ABSTRACT

DAYSTAR, JESSE SKY. Environmental and Economic Analysis of Biofuels Conversion Technologies. (Under the direction of Richard Venditti and Hasan Jameel).

Mandated production of second generation biofuels has recently stimulated much activity in the area of biofuels. However, both economic and environmental barriers blocking the success of second generation biofuels currently exist. The purpose of this work was to first identify the current knowledge base and identify the knowledge gaps surrounding the environmental impacts of biofuels and bioenergy. The second aim of this study was to determine the gate-to-gate differences in greenhouse gas (GHG) emissions of ethanol produced via biomass gasification for different feedstocks. The last objective was to identify the cellulosic feedstocks resulting in the highest financial return when processed by biomass gasification to produce ethanol.

A detailed literature survey was performed utilizing many publication databases and internet search engines. A corresponding publication database was created as a tool to identify environmental knowledge gaps. In the publications surveyed, the effects of feedstock type on the GHG emissions from cellulosic ethanol conversion processes were not thoroughly explored, especially for the thermochemical conversion pathway. Within the literature, many publications stressed the need for more detailed GHG analyses examining feedstock production and corresponding land use changes (direct and indirect). It was also noted that feedstock production and land use change are the divers of environmental success and GHG reductions through the production and use of biofuels. However, ethanol yield (gal/ton) from conversion processes is a major area of uncertainty and varies for each process conversion technology and feedstock type. Additional research should identify and compare GHG emissions from promising conversion technologies using consistent boundaries and assumptions.

To determine the impacts of ethanol produced from biomass gasification, the National Renewable Energy Labs (NREL) thermochemical ethanol production simulation and literature data were used. Six feedstocks including natural hardwoods, eucalyptus, loblolly pine, corn stover, switchgrass and miscanthus were compared to hybrid poplar (the NREL model original feedstock) examining GHG emissions on a gate-to-gate basis. Loblolly pine and corn stover emitted the least and most GHGs on a per liter basis, respectively, differing by 5%. All six feedstocks when run through the simulation model produced fewer GHG emissions than the baseline comparison of hybrid poplar. In addition, the results of this study also indicate that the conversion process contributed 62% of the overall emissions

on a cradle-to-grave basis relative to gasoline. As the conversion process represents the majority of the overall emissions, further analysis around the conversion was considered critical to the reduction of the overall GHG emissions.

Financial analysis was performed using the NREL simulation as well as updated capital cost data from Phillips et al. 2007. Feedstocks of natural hardwoods, eucalyptus, loblolly pine, corn stover and switchgrass were examined. Key financial indicators, IRR and NPV, were calculated to quantify the financial outcome for each feedstock. Loblolly pine produced the highest financial return of 21.4% IRR and corn stover produce the lowest at 14.2% IRR. Additionally, both moisture and ash content were found to negatively impact alcohol yields and have resulting in higher GHG emissions and lower financial returns. . A combined economic and environmental parameter was proposed to evaluate biofuel systems, NPV/GHG emissions. Forest based feedstocks resulted in higher values than switchgrass or corn stover for the thermochemical conversion of biomass to ethanol.

Environmental and Economic Analysis of
Biofuels Conversion Technologies

by
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DEDICATION

For losing countless tools in the yard and asking a million questions about everything, I dedicate this to my father. I dedicate this to my three sisters for taking apart bikes, toys, or anything else with moving parts and very rarely reassembling them. Finally, I dedicate this work to my mom, who in sixth grade made me question my path in life and realize my full potential.

BIOGRAPHY

Jesse received undergraduate degrees in pulp and paper engineering and chemical engineering. With these degrees, he worked with PESCO-BEAM as the technical director of biofuels evaluating and developing ethanol production methods. While an undergraduate student, he also interned with both Mead WestVaco and Kemira Chemical Company. Jesse was first exposed to research by receiving an undergraduate research grant and conducting a series of experiments analyzing different biomass feedstock pretreatment methods for improved ethanol yield. As a graduate intern, Jesse worked with the National Council for Stream and Air Improvement (ncasi) assisting in the development of greenhouse gas analysis tools. During graduate school, Jesse started Triangle Life Cycle Assessment LLC to provide environmental assessments of goods, services and fuels.

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I cannot write this thesis and complete my work without thanking two of my high school teachers. Through patiently watching me make mistakes and allowing me to find my own solutions, I thank you Dean Knick for helping me realize the value of persistence and self-learning. Without an observant chemistry teacher recognizing my somewhat disguised potential, I would have never attended NC State and learned the wealth of knowledge I now possess. Thank you Chip Coalter for taking me to the NC state open house and encouraging me to pursue an education in engineering. Never underestimate the impact you can have in developing minds.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1 Thesis introduction

"The evidence of human-induced climate change goes beyond observed increases in average surface temperatures; it includes melting ice in the Arctic, melting glaciers around the world, increasing ocean temperatures, rising sea levels, acidification of the oceans due to excess carbon dioxide, changing precipitation patterns, and changing patterns of ecosystems and wildlife" (Jackson). This quote from Lisa Jackson's (the EPA administrator) announcement of *Greenhouse Gases Threaten Public Health and the Environment* outlines a few of the impacts of global warming. These and unanticipated impacts to the world are the motivating force behind greenhouse gas (GHG) monitoring/regulations and renewable fuels initiatives. Responding to the current and potential impacts of global warming, the EPA has determined that GHG are harmful to human health and will be regulated under the Clean Air Act (CAA).

The Energy Independence and Security act of 2007 (EISA) outlined a set of goals to increase energy security as well as reduce GHG emissions. As biofuels are seen as a key component of energy security and GHG reduction, the Renewable Fuels Standard (RFS) requires production of 36 billion gallons of blended renewable transportation fuels by 2022. As there is much controversy over the GHG reductions due to first generation biofuels production and use (Davis, Anderson-Teixeira et al. 2009); EISA also required the EPA to apply life cycle GHG threshold standards to ensure reductions through the use of renewable fuels. Through following these threshold requirements, 60% GHG reduction for cellulosic ethanol and 20% for other biofuels, the use of biofuels will decrease anthropogenic GHG emissions and create a more sustainable path forward.

It is clear that forests, durable wood-based products and forest biofuels produced from sustainably managed forests can have a significant impact on global carbon cycles. This impact includes a complex array of factors including carbon stored in the forests, durable wood products, and fossil carbon displaced by these durable wood products and forest biofuels. The overall impact depends on the region (water, soil and growing season) and forest type, specific aspects of the conversion technology and the characteristics of the materials that are displaced by the wood material or energy product. The complexities of forests and the conversion technology options, and the subsequent displacement of fossil carbon, makes determining of the overall impact of specific biomass use alternatives extraordinarily difficult, but also extremely valuable.

The difficulty of this type of analysis and inconsistencies in assumptions yields a wide range of reported impacts and carbon balances within literature. Due to the nature of life cycle assessment and GHG analysis, system boundaries and specific assumptions will vary for individual studies depending on the goal and scope of the work. However, when inconsistent system boundaries and assumptions are made, the outcome of LCA studies are greatly varied.

Due to the high dependence on study assumptions and system boundaries, it is extremely difficult to compare various studies without verifying identical assumptions and boundaries or correcting them to match other studies. However, some insight can be gained through surveying literature and compiling study results to gain an overall literature consensus. Additionally, much knowledge can be gained through observing study assumptions and resulting study conclusions. From this type of analysis, system boundary and process assumptions can become more accurate and consistent within future studies.

Within this thesis, three topics surrounding biofuels were explored. First, a knowledge gap analysis was performed surveying literature on GHG analysis and LCA of biofuels to gain an understanding of the current knowledge base and to identify knowledge gaps, Chapter 2. Second, GHG emissions due to ethanol production via biomass gasification for cellulosic feedstocks were determined, Chapter 3. The third aspect of this thesis diverges from an environmental to an economic focus to identify the most economically feasible feedstocks to produce ethanol via biomass gasification, Chapter 4. Figure 1-1 depicts all three aspects of the following research.

A reader of this thesis will: 1) become familiar with the different aspects of life cycle assessments and many of the common assumptions used, 2) understand the knowledge gaps in the area of LCA and GHG analysis of biofuels/energy, 3) become familiar with the various biofuels processing technologies, 4) understand biomass types and characteristics that produce the fewest environmental impacts when processed into ethanol via gasification, and 5) understand biomass types and characteristics that produce the best financial return on investment for ethanol production via biomass gasification.

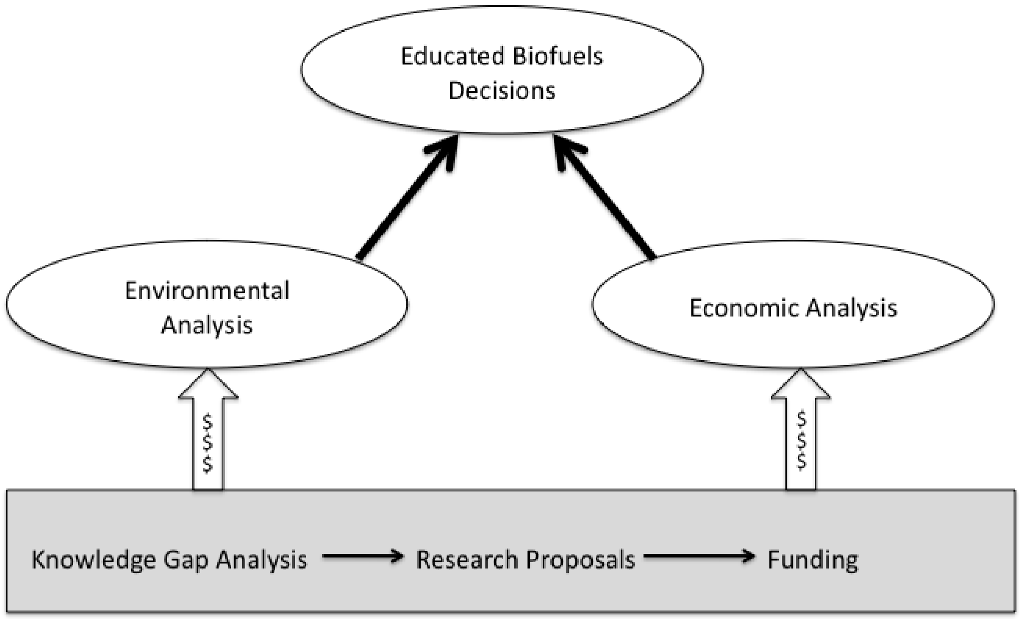

Figure 1-1: Research approach diagram

2 Biofuels LCA literature review and knowledge gap analysis

2.1 Overview

2.1.1 Project motivation

This work was contracted by the United States Forest Service to accomplish several goals. First, knowledge gaps within life cycle assessment literature were to be discovered and reported. Additionally, the assumptions and study methods that impact results significantly were to be identified. To accomplish these goals, a literature survey, covering more than 50 publications, was performed. From this survey, a review of pertinent articles extensively covering a sampling of the process and life cycle assessment methods was written. To provide additional utility for future grant writing and research, a literature database and annotated bibliography was created. This document in conjunction with the literature database will be an invaluable tool for teaching life cycle assessment of biofuels and identifying future research opportunities.

2.1.2 Publication collection methods

The aim of this study was to identify topics thoroughly covered within literature and knowledge gaps within the field of life cycle assessment of biofuels/energy. An extensive literature search was conducted yielding a total of 56 sources. The majority of these sources come from peer-reviewed publications while a few come from CRISS reports. CRISS reports outline research currently being conducted that will soon be published. Databases Web of Science, Compendex, Google Scholar, and SciFinder Scholar were used to search for articles within the area of LCA of biofuel/energy. Key words used for these searches include: biomass, thermochemical, gasification, biochemical, dilute acid, enzymatic, ethanol, lignocellulosic, 2nd generation, wood, cellulose, biorefinery, LCA, life cycle assessment, and green house gasses.

The literature surveyed contained a disproportionate weighting of studies surrounding biofuels. Despite this, a good sampling of articles was found for each production process and final energy product. To record these findings, Microsoft Access was used to organize and enter data on each publication. Within this database, the major findings, knowledge gaps, methodology, location, citations and other data were collected and tabulated for each article. The results from these fields will be converted into an annotated bibliography. In addition to organizing the articles, the database serves as a useful tool for LCA education.

2.1.3 Publications and literature examined

The publications collected can be categorized in seven categories: 1. review articles, 2. ethanol, 3. biodiesel, 4. electricity, 5. other biofuel products, 6. LCA sub-process, 7. LCA methodology and policy. Of these seven categories, the majority of the articles were focused on ethanol production process, Table 2-1. In addition to the publications focused on LCA of ethanol production, most of the biofuel review papers included ethanol biofuels as well.

Table 2-1: Publications by topic group

Topic area	# of articles
Review	8
Ethanol	16
Biodiesel	5
Electricity	7
Other biofuel products	4
Sub-processes	11
Biofuel LCA Methods and policy	5
Total	56

Some LCA studies investigated only one aspect of a full biofuel production process. These articles were grouped within the sub-process category. Other articles focusing on LCA methodology, techniques and policy related to biofuels were also found. These were grouped within the biofuel LCA methods policy category.

The majority of the studies were conducted within the United States, Table 2-2. Many European publications discussing the techniques of LCA were found but are included in the not specified category, as the technique was not being applied within a particular region.

Table 2-2: Publications by study location

Location of study	# of articles
USA	22
Europe	14
Asia	4
Not specified	16
Total	56

Language filters of the performed searches likely influenced the number of publications for each country. Publications in languages other than English were not considered.

Table 2-3: Publication by dates (note: the search was primarily conducted in 2009)

Publication date	# of articles	Publication date	# of articles
2010	1	2002	1
2009	27	2001	1
2008	7	2000	0
2007	7	1999	0
2006	3	1998	0
2005	2	1997	0
2004	2	1996	2
2003	3		
Total	56		

The majority of the literature search was performed in 2009. As a result, few articles from 2010 are within the review. Nearly all, of the articles found were published within the last ten years, Table 2-3.

