</tbody>
</table>

**Note:** Volume of CO\(_2\) excluded while calculation the CGE.