2.2 LCA of ethanol from forest resources/lignocellulosics

Ethanol production can be broken down into two categories: 1st and 2nd generation biofuels. 1st generation biofuels are produced from starches and sugars typically from corn, while second generation ethanol is produced from non-food sources such as cellulose. Within the review of ethanol studies, processes with forest based biomass feedstocks were the primary focus. Other biomass feedstocks were considered including crop residuals, waste cellulose, and corn, but were not fully explored. In particular, LCA studies based on corn ethanol are numerous but were not thoroughly explored. In total, 16 LCA related publications were found on ethanol production, Table 2-4.

Table 2-4: LCA of ethanol production by biomass type

Ethanol Production	**# of articles**
Cellulose based ethanol	12
Forest biomass	5
Corn stover	3
Variety cellulosic materials	4
Corn based ethanol	4
Total publications	**16**

2.2.1 Conversion technologies

2.2.1.1 Biochemical conversion

The biochemical conversion process is defined by the use of living organisms to produce a final biofuel product. There are many different technologies being developed utilizing the biochemical pathway. This ethanol production pathway converts either cellulose or starch from a raw form, chips or corn, to a final product of ethanol. For cellulosic ethanol conversion, the main steps often include: feedstock preparation (chipping), pretreatment process, saccharification, fermentation, purification, and power production, Figure 2-1.

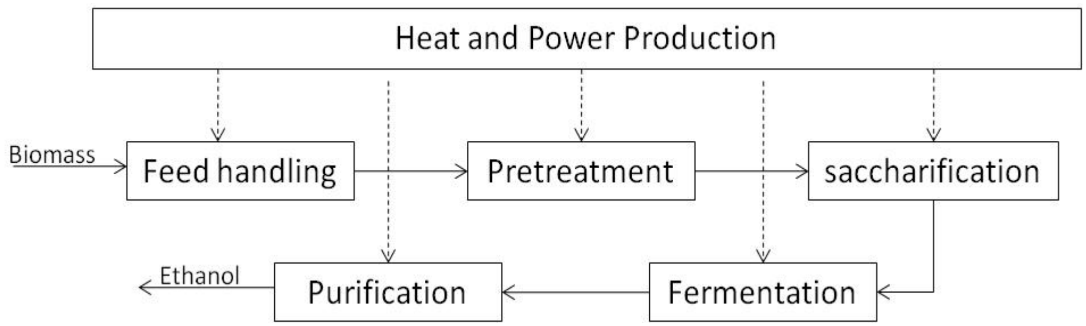

Figure 2-1: Biochemical conversion pathway block diagram

Feedstock preparation / chipping

To insure proper chemical penetration and accessibility, the incoming biomass must be mechanically treated to insure a small and uniform chip size. Small chip sizes increase the chemical accessibility of the biomass through increasing the available surface area. However, there is an optimum chip size that insures proper chemical penetration to maximize sugar yields while conserving chipping energy.

Pretreatment

The pretreatment step has been an area of intense research within the biofuels field. Many scientists have developed novel chemical and mechanical pretreatment processes claiming to increase enzymatic hydrolysis sugar yields. The common aim of all these methods include (Jorgensen, Kristensen et al. 2007):

- Maximize enzymatic convertibility, minimize sugar loss,
- Maximize the production of other valuable by-products, e.g. lignin,
- Not require the addition of chemicals toxic to the enzymes or other fermenting microorganisms,
- Minimize the use of energy, chemicals and capital equipment,
- Be scalable to industrial size

These pretreatment process are often chemical and energy intensive but are required to achieve reasonable hydrolysis yields. From an economic standpoint, low chemical cost or high chemical recovery is critical (Jorgensen, Kristensen et al. 2007).

The dilute acid pretreatment has been heavily promoted by NREL and is often compared as a benchmark to other pretreatment processes. This process uses sulfuric acid and moderate temperatures to increase the feedstock enzymatic accessibility. As this process is most prominent within the published literature and process models are publicly available through NREL, there have been a many economic and environmental publications based on this technology pathway.

Saccharification

The saccharification process employs enzymes to break down cellulose and hemicellulose polymers to monomer sugars, glucose and pentose. Sugars monomers are formed by cleaving the glycosidic linkages using a variety of enzymes such as end-glucanase, exo-glucanase and glucosidase (Jorgensen, Kristensen et al. 2007). Of all the processes within the biochemical pathway, the hydrolysis or saccharification step is serving as the "gate keeper" to economic successes. High sugar yield within this unit process is critical, influencing both the economics and environmental performances dramatically.

Fermentation/purification

Sugars from the saccharification process are fermented to alcohol. Commonly used yeast includes Z. Mobolisis and Saccharomyces cerevisia. Z. Mobolisis yeast has the ability to ferment sugars to a higher concentration, but is unable to convert 5 carbon sugars to ethanol. The increased alcohol concentrations attained with this yeast can dramatically decrease the purification energy requirements. This is favorable for both economics and environmental parameters. The Saccharomyces cervisia yeast, however, has been used to ferment alcoholic beverages for thousands of years and is a well understood microorganism. In addition to this, it is able fermenting five carbon sugars from hemicellulose into sugars.

Alcohol purification is usually done through the use of distillation columns and molecular sieves. Distillation is an energy intensive process that utilizes the different vapor pressures of water and alcohol to separate the two components. Increased alcohol concentration entering the distillation process decreases energy usage and equipment cost. Higher incoming alcohol concentration can be achieved through high alcohol yielding yeasts, increased fermentation solids, and increased saccharification solids. After the alcohol is purified to around 95%, a molecular sieve is used to increase the alcohol concentration to around 99.9%.

Power generation

Within previous unit processes, lignin hinders reactions and is generally an undesirable component. However, lignin is a good fuel source to create process steam and energy. Not all processes create burnable lignin, however. These processes often rely on natural gas or coal boilers to power facility operations. In order to avoid using fossil fuels, some processes utilize a hog fuel boiler burning biomass rejects, bark, and residuals from the process.

2.2.1.2 Thermochemical conversion process

Thermochemical conversion technology produces ethanol in absence of microorganisms. Instead of microorganisms, the thermochemical pathway utilizes heat and/or physical catalysis to convert biomass to intermediate gases then to biofuel (Foust et al. 2009). Thermochemical conversion processes are generally split into three main categories: gasification, pyrolysis and torrifaction. The gasification process is described in the subsequent sections.

2.2.1.2.1 Biomass gasification

The biomass gasification pathway to biofuels is very complex and requires many unit processes. As a result of this, the process requires a large capital investment and is generally less understood than the biochemical process. Despite this, NREL and others have developed biomass gasification process models used for environmental and economic analysis. The NREL biomass gasification process is described in further detail here and can be found in full detail in Phillips et al. 2007. A simplified flow sheet of the biomass gasification production ethanol pathway is given in Figure 2-2.

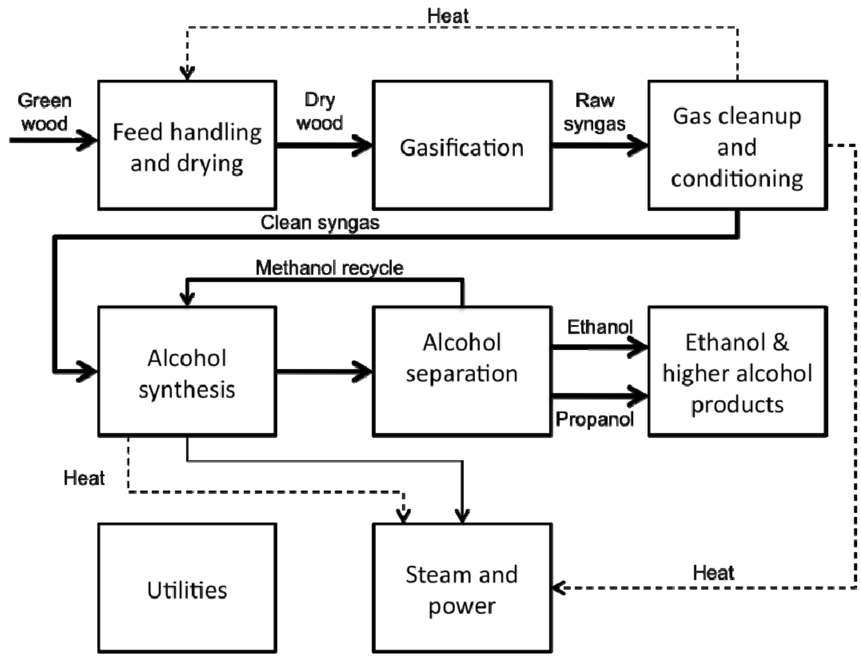

Figure 2-2: Major unit process for NREL thermochemical alcohol conversion process (S Phillips 2007)

The thermochemical process is broken down into seven major process areas, Figure 2-2. Each process area is comprised of multiple unit operations such as reactors, separations, heat exchangers, and other operations that alter the matter within the process. Aspen Plus, a process simulation program, was used to simulate and group the conversion process into seven hierarchy groupings. The following describes the unit process areas within Figure 3-1.

A100 Feedstock handling and drying: The incoming feedstock is dried and screened to remove unusable biomass and contaminants. Flue gas from the char combustor and syngas boiler is the primary heat source for drying. Biomass moisture content is reduced to around 5%.

A200 Gasification: Incoming biomass is further heated by olivine, sand like substance, circulated from the char combustor. Endothermic reactions release syngas, primarily CO and H_2 in the gasifier.

A300 Gas cleanup and conditioning: tars and other hydrocarbons are reformed into CO and H_2, syngas is cooled/quenched, and acid gas is removed and reduced to sulfur. Syngas contaminants or "acid gases" such as CO2 and H2S are removed in a monoethanoamine-based scrubbing system. Finally, H_2S is further catalytically reduced to sulfur. These cleanup steps are critical to preventing both catalyst fouling and poisoning in the subsequent alcohol synthesis steps.

A400 Alcohol synthesis: Once the syngas is cleaned, it can then be converted to alcohols using a fixed bed reactor. In the NREL process, this is accomplished with a sulfur tolerant molybdenum disulfide catalyst. Unconverted syngas is primarily recycled back to the tar reformer for additional cycles through alcohol synthesis. A purge stream of unreacted syngas is sent to the tar reformer catalyst regenerator as fuel.

A500 Alcohol separation: Within this process area, the mixed alcohol stream is depressurized in preparation for dehydration using a molecular sieve. Once water is removed from the alcohol stream, a distillation column is used to separate methanol and ethanol from higher alcohols. A second distillation column separates the methanol from the ethanol final product. The higher alcohols are sold as a co-product, while most of the methanol is first recycled back to molecular sieve to flush adsorbed water, and then returned to the input of the synthesis reactor to help maximize ethanol production.

A600 Power and steam: Steam for process heating and shaft work is generated from the highly integrated reuse of process energy. Heat exchanging both boiler feed water and steam with high temperature flue and syngas streams is used in conjunction with heat recovered from alcohol synthesis to created superheated steam for power generation. Turbo generators then generate electricity as well as extract lower pressure steam to meet any remaining process energy requirements. The tar reformer catalyst regenerator is configured to burn raw syngas to provide any additional process energy, and allow the model biorefinery to be energy independent.

A700 Utilities: Low quality steam from power production and other unit processes are condensed using cooling towers fed by well water. The condensate is recycled back to the process for further use.

2.3 Literature reviewed: ethanol production

Several different conversion processes were studied to analyze the environmental impacts of biofuels. The biochemical process was the most common conversion technology used for these analyses, Table 2-5. The biochemical processes utilizes a pretreatment method followed by an enzymatic hydrolysis sugar conversion step. This conversion technology has been the main focus of the NREL and is the benchmark upon which other processes are compared. Only one article specifically focused on the thermo-chemical process while two compared the thermo-chemical process to the bio-chemical process.

Table 2-5: Ethanol production conversion processes studied

Ethanol Production Processes	# of articles
Bio-chemical conversion	9
thermo-chemical conversion	1
Bio/thermo chemical comparison	2
Corn-sugar fermentation	4
Total publications	**16**

Environmental and life cycle assessment analysis can be broken down into several categories. The two largest categories of analysis include (1) green house gas (GHG) emissions/energy analysis and (2) life cycle assessment (LCA). GHG emissions studies offer insight on these process' effects on global warming and energy production, while full LCA studies include a broader scope, which analyze the full environmental impacts of a process. To date, there are many more GHG and energy analyses of biofuels than full LCA studies (Cherubini 2009).

Despite the more focused scope of GHG analyses, they are still useful to review as GHG emissions reductions are under regulations as previously designated. In addition to this, data and methods from GHG analyses can be incorporated into further LCA studies. Within this review, the GHG and energy analyses will be reviewed first followed by individual LCA studies.

2.3.1 GHG literature review

Typically, all GHG emissions are reported in CO_2 equivalents. For each type of GHG, (CO_2 NO_x, CH_4, ect.) there are conversions to convert each pollutant to an equivalent CO_2 effects on global warming,

Table 2-6.

Table 2-6: CO_2 equivalent conversion factors (IPCC 2006)

Pollutant	CO_2 eq. multiplication factor
CO_2	1
C	3.3
CH_4	21
N_2O	281
HFC-23	10,614
CF4	5,897
SF_6	21,682

Note: (HFC-23=hydrofluorocarbon gases, CF4=perfluorocarbon gases, SF6=sulfur hexaflouride)

With uniform reporting standards of CO_2, studies are more easily compared. Davis et al 2009 performed a comprehensive biofuel GHG emissions literature review. Within this work, GHG emissions from many feedstocks, primarily using a biochemical conversion pathway, were tabulated and ranked from the most GHG savings to the least GHG savings, Table 2-7. Despite convenient reporting unit of GHG analyses, when studies with different scopes, boundaries, or assumptions are compared, a wide range of results often occurs. For example, within Table 2-7 corn based biofuel was reported from two different studies to either have an 86 percent GHG savings or 93% GHG burden.

Table 2-7: GHG emissions from varying feedstocks (biochemical conversion except as noted)

Feedstock	GHG Displacement %	S	Feedstock	GHG Displacement %	S
Switchgrass	-114	1	Corn	-86	9
Switchgrass combustion compared with coal combustion	-109	2	Corn-soy	-38	10
Miscanthus (gasification)	-98	3	Corn (starch)	-25	11
Switchgrass	-93	4	Corn (starch)	-24	12
Switchgrass	-73	5	Corn	-3	13
Switchgrass	-11	6	Corn (starch)	66	14
Switchgrass	43	7	Corn (starch)	93	15
Switchgrass	50	8			

Source: [1](Adler, Grosso et al. 2007), [2](Ney and Schnoor 2002), [3](Lettens, Muys et al. 2003), [4](Schmer, Vogel et al. 2008), [5](Wu, Wu et al. 2006), [6](Lemus and Lal 2005), [7](Delucchi 2006), [8](Searchinger, Heimlich et al. 2008), [9](Delucchi, 2006), [10](Adler, Grosso et al. 2007) [11](DiPardo 2004), [12](Wu, Wu et al. 2006), [13](Niven 2005), [14](Delucchi, 2006), [15](Searchinger, Heimlich et al. 2008) (Table modified from Davis et al 2009)

These vastly varying results illustrate the inconsistency between studies and the mishandling of the following factors (Cherubini et al 2008):

- Recognition of biomass carbon cycle
- Including carbon stock changes in biomass and soil over time
- Inclusion of nitrous oxide and methane emissions from agriculture activities,
- Selection of appropriate fossil reference system
- Homogeneity of the input parameters in life cycle inventories

- Influence of the allocation procedure when multiple products are involved
- Future trend in bioenergy

These mishandlings and inconsistency are not exclusive to GHG analysis. LCA studies offer an even larger spectrum and opportunity for inconsistent handling of these factors.

Despite these the inconsistency of the results, some trends can be observed. Nine out of the eleven cellulosic feedstock options report GHG savings with an average savings of 59%. Corn, however, only had five out of the seven reports indicating GHG savings with an average of 2.42% GHG displacement. These findings are in line with other GHG review studies such as Cherubini et al 2009.

2.3.2 Ethanol LCA review

Publications on LCA of cellulosic biofuels will are reviewed within this section. Articles focusing on biochemical pathways will be reviewed first followed by, thermochemical/biochemical comparison, and biorefineries. The selected articles were considered to be of higher quality than many others within the literature. They were considered to be more robust and thoroughly covered topics that other studies did not fully analyze. Articles not reviewed here that were considered and included in the knowledge gap analysis database, are found within an annotated bibliography not included within this manuscript.

The below review was written with the goal of informing the reader of general findings within the area of LCA of biofuels as well as illustrate techniques used, and present useful data. In addition to these goals, parameters that have large LCA impacts will be identified and explained. The following articles focus on several main topics including feedstock comparisons, conversion technologies, and chemical and enzyme usage from an LCA perspective. Through reviewing these articles, the reader will be exposed to the multifaceted nature of LCA as well as the general techniques followed within the LCA community. After presenting these studies, knowledge gaps found within the literature will be identified.

2.3.2.1 LCA biochemical process

Comparative Life-Cycle Assessment for Biomass-to-Ethanol Production from Different regional Feedstocks*,* by Kemppainen and Shonnard, performs a cradle to gate LCA around the biochemical ethanol production pathway. More specifically, the NREL dilute acid model

(Wooley, Ruth et al. 1999) was used to attain the production based emissions. In addition to Aspen Plus software used for the simulation, the Boustead model and Environmental Fate and Risk Assessment tool were used for life cycle inventory (LCI) and impact assessment (LCIA), respectively.

The goal of this study was to "compare the life-cycle (cradle-to-gate) energy consumption and environmental impacts for producing ethanol via fermentation-based process starting with two lignocellulosic feedstocks: virgin timber resources or recycled newsprint from an urban area (Kemppainen 2005). The model was run at a feedstock rate of 2,000 MT per day.

Nine commonly used environmental indices were considered for this study, Table 2-8. The life cycle composite index is total environmental score index that includes the other eight indices. As previously stated, a life cycle inventory was compiled using both Aspen Plus and the Boustead Model. Using these tools, 14 air emissions were tracked and quantified, Table 2-8

Table 2-8: Environmental indices and abbreviations (Kemppainen 2005)

Environmental Indices	Abbreviations
fish toxicity	I_{ft}
human ingestion toxicity	I_{ING}
human inhalation toxicity	I_{INH}
human carcinogenic ingestion toxi(	I_{CING}
human carcinogenic inhalation toxi	I_{CINH}
smog formation	I_{SF}
acid rain	IA_R
global warming	I_{GW}
life cycle composite index	I_{L-CC}

Table 2-9: Life cycle emissions to air: timber vs. newsprint (Kemppainen 2005)

chemical	upper Michigan timber (Mg/year)	newsprint (Mg/year)
acetaldehyde	2.73×10^{-6}	3.78×10^{-6}
acetic acid	8.24×10^{2}	3.76×10^{2}
ammonia	2.90×10^{3}	2.49×10^{3}
butane	9.87×10^{1}	7.26×10^{1}
carbon dioxide [b]	2.09×10^{4}	1.40×10^{5}
carbon disulfide	3.41×10^{-7}	4.54×10^{-7}
carbon monoxide	9.27×10^{2}	5.48×10^{2}
ethanol	1.50×10^{2}	7.35×10^{2}
hydrochloric acid	2.03×10^{0}	1.92×10^{0}
nitrogen dioxide	4.77×10^{2}	6.78×10^{2}
nitrous oxide	1.67×10^{-4}	2.24×10^{-4}
sulfur dioxide	2.71×10^{3}	2.74×10^{3}
TOC	-1.50	1.98
toluene	3.36×10^{-2}	3.79×10^{-2}
total	2.90×10^{4}	1.48×10^{5}

[a] Data obtained through use of NREL simulation results for the ethanol process and the Boustead Model for the emissions from the life-cycle stages prior to the ethanol process. Some emissions were obtained by inputting NREL results into EFRAT. [b] Climate-active C

Overall, the use of upper Michigan timber had a lower air emission rate than the use of newsprint. As presented earlier, not all emissions have the same effect on environmental indices. Impact assessment methods attempt to quantify each pollutant's relative environmental impacts and adjust these impacts to reflect the damage done to the environment. Kemppainen divided the production process into two categories: pre-manufacturing and manufacturing. Such processes as chemical production, feedstock harvesting and preparation are included in pre-manufacturing. The impacts of both pre-manufacturing and manufacturing are shown in Table 2-10.

The two processes produced relatively similar impacts in all categories except global warming and fish toxicity. The timber process produced more acetic acid due to the higher hemicellulose content of the feedstock. As a result of this, the fish toxicity more than doubled for the timber processes. The global warming impact, however, was more than three times higher for the newsprint process. Again, the major factor affecting the indices was the biomass composition.

Since newsprint has a low lignin content, less power can be produced from recovered lignin. As a result of this, power must be purchased from the grid, primarily fossil fuel derived energy. Lignin derived energy, in contrast to fossil fuel energy, has a lower carbon footprint due to carbon sequestration in feedstock/lignin production.

Table **2-**10: Environmental impacts for newsprint and timber (Kemppainen 2005)

	I_{FT}	I_{ING}	I_{INH}	I_{CING}	I_{CINH}	I_{GW}	I_{SF}	I_{AR}
Upper Michigan Timber								
premfg process[a]	3.83×10^{-6}	1.52×10^{-7}	0.129	1.83×10^{-11}	6.10×10^{-13}	0.526	1.85×10^{-5}	3.59×10^{-3}
mfg process	2.32	26.1	0.415	0.00	0.00	−0.330	6.66×10^{-4}	3.46×10^{-2}
total (kg/L EtOH)	2.32	26.1	0.542	1.83×10^{-11}	6.10×10^{-13}	0.196	6.68×10^{-4}	3.83×10^{-2}
Newsprint								
premfg process[b]	3.20×10^{-6}	1.65×10^{-7}	0.119	2.42×10^{-11}	8.08×10^{-13}	0.478	1.78×10^{-5}	3.36×10^{-3}
mfg process	1.02	26.9	0.433	0.00	0.00	0.291	5.44×10^{-4}	3.09×10^{-2}
total (kg/L EtOH)	1.02	26.9	0.552	2.42×10^{-11}	8.08×10^{-13}	0.769	5.60×10^{-4}	3.43×10^{-2}

[a] Impacts from producing chemicals used in the ethanol process, for felling, skidding, and transportation of timber and of chipping.
[b] Impacts from producing chemicals used in the ethanol process, of transportation of newsprint, and of pulping.

When the environmental indices are normalized and compared between the two processes, the newsprint process had a slightly lower overall environmental impact ($I_{L\text{-}CC}$), approximately 5%. Of the total impact, human ingestion toxicity (I_{ING}) contributed 83% and 91% for timber and newsprint processes, respectfully.

In conclusion, the overall impacts of both processes are relatively similar. While the timber process used more fossil fuel energy in the pre-manufacturing stage, the newsprint process used more fossil fuel intensive electricity in the production stage.

Life Cycle Assessment of Bio-ethanol Derived from Cellulose by Fu et al. (Fu 2003) performed a full LCA of bioethanol produced from wood and agriculture wastes. SimaPro 4.0 was used to perform a life cycle inventory (LCI) and an impact assessment. This ethanol conversion process utilized a steam explosion pretreatment method followed by subsequent enzymatic treatment to produce sugars fed to the fermentation system. The alcohol stream from the fermentation process is then distilled to attain an ethanol purity of 99.5 wt %. The study was conducted at a production scale of 6.62 million gallons per year. The main objective of the study was to determine the potential for reducing GHG by producing a 10% bioethanol/gasoline blend as a transportation fuel (Fu 2003).

For this analysis, four different operating scenarios were examined. To examine the effects of feedstock production as well as energy production the following scenarios were studied, Table 2-11.

Table 2-11: LCA scenarios for bio-ethanol fuel studied (Fu 2003)

Feedstock	Process energy source
Hay	E10-a: fossil electric grid
Wood and agricultural waste	E10-b: fossil electric grid
Hay	E10-c: waste biomass (lignin, etc.)
Wood and agricultural waste	E10-d: waste biomass (lignin, etc.)

The cultivated feedstock was hay produced in Ontario while the waste biomass was composed of wood and agriculture waste.

Fuel economy was assumed to be the same for both E10 and pure gasoline, although, in reality there is a 1% fuel economy penalty. The co-product and byproducts of this process are recognized but do not carry any of the environmental burdens. This 100% burden allocation to ethanol was justified by lack of a market for the co-products and their currently valueless nature. Figure 2-3 illustrates the system boundaries and information sources of this study.

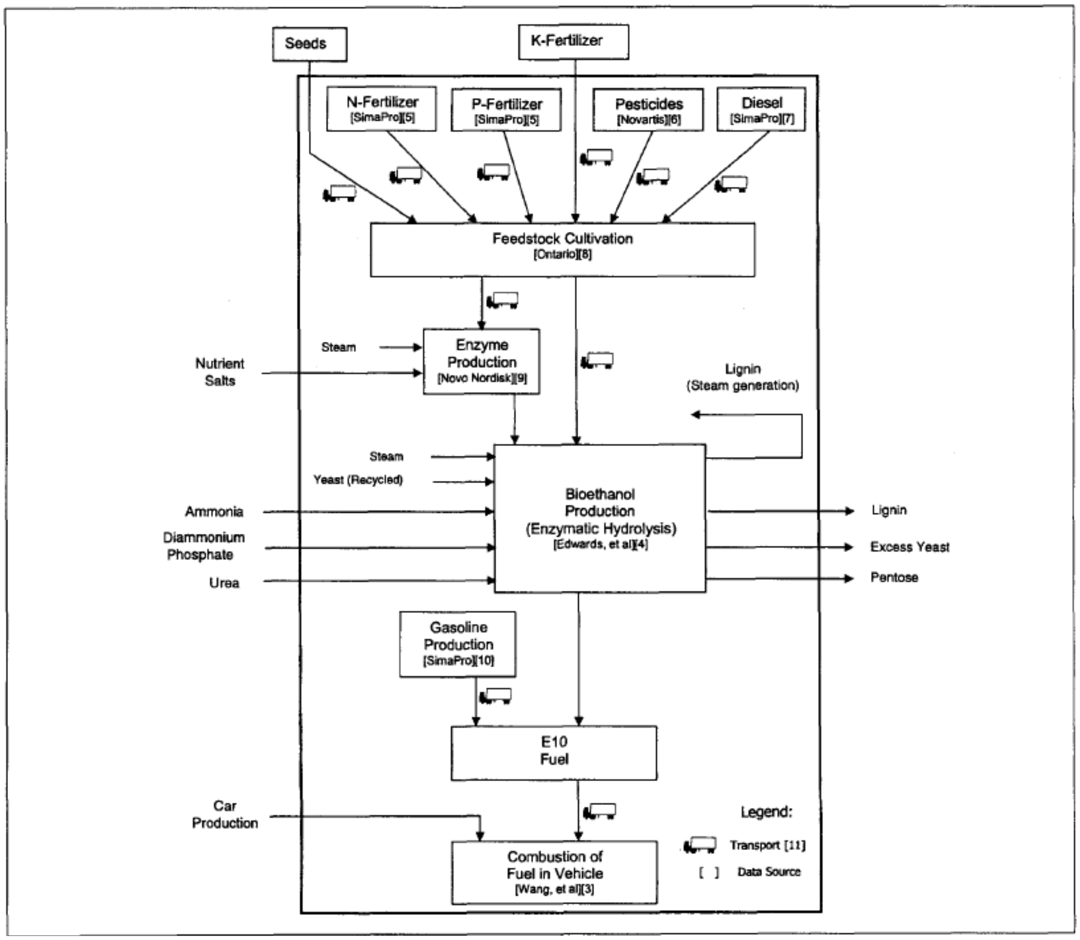

Figure 2-3: Fu et al. system boundaries (Fu 2003)

The results from this study were presented in several methods. The actual emissions for E10-a scenario were given and then compared to the other three scenarios. The emissions were also broken down to reflect releases based on six categories: 1. Transportation, 2. Feedstock cultivation, 3. Steam production, 4. Enzyme production, 5. Gasoline manufacturing, and 6. Fuel combustion. The fuel combustion dominated many of the emission categories.

Table 2-12 includes the emissions and energy usages from the cultivated feedstock / fossil power scenario.

Table 2-12: Inventory for biofuels produced from cultivated feedstocks using fossil fuel power (Fu 2003)

Inventory	Value	Equivalent unit/compound
Green house gases	0.256	kg CO2
Acidifying gases	1.88	g SO2
Eutrophication	0.278	g PO4
Winter smog	0.689	g dust
Summer smog	1.08	g C2H4
Ozone depleting gases	0.318	mg CFC11
Heavy metals	0.654	mg Pb
Carcinogenic	0.00608	mb benzo (a) pyrene
Solid wastes	0.719	g
Energy consumption	5.1	MJ

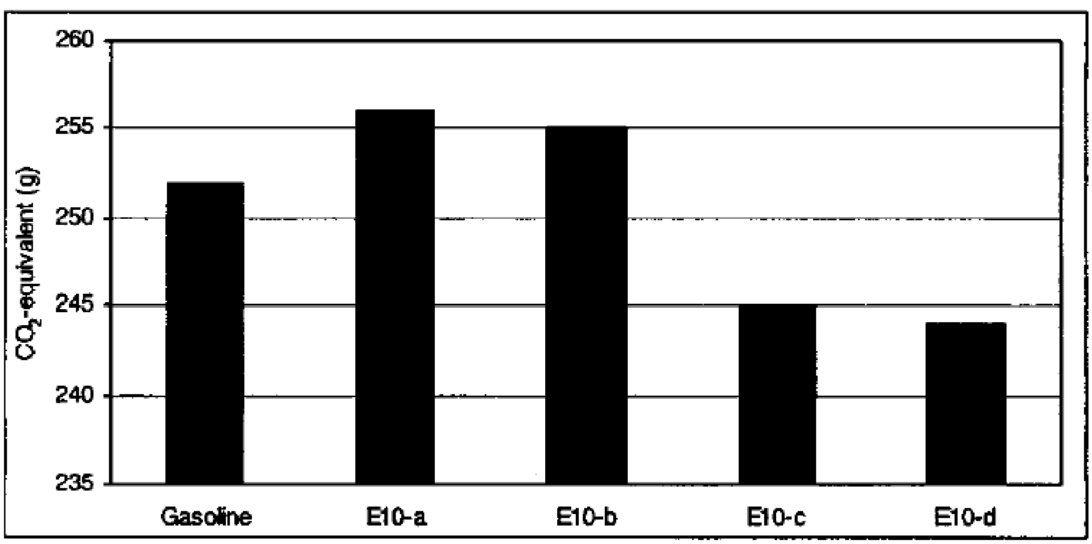

Figure 2-4: LCA GHG emissions for E10 fuels compared to gasoline (per km driven basis) (Fu 2003)

Based on these findings, only when waste biomass was used as the energy source did GHG emission reductions occur. Further GHG emissions reductions were experienced with the waste biomass feedstock, scenario E10-d. Ten different parameters were compared in a qualitative manner in Figure 2-5. Eutrophication, winter smog, acidification, and solids were worse for the four ethanol blend scenarios relative to gasoline whereas heavy metals, ozone, summer smog and energy in manufacturing were all more favorable.

In conclusion, when hay biomass was specifically grown for ethanol production, the use of E10 increased environmental degradation in many categories and was more harmful to the human population than gasoline. E10 production using biomass energy and waste biomass feedstocks, however, offered benefits in many categories, (energy in manufacturing, GHG, summer smog, ozone, and heavy metals) while increasing the burdens in several others (eutrophication, winter smog, and solids).

	E10-a	E10-b	E10-c	E10-d
Energy in manufacturing	+	+	++	++
GHGs	-	-	+	+
Acidification	--	-	--	-
Eutrophication	--	-	--	-
Winter smog	--	--	-	-
Summer smog	+	+	+	+
Ozone	++	++	++	++
Heavy metals	+	++	+	++
Carcinogens	---	o	---	o
Solids	--	--	--	--

--, -, 0, +, ++ : from 'more severe,' to 'same,' to 'less severe' environmental impact relative to gasoline

Figure 2-5: Qualitative difference compared to gasoline for each operation scenario (Fu 2003)

The contribution of enzymes and process chemicals to the life cycle of ethanol by MacLean and Spatari 2009 analyzed the effects enzyme and chemical usages often overlooked in other LCA studies. The objective of this analysis was to determine if this omission or lack of resolution is warranted within other studies. Environmental burdens of bioethanol process chemicals were analyzed on a well-to-tank basis for both mature lignocelluosic and corn feedstocks. The metrics examined were fossil derived energy and GHG emissions on a per MJ of ethanol basis.

There are many novel biochemical conversion pathways which utilize different pretreatment processes. Each pretreatment process will affect the enzyme accessibility and efficiency. As a result of this, chemical usages and enzyme addition rate will vary for each process, Table 2-13 Based on the numbers reported here for commercial ethanol production, it is clear that the pretreatment process had a large effect on the chemical usage as well as the associated GHG emissions.

Table 2-13: Chemical usage for different biochemical conversion pathways

Conversion process	Chemical	Chemical input (kg/dry metric ton feedstock)	Assumptions and data sources
	Starch-based technology:		
Corn dry-milling	NH_3	2.1	Chemical loading specifications taken from [10].
	NaOH	5.2	
	CaO	1.2	
	Enzymes:		
	alpha-amylase	0.8	
	gluco-amylase	1.1	
	Lignocellulosic technologies:		
DA–SSCF	H_2SO_4	26.0	Chemical loading specifications for H_2SO_4, cellulase and DAP taken from [19]; specifications for $Ca(OH)_2$ taken from [20].
	$Ca(OH)_2$	29.0	
	Cellulase	9.2	
	DAP	1.9	
AFEX–SSCF	NH_3	20.0	Chemical loading specifications taken from [21, 22].
	Cellulase	9.6	
	DAP	2.2	
Advanced AFEX–CBP	NH_3	8.1	Chemical loading specifications taken from [23, 24].
	DAP	2.2	

(note: SSCF=simultaneous saccharification and co-fermentation. AFEX=amomonia fiber explosion. CBP= consolidated bioprocessing, diammonium phosphate is abbreviated as DAP) (MacLean and Spatari 2009)

The process chemicals are purchased from industrial producers using traditional feedstocks. Enzyme emissions, however, were calculated in Sheehan et al, 2002, based on NREL reports from (Wooley et al. 1999) and (Aden et al. 2002). Cellulase enzymes were assumed to be purchased from a producer using submerged fermentation technology located at the production site. The cellulose cocktail studied here included endoglucanases, exoglucanases, and B-glucosidases produced by the fungus Trichoderma reesei.

Based on the chemical and enzyme production processes and assumptions, the emissions associated with these materials are shown in

In conclusion, this article found that process chemical and enzyme usages did not contribute significantly to corn based technologies or futuristic n^{th} facilities that do not require large enzyme loadings. The study indicated that only lignocellulosic technologies that do not require high enzyme dosages will be economically profitable, therefore the initial assumption of many studies may be valid depending on the scope of future studies. However, GHG emission from near term technologies for converting cellulose to ethanol are not trivial. They were found to contribute between 30%-40% of the total fossil energy requirements as well as 30%-35% of the GHG emissions. Improved enzyme production processes and overall enzyme conversion efficiency were emphasized as being critical to decreasing the economic and environmental cost of bioethanol.

Table 2-14. The use of process chemicals and enzymes to produce corn-based ethanol resulted in the lowest GHGs emissions. This is due to the easily degraded starches used as feedstocks. Wood, on the other hand, consists of cellulose, which is more recalcitrant than starches and requires more energy and chemicals to break down into fermentable sugars. This study found that GHG emissions due to these process chemicals and enzymes to be less than reported in other studies. This data discrepancy results from different enzyme loading requirements. NRCan (Natural Resources Canada assumed a loading of 41-45 g enzyme/kg feedstock while Spatari and MacLean assumed 9-10 g enzyme/kg feedstock. These vastly different assumptions are due to the type of enzymes each study assumed were available. NRCan used enzymes that are currently available while this study examined the use of enzymes at the n^{th} plant. Enzymes at the n^{th} plant produce a higher biomass to sugar conversion with lower enzyme dosages. As a result of this enzyme productivity assumption, NRCan enzyme GHG emissions for lignocellulosic biomass conversion are around 13 times higher than emissions found within this study.

In conclusion, this article found that process chemical and enzyme usages did not contribute significantly to corn based technologies or futuristic n^{th} facilities that do not require large enzyme loadings. The study indicated that only lignocellulosic technologies that do not require high

enzyme dosages will be economically profitable, therefore the initial assumption of many studies may be valid depending on the scope of future studies. However, GHG emission from near term technologies for converting cellulose to ethanol are not trivial. They were found to contribute between 30%-40% of the total fossil energy requirements as well as 30%-35% of the GHG emissions. Improved enzyme production processes and overall enzyme conversion efficiency were emphasized as being critical to decreasing the economic and environmental cost of bioethanol.

Table 2-14: Comparison of GHG emissions related to enzyme inputs in current and near-term ethanol conversion processes.

Model	Spatari and MacLean				NRCan [4]			EUCAR *et al* [2]	
Feedstock Process	Corn dry-mill	SG AFEX SSCF	SG DA SSCF	SG AFEX CBP	Corn dry-mill	SG DA SSCF	WD DA SSCF	WD NREL SSCF	WS Iogen SSCF
Enzymes	1.1	3.3	3.6	0	1.9	49	49	See footnote	See footnote
Sulfuric acid	0	0.13	0.59	0.0	0.14	2.8	1.4	0.74	0.87
Lime	0.17	0	4.7	0	0	0	2.8	1.5	1.7
Ammonia	0.4	5.4	0	1.5	2.0	4.3	0.52	6.6	2.5
Nutrients	0	0.21	0.22	0.15	0	0.03	0.03	0.58	0.22
Yeast	0	0	0	0	0.05	0.05	0.05	0	0
Sodium hydroxide	0	0	0	0	0	0	0	0	0
Antifoam	0	0	0	0	0	0	0	0.43	0.16
CSL	0	0	0	0	0	0	0	0.03	0.03
Total GHG emissions	1.6	9.3	9.8	1.9	4.1	56	54	9.8	5.5

(MacLean 2009) (Notes: SG = switchgrass; DA = dilute acid pretreatment systems; AFEX = ammonia fiber explosion pretreatment system; SSCF = simultaneous saccharification and co-fermentation; CBP = consolidated bioprocessing. Spatari and MacLean are pathways developed in this study. NRCan uses data from [29]. FPU = international filter paper unit. GWI = global warming intensity; N/A = not available. The lower heating value for ethanol is utilized to convert values from a /MJ basis to a /l basis and then values are rounded.)

2.3.2.2 Thermochemical / Biochemical Comparison

Within this section, the biochemical ethanol production pathway will be compared to the thermochemical production pathway. Foust et al. 2009 performed an economic and environmental comparison of a biochemical and a thermochemical lignocellulosic ethanol conversion process primarily focused on economic and energy requirements. However, environmental impacts of each process are addressed. The two production processes analyzed are summarized in the beginning of the literature review section. Both processes were developed by NREL and are reported in (Phillips 2007) and (Aden et al. 2002), for the thermochemical and biochemical conversion pathways, respectfully.

This study took extensive efforts to apply consistent economic and environmental assumptions to both processes. With these consistent assumptions, true comparisons between the processes can be made illustrating the major economic and environmental differences. Both processes were simulated in Aspen Plus using the same biomass feed rate of 2000 dry metric tonnes per day. However, switch grass was the considered feedstock for the biochemical process while hybrid poplar was the feedstock for the thermochemical process. Both feedstocks are assumed to be optimal for each conversion process.

Based on the given assumptions and processes, an LCI was tabulated for each process. Table 2-15 includes all emissions and wastes from both processes. However, within the report, the emissions description of "Other" was not fully explained. Within this category, significant air emissions occur, although, often in smaller amounts. In most of the categories, both conversion processes yield similar results. Although, the thermochemical process does emit slightly more CO_2 and produce a waste stream sent to offsite treatment. In addition to this, the thermochemical process has a sulfur stream that can be refined to produce a saleable product while the biochemical process produces gypsum that must be disposed as waste.

The inputs of both processes are not identical in all regards. Though both processes were run at the same feedstock flow rate, the biochemical process will require chemicals and enzymes while the thermochemical process only utilizes a catalyst replaced every 5 years and a sand like substance referred to as olivine. As previously reviewed within MacLean and Spatari, these chemical and enzyme usages often have a significant effect on the overall GHG emissions and environmental impacts. These factors were not considered within this study despite their possible significance.

Overall, the direct production emissions from both processes are similar. However, the water usage and chemical usage for the biochemical pathway are far higher than the thermochemical pathway. In addition to this, this study does not fully analyze the impacts of both processes as upstream emissions from process chemicals and feedstocks were not considered. Additional review and further refining of the work presented here could yield a more thorough environmental assessment of both processes.

Table 2-15: Emissions and wastes from different ethanol production pathways (Foust et al. 2009)

Description	Solids		Liquid (N/A)	Vapor	
	Gypsum waste	Boiler ash		Scrubbed fermentation offgas	Flue gas
Biochemical					
Total flowrate (kg/h)	7,347	4,492		24,013	352,975
Component flowrates (kg/h)					
Water	1,261	0		432	68,775
N_2	0	0		0	206,380
O_2	0	0		196	10,278
CO_2	0	0		23,381	65,695
CO	0	0		0	61
CH_4	0	0		0	3
NO_x	0	0		0	61
SO_x	0	0		0	100
Other	452	177		4	1,622
Ash	0	4,287		0	0
Gypsum	5,634	28		0	0

Description	Solids		Liquid	Vapor	
	Sand and ash	Sulfur	Wastewater	Flue gas	CO_2 vent
Thermochemical					
Total flowrate (kg/h)	1,101	49	528	452,822	23,878
Component flowrates (kg/h)					
Water	110	0	528	102,108	0
N_2	0	0	0	240,887	0
O_2	0	0	0	10,978	0
CO_2	0	0	0	80,955	23,878
CO	0	0	0	0	0
CH_4	0	0	0	0	0
NO_x	0	0	0	122	0
SO_x	0	0	0	51	0
Other	<1	49	<1	17,721	<1
Sand and ash	991	0	0	0	0

Life Cycle Assessment of Second Generation Bioethanol Produced From Scandinavian Boreal Forest Resources by (Bright and Stromman 2009), compares the impacts of the biochemical conversion pathway to the thermochemical pathway. This is done on a well-to-wheel basis utilizing an ethanol blend of 85% ethanol to 15% petroleum, E85. The impacts are calculated on a per km driven in a flex fuel vehicle. The study is performed based on resources and standard emission factors within Norway. Four different scenarios were examined, both worst and best case scenarios for both biochemical and thermochemical conversion pathways.

The goal of this study was to examine the global warming mitigation potential of bioethanol produced within one particular region in Norway. Literature findings were utilized for biomass production and impacts within this region. Feedstocks include surplus wood, residuals generated by wood products and processing industries and all logging activities. This feedstock mixture was chosen to avoid the effects of competing with established wood markets and the unpredictable consequences based on economic incentives that eventually impact the environment. Only wood from productive natural forests was used.

The biochemical process is similar to the previously described biochemical conversion pathway with one major exception. This process utilized a system known as simultaneous saccharrification and co-fermentation (SSCF). This process breaks down cellulose to sugar monomers while simultaneously fermenting these sugars as they become available. More information based on this process can be found in (Wooley et al. 1999). The thermochemical process model was similar to the process previously described. More detailed process information can be found in (Phillips 2007).

To avoid process simulation complications, this study assumed the same yields for the Norway feedstock consisting of mostly softwoods. This assumption for the biochemical process is supported by data from (Huang et al. 2009) that determined ethanol yields scaled linearly with increasing holocellulose. Both the Norway feedstock and poplar have similar holocellulose compositions. The same conversion assumption was made for the thermochemical conversions. This assumption was backed by work done (Prins 2005) supporting that yields from thermochemical processes depended primarily on heating value, moisture content, and the ratios of hydrogen, carbon, oxygen, nitrogen, sulfur and ash. These parameters were found to be similar for both the studied biomass and poplar used in the thermochemical model. In addition to process models built in Aspen Plus, SimaPro 7.0 was used to perform an impact analysis and contribution analysis.

Table 2-16 outlines the different scenarios considered within this study. The yields for the biochemical process were based on data from Wooley et al. 1999 that utilized enzymatic hydrolysis efficiencies for near term technologies and n^{th} facility technologies. For the thermochemical model, the process conversion efficiencies were not modified to avoid additional process modifications required to maintain energy self-sufficiency. In addition to varying the processes to examine worst and best case scenarios, the effects transportation distances were analyzed.

The impacts of the thermochemical conversion pathway for both scenarios are presented in Figure 2-6. For logical reasons, the overall impacts increased with greater transportation distances. The impacts due to upstream transportation increased from 23% to 31.5% resulting from a 34% increase in primary forest residuals transportation distance. The acidification and eutrophication potentials categories experienced the largest percentage increase, though the absolute change was small. The global warming index experienced the largest absolute change. It was also found that wood chip storage contributed from 33%-39% of the total well to tank GHG emissions, the largest contribution of all unit processes.

Table 2-16: Well to tank system parameters (Bright and Stromman 2009)

Characteristic	*Best case biochemical*	*Best case thermochemical*	*Worst case biochemical*	*Worst case thermochemical*
Notation	BCBCh	BCTCh	WCBCh	WCTCh
Conversion process	SSCF "best of industry"	Allotherm. gas.-mixed alc. syn.	SSCF base case	allotherm. gas.-mixed alc. syn.
Yield (liters/tonne feed)	261	276	235	276
Conversion efficiency (%)	43	46	38	46
F, PR biomass transport	120 km	120 km	170 km	170 km
SR biomass transport	2 km	2 km	50 km	50 km

(note: Biomass-to-ethanol thermal conversion efficiency is based on a lower heating value (LHV) of 21.5 megajoules per kilogram dry matter (MJ/kg DM) biomass. Allotherm. gas.-mixed alc. syn. = allothermal gasification of wood chips into synthesis gas followed by catalytic synthesis into ethanol and other higher weight mixed alcohols; SSCF = simultaneous saccharification and cofermentation; F = surplus forest growth; PR = primary forestry residual; SR = secondary industry residual.)

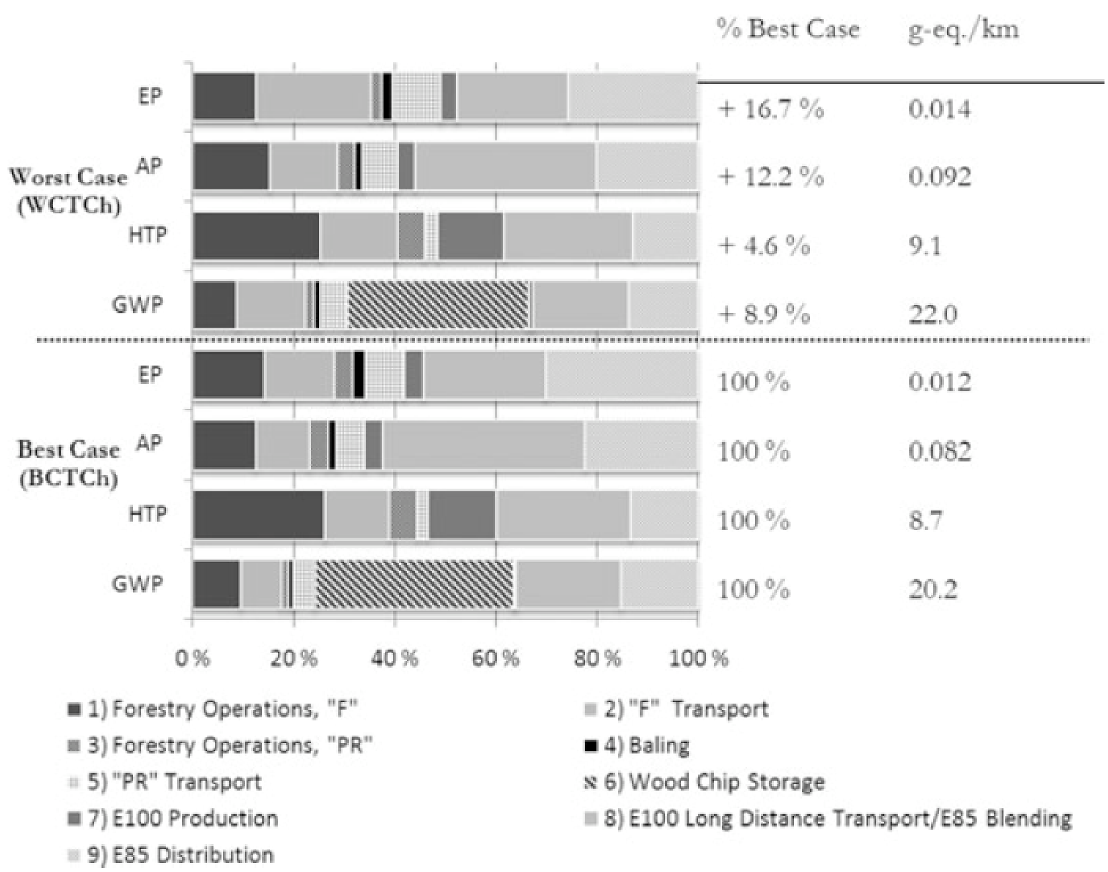

Figure 2-6: Well-to-tank (WTT) thermochemical ethanol conversion impacts (Bright and Stromman 2009). (Note: impacts based on the emissions required to operate a flex-fuel vehicle (FFV) over a distance of 1 km. Processes contributing less than 1% were not considered. WCTCH= worst case thermochemical; BCTCH= best case thermochemical; EP= eutrophicatoin potential; AP= acidification potential; HTP= human toxicity potential; GWP= global warming potential; F=surplus forest growth; PR= primary forestry residuals)

The impacts of the biochemical conversion process are listed in Figure 2-7. These impacts are shown for each unit process for all scenarios. Unlike the thermochemical process, it was found that the biochemical process contributed significantly to the global warming impact relative to the other processes. This results from natural gas based ammonia usage. Another contributing factor is the methane released from the waste treatment plant. It was also found that the variations feedstock transportation distances impacted overall emissions by 17% in the best case and 27% in the worst-case scenario. These findings support that feedstock transportation not only contributes significantly to the overall emissions, but also is effected greatly by transportation distances. Of the 39% total emissions increase for the worst-case scenario, 10% was attributed to biomass transportation and the remaining 29% was attributed to decreased conversion efficiencies. This 29% emissions increase created by an 11% decrease in yield illustrates the large impact and importance of process conversion yields.

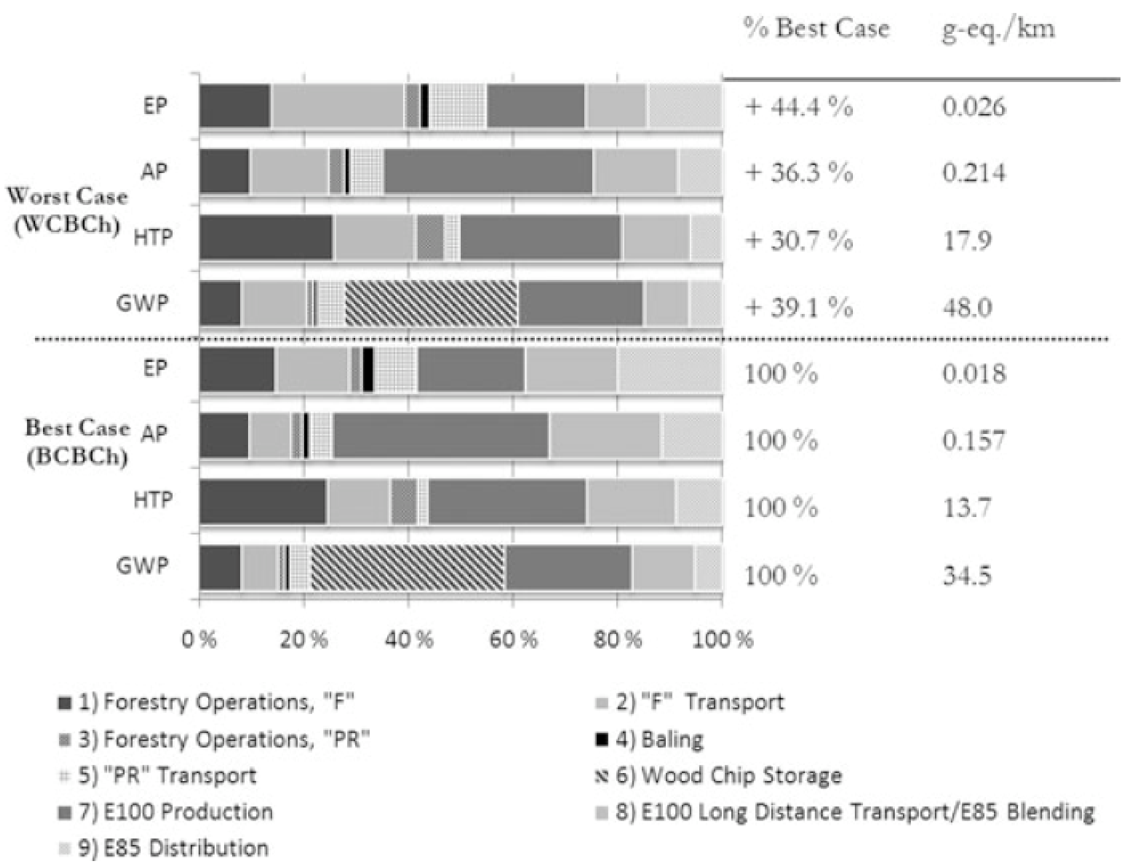

Figure 2-7: Well-to-tank (WTT) relative and absolute impacts, biochemical cases. Note: Impact scores are scaled to the operation of a flex-fuel vehicle (FFV) over a distance of 1 km. Only processes contributing at least 1% to any impact category are presented. WCBCh = worst-case biochemical; BCBCh = best case biochemical; EP = eutrophication potential; AP = acidification potential; HTP = human toxicity potential; GWP = global warming potential; F = surplus forest growth; PR = primary forestry residuals. (Bright and Stromman 2009)

When compared to gasoline on a well to wheel basis, Figure 2-8, ethanol produced by these methods was found to reduce GHG emissions by 44% to 62% per km driven. The majority of these savings resulted from tail pipe emissions reductions. Biogenic carbon emissions, emissions due to combustion of plant materials, are not generally accounted for in the overall GHG total.

This accounting practice is based on the logic that biogenic carbon was once sequestered from the atmosphere. With this logic, the net atmospheric carbon change is null.

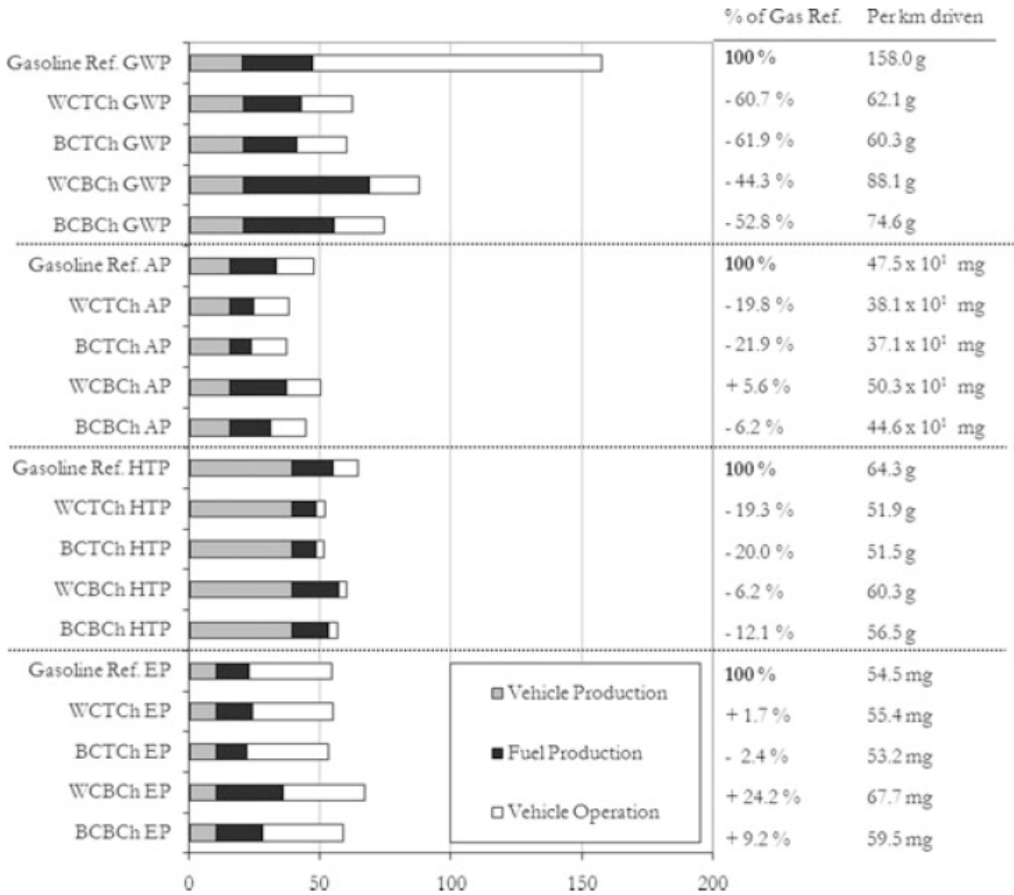

Figure 2-8: Well-to-wheel (WTW) absolute impacts compared to fossil fuel reference, all cases. Gas Ref. =gasoline reference; GWP = global warming potential; WCTCh = worst case thermochemical; BCTCh =best case thermochemical; WCBCh = worst case biochemical; BCBCh = best case biochemical; AP =acidification potential; HTP = human toxicity potential; EP = eutrophication potential. (Bright and Stromman 2009)

The process conversion pathway also had an effect on the overall emissions. The biochemical pathway had higher emissions in both acidification and eutrophication potential categories. These higher impact levels are due to the high ammonia usage and methane emissions from the effluent processing of the biochemical process.

In addition to studying the impacts of the fuels, this study analyzed the impacts of vehicle production and maintenance. This analysis found that 75% of the human toxicity potential resulted from vehicle production. Steel and copper material used in vehicle contributed 38% and 56% respectfully, to the HTP.

In conclusion, the conversion has a significant effect on the overall environmental impacts. The emissions due to these conversion pathways are particularly sensitive to process yields. Additionally, chip storage was found to be the largest emissions contributor within a well-to-tank scope. When comparing ethanol produced through these processes to petroleum, a GHG emissions savings of 51%-71% were found. Based on these findings, ethanol use as a transportation fuel could reduce GHG emissions and decrease the overall impacts of vehicular transportation.

2.3.2.3 Biorefinery

LCA of a biorefinery concept producing bioethanol, bioenergy and chemicals from switchgrass by Cherubini and Jungmeier (Cherubini and Jungmeier 2010) examines the life cycle impacts of a hybrid conversion pathway often referred to as the biorefinery concept. This process has the economic benefits of multiple products from a common feedstock. This product spread allows for optimal usage of the incoming carbon while decreasing the economic dependence on the markets of any one product. Not only are the multiple products potentially beneficial to the economics, the environmental burden for each product can be decreased due to burden allocated to multiple products.

The biorefinery process was not previously discussed but will be reviewed here. Petroleum based refineries produce many products ranging from asphalt to gasoline utilizing nearly all possible carbon within the incoming feedstock. The biorefinery, utilizing biomass feedstocks, can produce a wide range of products including, heat, bioethanol, electricity, phenols, lignin, hemicelluloses and other chemicals. Through producing multiple products, the production process can be optimized to reflect current product markets resulting in increased revenue. Within the refining process, there are many different unit processes, Figure 2-9. The petroleum and biomass based refining systems have many similarities and products. Both systems convert a carbon feedstock source of lesser utility to several more useful carbon based materials or energy derived from these carbon sources.

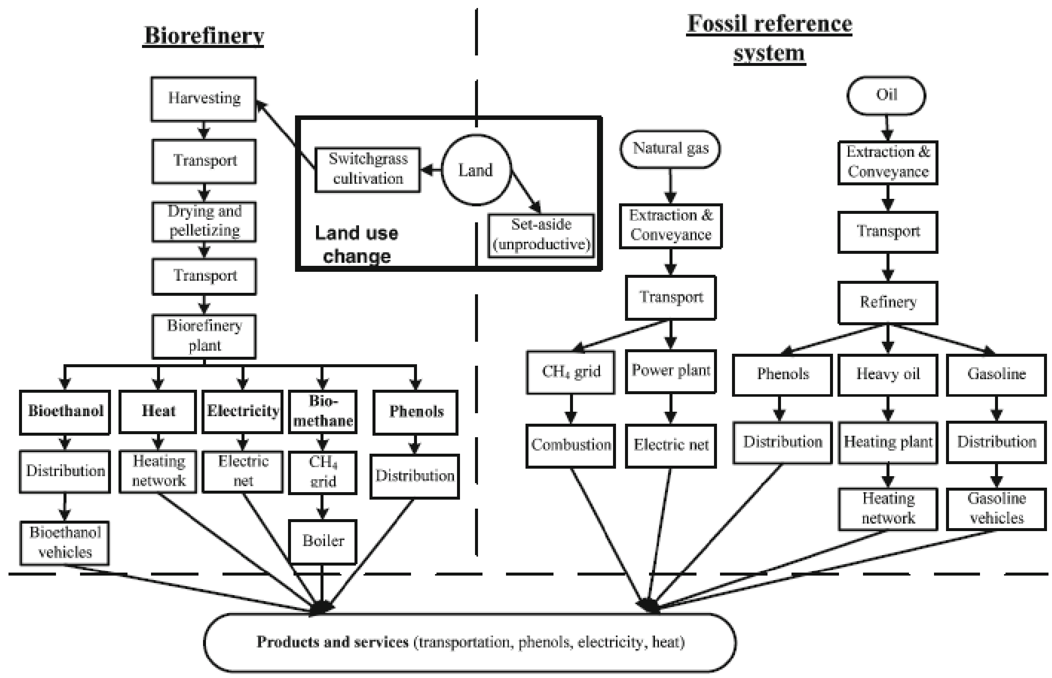

Figure 2-9: Production chain for biorefinery and fossil fuel refinery (Cherubini and Jungmeier 2010)

The incoming switchgrass is converted through the following major unit processes extracted from (Cherubini and Jungmeier 2010).

- Pretreatment (uncatalyzed steam explosion) of the raw material in order to depolymerize hemicellulose and separate lignin ((Sun and Cheng 2002); (Lynd 1996));
- Enzymatic cellulose hydrolysis to glucose monomers (Palmqvist and Hahn-Hägerdal 2000; Hamelinck et al. 2005);
- Fermentation and distillation of sugars to bioethanol (Hamelinck et al. 2005);
- Anaerobic digestion of wastewaters (Berglund and Börjesson 2006; Romano and Zhang 2008);
- Flash pyrolysis of lignin (20%) followed by phenol separation from the resulting pyrolytic oil (Zhang et al. 2007; Meister 2002);
- Final combustion (for heat and power production) of process residues, fraction of lignin that is not pyrolyzed (80%), pyrolytic char, and the remaining pyrolytic oil after phenol extraction (Senneca 2007; Gani and Naruse 2007).

A simplified process flow diagram illustrates the above unit processes and products produced, Figure 2-10. This biorefinery process is one of many emerging biomass conversion technologies. Some systems include a combination of biomass gasification and biochemical conversions technologies. These hybrid conversion technologies often boast high carbon conversions and more flexibility for varying feedstocks.

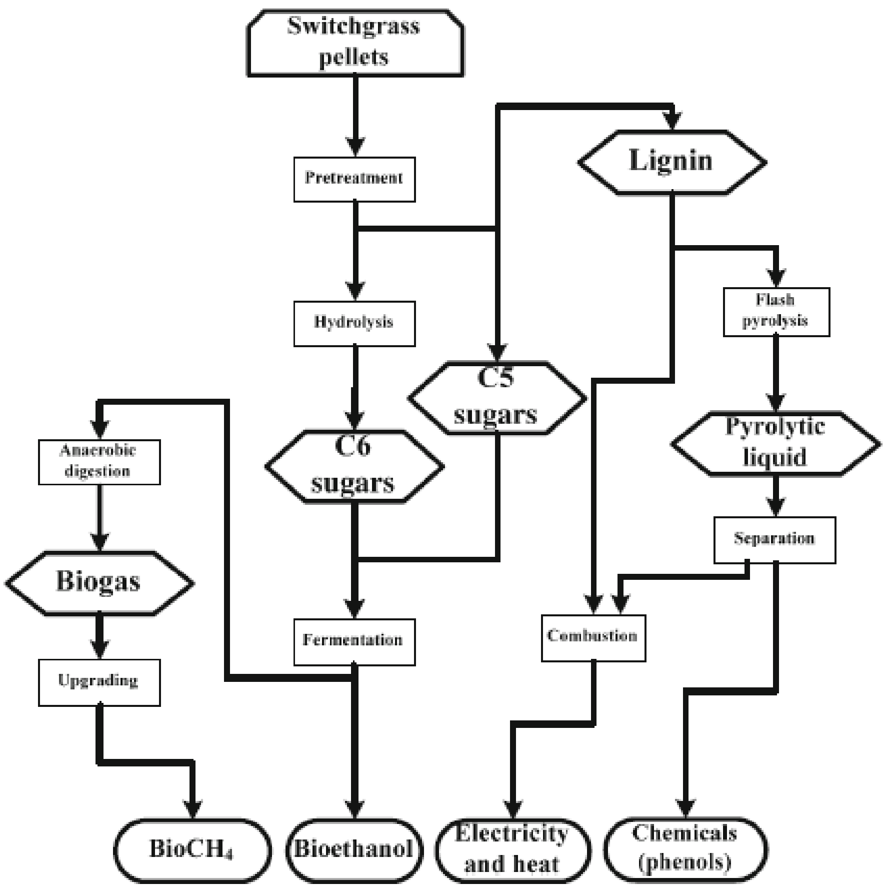

Figure 2-10: Simplified process flow diagram of a biorefinery (Cherubini and Jungmeier 2010)

Before moving into the details of this study, the goal and scope should first be addressed. This study focused on analyzing the potential to reduce GHG emissions and the ability of the process to produce domestic energy. These two factors are of primary interest as global climate change and energy independence are the two largest driving forces for the development of the biofuels industry (Cherubini and Jungmeier 2010). In addition to these two parameters, an impact assessment was performed using SimaPro 7 to quantify the entire environmental effects of biorefinery products. The biorefinery process and corresponding products were compared to similar products produced from petroleum based refineries. These petroleum based products include: gasoline, heat from natural gas (instead of biomethane), conventional phenols from oil refining, electricity from natural gas, and heat from heavy oil.

The system boundaries of the biomass-based refinery include all input and output flows occurring within the production chain. Processes that are included in the production chain are shown in Figure 2-9 and include: planting and harvesting crops, processing feedstocks into biofuel, feedstock transportation and storage, distribution and final use of biofuels and any upstream emissions that occur as a result of these processes. The fossil fuel system boundaries start with fossil fuel extraction and include conveyance of raw materials, raw fossil fuel production, refining, storage, distribution, and combustion.

The important issue of land use change emissions and accounting was taken into consideration within this study. The fossil fuel system, however, does not account for any land use change or land based emissions due to drilling and other disturbances that may occur during oil production activities. Land use change can be categorized in two ways: direct and indirect. Direct land use emissions result from conversion of land used for other proposes to land used for biomass production. Indirect land use change accounts for the emissions that occur due other parties actions that resulted from actions done by the reference system (Wakeley et al. 2009). Only direct land use change emissions were analyzed within this study.

Switchgrass was the chosen feedstock for this study for several reasons. Low nutrient demand, high energy yields, and diverse geographical growing range make switchgrass a favorable energy crop (Sokhansanj et al. 2009). Within the carbon cycle of the entire process, biomass production had a large impact. By planting switchgrass on “set aside land” the soil carbon and overall soil quality can be increased (Downing M 1995, Mitchell et al. 2008). Additionally, some studies supported that surface soil CO_2 emissions did not increase due to nitrogen fertilizers (Mulkey et al. 2006).

Several soil treatments including liming and fertilizing must occur in the production of switchgrass. Once the switchgrass is grown and harvested at a moisture content of 20%, it is further processed into dried pellets. The required materials and energy to produce the switchgrass pellets as well as emissions from land are shown in Table 2-17. Each chemical input is accounted for within this table. This inventory was used to calculate the emissions due to upstream chemical production. The emissions from soil within this section are worth a considerable amount of attention.

There has been much controversy over the amounts of N_2O emitted as a result of nitrogen fertilizers. N_2O is an especially potent GHG with the equivalent impact of more than 300 times that of CO_2. Within this study, the N_2O emission rate calculated by the International Panel for Climate Change (IPCC) is used. Methane oxidation rates within the soil are also affected by land conversion. This change in soil functionality is accounted for within the life cycle inventory. Below are the default emission factors from the IPPC 2006.

- Direct soil emissions of N as N2O, at 1% of synthetic N application (mean value);
- Volatilization of N as NH3, at a rate of 10% of total N of synthetic N application. One percent of N in NH3is then converted to N2O;Table 2-17.
- Leaching to groundwater as nitrate (30% of total N applied); 0.75% of it is converted to N2O;

Table 2-17: Chemicals and energy requirements and emissions of switchgrass pellet production (Cherubini and Jungmeier 2010)

Flow	Unit/yr	Value	Source
Cultivation			
Seed	kg/ha	15	Bullard and Metcalfe 2001
Fertilizers			
N	kg/ha	112	Smeets et al. 2009
P	kg/ha	17	Smeets et al. 2009
K	kg/ha	54	Smeets et al. 2009
Lime	kg/ha	150	Bullard and Metcalfe 2001
Herbicides	kg/ha	2.5	Smeets et al. 2009
Emissions from land			
N_2O	g/gN	0.042	IPCC factor
CH_4	g/kgN	10	Delucchi and Lipman 2003
Processing and transport			
Drying	MJ/t_{water}	2.26	Smeets et al. 2009
Pelletizing	MJ_e/MJ	0.015	Gemis 2009
Transport	Mt*km	57.2	Assumption

The first and one of the largest GHG impacts of this process come from soil carbon content. For the first 20 years, the switchgrass production increases carbon stores within the soil, Figure 2-11 This increased carbon content offsets much latter emissions due to biomass conversion and combustion. GHG emissions from the entire process are shown within Table 2-18 on a 1-20 year basis and an after 20 year basis compared to a fossil fuel reference. The GHG emissions after 20 years do not account for carbon soil sequestration. As a result of this, GHG savings drop from 79% to 55%. This 24% GHG savings decrease illustrates the large impact of soil carbon sequestration.

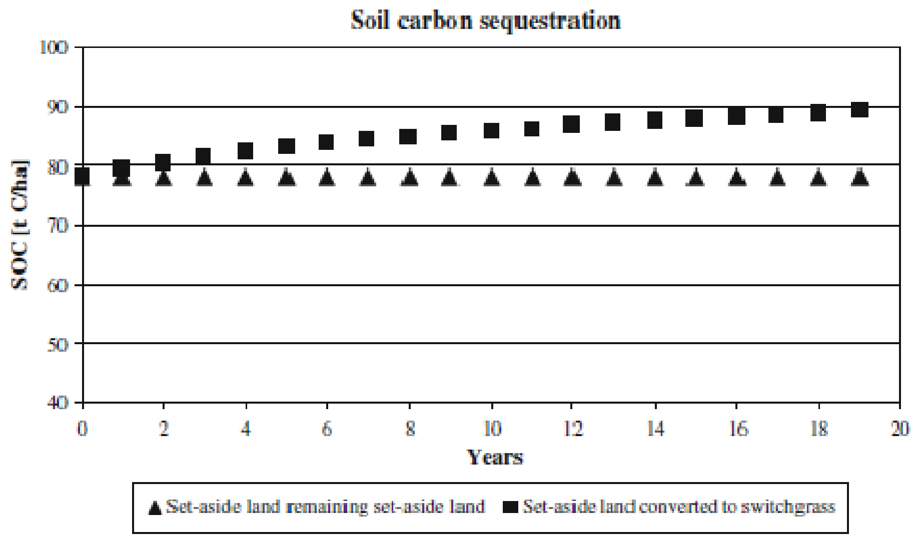

Figure 2-11: Soil carbon levels for converted and non converted land (Cherubini and Jungmeier 2010)

Table 2-18: GHG emissions, biorefinery scenarios compared to fossil fuel reference (Cherubini and Jungmeier 2010)

	Unit/a	Biorefinery 1–20year	Biorefinery >20years	Fossil reference system
GHG emissions				
Total	kt CO_2-eq	60.5	126	281
CO_2	kt CO_2-eq	−8.6	58.2	266
N_2O	kt CO_2-eq	64.2	64.2	6.56
CH_4	kt CO_2-eq	4.86	4.86	8.91
GHG savings				
per year	kt CO_2-eq.	221	155	–
per year	%	79%	55%	–
per t_{dry} feedstock	t CO_2-eq./t_{dry}	0.46	0.33	–
per hectare	t CO_2-eq./ha	7.41	5.21	–

Impacts by categories are listed in Table 2-19 for both the fossil fuel reference and the biorefinery. However, in Figure 2-12 the process impacts are normalized to 100% to better illustrate the overall differences between the processes. The biorefinery produced fewer impacts in all categories except acidification and eutrophication. Nitrogen fertilizers and resulting NH_3 production within the soil are the main contributors to both these impact categories. The biorefinery produced lower impacts in most categories; Figure 2-12 displays the relative difference of each impact category. The relative difference is largest for eutrophication with 90% higher impact than the gasoline reference system due mostly to nitrogen fertilization. The global warming index for the biorefinery is only slightly more than 20% of the global warming index for the fossil fuel reference. The contributing pollutants for the global warming index can be seen in Figure 2-13. The emissions from N_2O dominate for the biomass refinery scenario while CO_2 is the main pollutant for the fossil fuel reference system.

Table 2-19: Impact assessment using CML method for years 0-20 (Cherubini and Jungmeier 2010)

Impact category	Unit/a	Biorefinery	Fossil reference system
Abiotic depletion	kt Sb eq	0.42	1.94
Global warming (GWP100)	kt CO_2 eq	60.5	281
Ozone layer depletion (ODP)	kg CFC-11 eq	10.5	31.2
Human toxicity	kt 1,4-DB eq	34.2	187
Fresh water aquatic ecotox.	kt 1,4-DB eq	4.08	16.8
Marine aquatic ecotoxicity	Mt 1,4-DB eq	22.8	50.1
Terrestrial ecotoxicity	kt 1,4-DB eq	0.35	0.62
Photochemical oxidation	kt C_2H_4	0.06	0.28
Acidification	kt SO_2 eq	1.23	1.17
Eutrophication	kt PO_4-eq	2.82	0.17

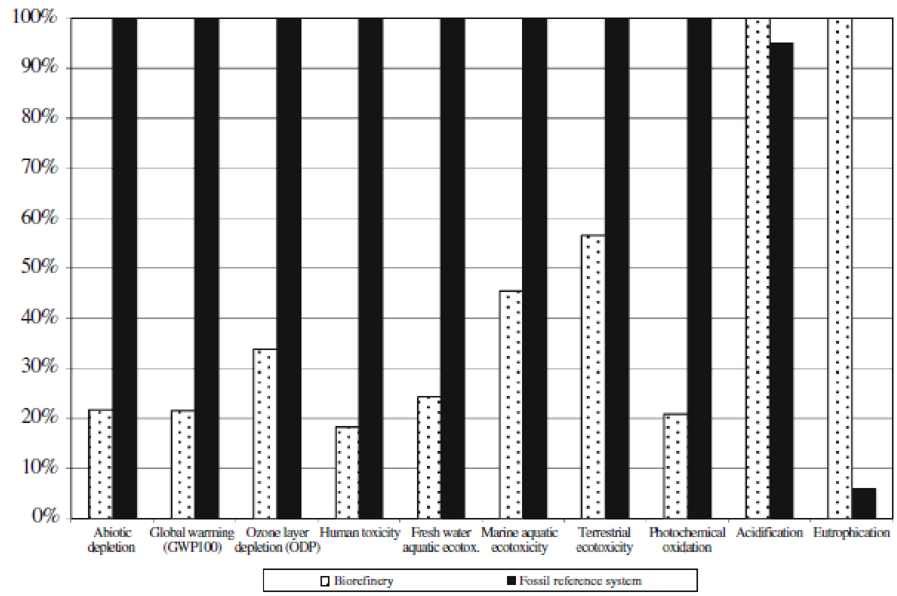

Figure 2-12: Impact assessment comparison using CML method (Cherubini and Jungmeier 2010)

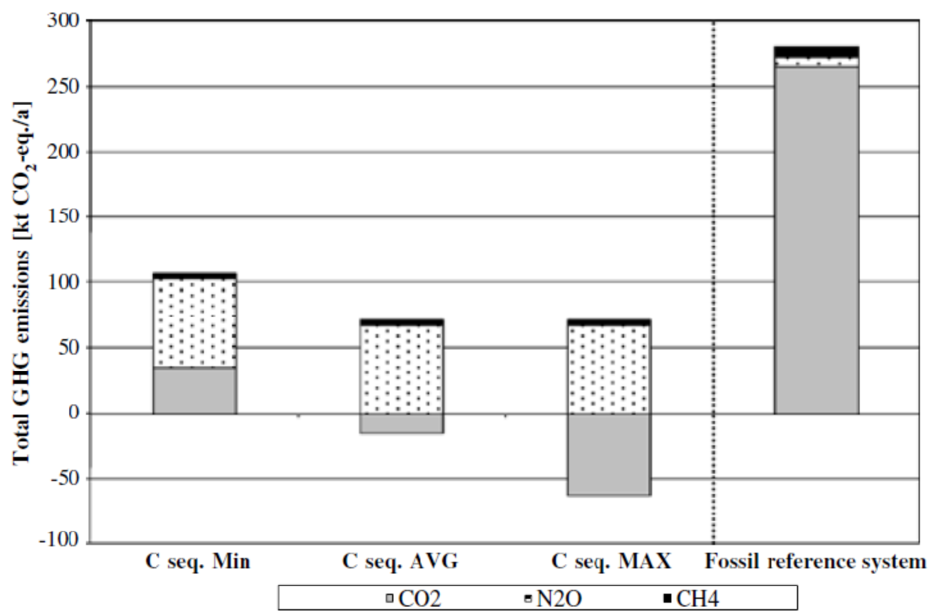

Figure 2-13: GHG emissions by component: CO2, N20, and CH4 (Cherubini and Jungmeier 2010)

Due to the large impact of N_2O emissions and the predicted nature of the N_2O emissions factors, a sensitivity analysis was done to demonstrate the effects of varying emission factor assumptions,

Figure 2-14. The use of the emission factors from the IPCC resulted in the lowest overall N_2O emissions while emission factors from a study by Crutzen et al. 2007 indicated resulted in significantly higher N_2O emissions and overall GHG emissions. Based on these emissions factors, Crutzen et al. supported that the use of biofuels was not an effective means of mitigating global warming. However, other studies assert that the methods used by (Crutzen, Mosier et al. 2008) to calculate these factors were based on uncertain approach and questionable (North Energy 2008; RFA 2008). Additionally, the conclusions of Crutzen et al. 2007 were based on "inappropriate and selective comparisons" (Cherubini, Jungmeirer 2010). The emissions factors below were extracted from Cherubini and Jungmeier 2010:

- 1.325%, as derived from IPCC guidelines (an assumed in this analysis); i.e., 0.042 g N2O/g N.
- 3%, lowest limit in Crutzen et al. (2007); 0.094 g N2O/g N.
- 4%, average value in Crutzen et al. (2007); 0.13 g N2O/g N.
- 5%, maximum limit in Crutzen et al. (2007); 0.16 g N2O/g N.

In addition to N_2O emissions, the overall GHG balance is highly sensitive to the soil carbon sequestration. For this study, a literature review was done surveying the carbon sequestration rate for converting grassland. Based on this literature survey, this study used an average value of 0.6 t*C / (ha*a). A sensitivity analysis was performed using the upper and lower boundaries carbon sequestration rates of 0.2 t C / (ha*a) and 1.1 t C / (ha*a). The effects of these sequestration rates can be seen in Figure 2-15.

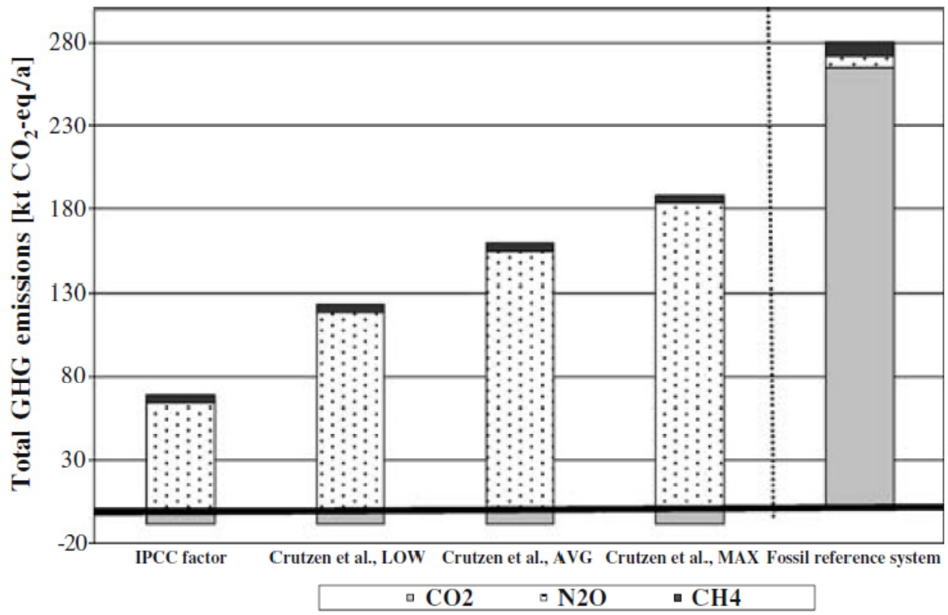

Figure 2-14: The effects of different N2O emission factors (Cherubini and Jungmeier 2010)

The soil carbon sequestration has a large impact on the overall GHG emissions. When the maximum sequestration rate is considered, the process approaches carbon neutrality. This sensitivity analysis illustrates the large impacts that both $N_2 0$ and carbon sequestration rates have on the overall GHG emissions.

In conclusion, based on these findings, alternative fuels and bio-based chemicals produced from a biorefinery can help mitigate global warming. The extent to which GHG and environmental impacts can be reduced depends highly on N_2O emission factors and soil carbon sequestration factors. When sensitivities around these two factors were examined, GHG emissions were lower than the fossil fuel references in all scenarios. Despite the possible GHG reduction, other impact categories increased. Both eutrophication and acidification impacts were significantly higher for the biomass based biorefinery. Nitrogen based fertilizers are the main contributors to these two impact categories.

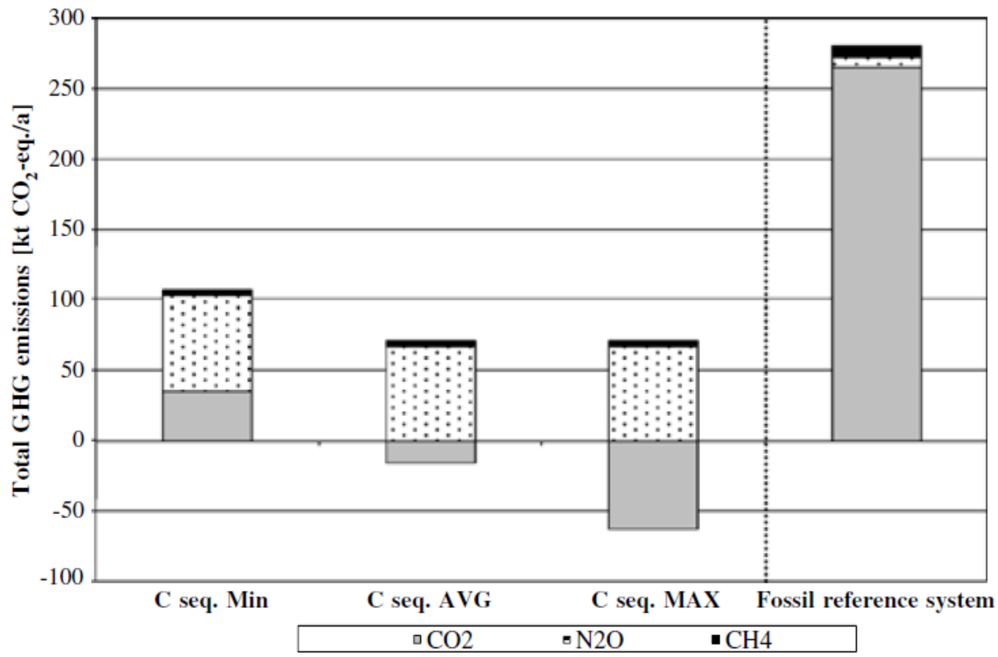

Figure 2-15: Sensitivity analysis of soil carbon sequestration on GHG emissions (Cherubini and Jungmeier 2010)

2.3.2.4 Ethanol LCA Literature Summary

From reviewed literature and literature considered but not reviewed here, the following conclusions can be made. Cellulosic biofuels have a high potential to reduce GHG emission potentially slowing global climate change. However, most studies support that other impact categories may be higher for biofuels when compared to a fossil fuel reference. These impact categories include eutrophication and acidification. The primary contributors to these impacts result from feedstock production and fertilization.

Within each study, several process parameters had the largest influence. The environmental impacts were highly sensitive to both process conversion yields and feedstock productivity. Both these factors are a measure of efficiency for land and carbon usage. Additionally, the overall impacts were highly sensitive to soil carbon sequestration rates. However, after a certain period of time, the soil reaches a steady state carbon concentration. As a result of this time based parameter, it is important to analyze the effects of time within an LCA. N_2O emissions also played a large role within the overall environmental impact. These emissions result from fertilization and are more than 300 times more potent as a GHG than CO_2.

Another major factor affecting the overall GHG balance was the process energy source. In many cases, biomass based energy was used while in scenarios where biomass was unable to supply all energy requirements electricity was purchased. Fossil fuel based electricity usage decreases environmental benefits.

2.3.2.5 Knowledge Gaps

Within the previous review of bioethanol LCA studies, many of the major concepts and techniques were presented. These articles were selected based on the quality and topic areas. These topic areas included: feedstock comparisons, process chemical contributions, conversion pathway comparisons, and biofuel to gasoline comparisons. By reviewing these higher quality articles, an understanding of techniques and current knowledge can be attained. Other articles were considered within the scope of this study but were not reviewed. It was thought that by presenting the techniques and findings of the high quality studies, a clear presentation of the knowledge base would be achieved. Additionally, these reviewed articles often provided useful literature reviews as well as identified knowledge gaps.

Varying boundary conditions, assumptions, functional units, and emissions factors are presented within the reviewed articles. Some of these variations result from questionable or unsubstantiated data. By further studying these underdeveloped topic areas, future analyses may produce more consistent results. Based on the reviewed articles, the following topics within the feedstock production process deserve further review and development:

- Soil carbon sequestration for bioenergy feedstocks
- N_2O emission factors due to fertilizer usage
- The impacts of high efficiency and proprietary fertilizers
- Ecological effects of bioenergy feedstock production
- Land use efficiency

As perspective conversion technologies are created, they will need to be analyzed from an LCA standpoint. Within these process analyses, several assumptions affect the process performance the most but are often inconsistent or based on questionable data. These inconsistent assumptions include:

- Enzyme conversion efficiency
- Facility assumptions, n^{th} facility vs. near term facility
- Biomass storage emissions
- Process energy source
- Process chemical usages and impacts
- Product allocation
- Process conversion yields

The area of bioethanol produced from cellulosic biomass are far more developed and analyzed from a technical and economic standpoint. Within the current LCA literature base, different biomass sources have been analyzed but to a lesser degree than the technical and economic analyses around these different feedstocks. Different feedstocks impact the overall LCA in several ways. Large impacts can result from feedstock production that is unique to the feedstock source and often growing location. In addition to this, feedstock composition often affects process material and energy balances. In order to understand the full effects of these feedstocks on conversion technologies, simulations or pilot scale studies should be performed.

Transportation emissions for different feedstocks were moderately covered within the literature. However, more analysis may be needed to determine the impacts of transporting different feedstocks. Additionally, environmental impact optimization based on production rate and transportation distances should be considered for future studies. As genetically modified feedstocks are further developed, more analysis will be required to understand the impacts on the overall LCA of the process.

As presented within the previous review, conversion pathways have a significant effect on the overall environmental impacts. LCA studies often cover the several mainstream conversion technologies, such as processes outlined by NREL, but do not consider other process conversion technologies that have promising futures. This lack of analysis may come from the proprietary nature of many novel conversions technologies. As these technologies are released as patents or through publications, more LCA studies will be needed to assess the impacts of these new processes.

2.3.3 Bioenergy

Bioenergy conversion technologies will be reviewed within this section. The two most common conversion technologies are combustion and biomass gasification. Once the technical aspects of the gasification process are presented, a review of LCA studies will follow. The studies covered in detail perform comprehensive review and analysis of many aspects of bioenergy. By reviewing these high quality studies, an overview of bioenergy LCA will be presented. Other articles that are not thoroughly reviewed here are included within LCA database.

2.3.3.1 Biomass Gasification and Combined Cycle Systems

The biomass gasification and combined cycle process is similar to the bioethanol gasification pathway in many ways. However, the later aspects of the ethanol pathway are not needed for energy production. The major unit processes include feed preparation, gasification, char combustion, syngas cleaning, gas turbines and cooling towers/condensing. This processes description is based on (Mann and Spath 1997) and is reviewed in further detail below. The major unit processes are seen in Figure 2-16.

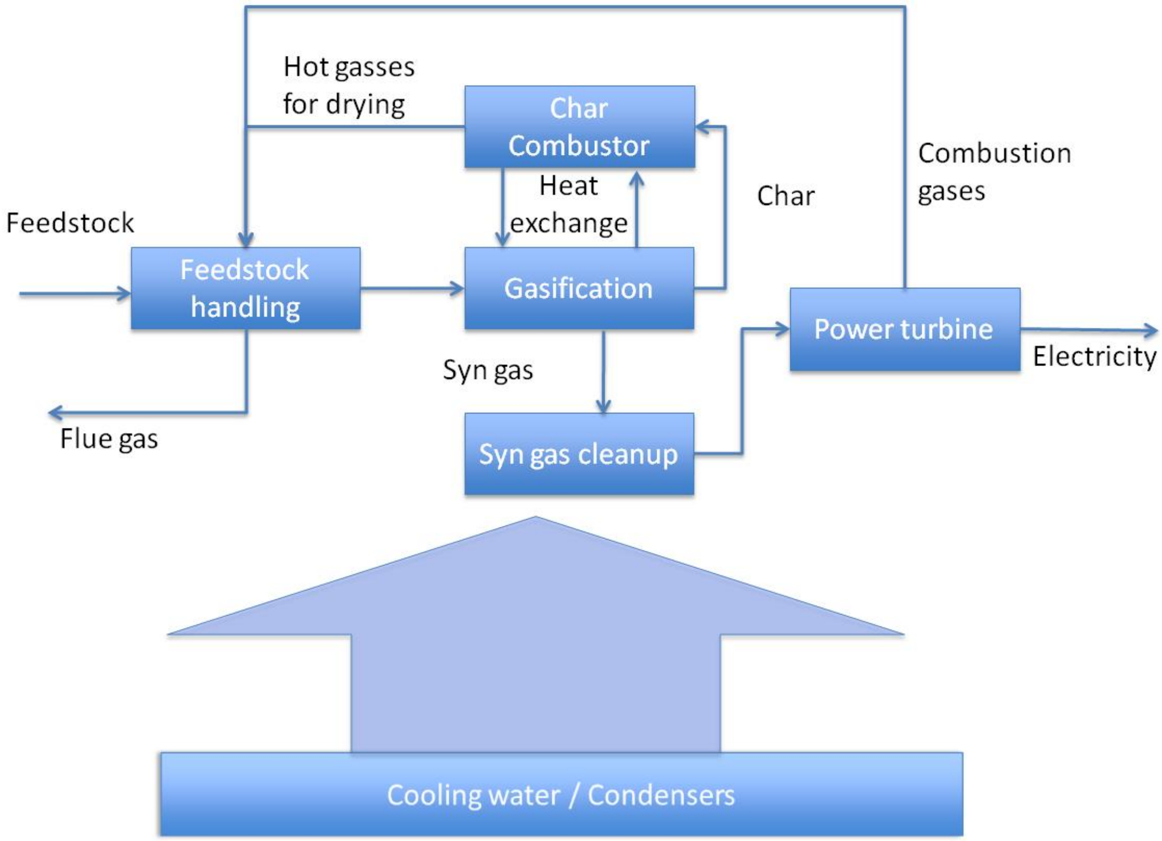

Figure 2-16: Electricity production via gasification: Process flow (Mann and Spath 1997).

Feed Preparation

In the feed preparation section, either round wood or chips are processed. If round wood is the primary feedstock, it is chipped. Chip sizes vary but pass through a two inch screen. This chipping energy is negatively correlated with chip size. This energy usage is substantial as chipping motors are often 1,000 HP or more Watson et al. 1986.

Wet chips are then dried to a moisture content ranging from 10-20%. This is generally done using flue gasses from the char combustor. These flue gasses enter the drying system at temperatures around 200 °C to avoid dryer fires. In some cases, a slipstream of dryer gas is recycled back to the char combustor to reduce VOC emissions. The remaining flue gas is filtered to remove particulate and then released to the atmosphere.

Gasification

The dried biomass is converted to syngas within the gasification section. This is done through a partial oxidation under an oxygen deprived high temperature environment. Steam, oxygen, and ambient air, depending on gasifier design, can be injected along with the biomass. However, steam and oxygen blown gasifiers produce cleaner syngas streams due to lower incoming impurities that are in ambient air.

The operating parameters will vary depending on the gasifier design. Generally, gasifers operate at temperatures around 800-900 °C at varying pressures. Using the indirect heating design, heat is transferred from the char combustor using a sand like substance olivine. This olivine is circulated from the char combustor to the gasifier then back to the char combustor with a small purge stream to prevent ash buildup. The products of the gasifier include H_2, CO, CO_2, CH_4, C_2H_2, C_2H_4, C_2H_6, tars, H_2S and NH_3. However, in many cases, over 90% of the product gasses consist of H_2, CO, CO_2 and CH_4.

Char Combustor

A char combustor provides heat required for the highly endothermic reactions in the gasification process. Char from the gasifier is the primary fuel for char combustor. The combustion process creates heat and ash. Cyclone filters separate the ash and olivine from the exiting flue gas. The resulting flue gas stream is circulated to back to the feed preparation section to dry the incoming biomass.

Syngas Cleanup

Within this section, impurities in the syngas are removed. These elements, originating from either the blown air or from the sulfur within the wood, include particulate and sulfur compounds. Scrubbers are used to clean the gasses before they are sent to the gas turbine.

Power turbine

This unit process takes the intermediate product of syngas and converts it to mechanical energy and electricity. Up until this point, the gasification for ethanol production is very similar to gasification for energy. Within the energy process, syngas is burned instead of reacted to form alcohols. Compressed air and syngas are combusted in the turbine at temperatures of around 370 °C. The mechanical energy created in this combustion is then transformed into electrical energy via generators.

Cooling and condensers

Process and low quality steam must be cooled and condensed before reuse. This is done through condensers and cooling towers. The cooling towers use latent heat of water to cool the closed water/steam system.

2.3.3.2 Bioenergy LCA Review

Life Cycle assessment of a Biomass Gasification Combined-Cycle Power System, by man and Spath 1997, evaluates the LCA impacts as well as economic feasibility of the Battelle/FERCO gasifier and combined cycle power generation system. The study was performed on a cradle-to-grave basis. Much emphasis was placed on the inventory analysis while the impact assessment was done in a fairly rudimentary way, as many of the current impact methods had not been developed at the time of publication. However, this study did take a unique inventory approach estimating the emissions for each year, from beginning of constructing to decommissioning. This detailed analysis gives some insight that many other studies do not.

The goal of this study was to analyze the CO2 emissions and energy usages as well as identify what environmental effects may become important if the technology was brought into a mature state. In addition to this, the LCA was used to environmentally optimize the process. An economic analysis was performed to quantify the process changes in terms of profitability.

The process used within this study is very similar to the previously described process. The feedstock fed to the system was hybrid poplar, the same as the previous ethanol production via gasification (Phillips 2007), (Foust et al. 2009). Table 2-20 lists the operation parameters used by the simulation.

Table 2-20: Operating Parameters for gasification electricity production (Mann and Spath 1997)

Gasifier temperature	826 °C (1519 °F)
Gasifier pressure	0.17 MPa (25 psia)
Dried wood feed to gasifier (11% moisture, 100% capacity)	1,498 Mg/day (1,651 t/day)
Dried wood moisture content	11%
Gasifier internal diameter	2.93 m (9.6 ft)
Steam / wood ratio (wt/wt, MAF)	0.45
Sand / wood ratio into gasifier (wt/wt)	19.5

From this process, twenty air, twenty-five water and seven solid emissions were tracked. In addition to this, seventeen natural resources and six types of energy were tracked and quantified. However, the most emphasis was put on the CO_2 emissions within this study.

Of all the air emissions, CO_2 made up more than 66% of the total emissions, Table 2-22. Isoprene a rubber like compound found in plants, was the second largest compound released. Despite the lower amount of NO_x emitted, 1% of total, it is still a very significant emission as NO_x is more than 300 times more potent than CO_2 as a green house gas according to the IPPC. VOCs and sulfur also contribute significantly to the overall air emissions from this process.

Table 2-21: Average air emissions per kWh of net electricity produced (Mann and Spath 1997)

	% of Total in this Table	% of Total in this Table Except CO2	% of Total in this Table Except CO2 and Isoprene	Total (g/kWh)	% of Total from Feedstock	% of Total from Transportation	% of Total from Power Plant
(a) Aldehydes	0.0%	0.0%	0.0%	1.68E-04	78.7%	17.9%	3.4%
(a) Ammonia (NH3)	0.1%	0.2%	2.0%	3.52E-02	99.9%	0.0%	0.0%
(a) Carbon Dioxide (CO2)	66.7%	0.0%	0.0%	4.59E+01	61.8%	12.0%	26.2%
(a) Carbon Monoxide (CO)	0.1%	0.4%	4.7%	8.30E-02	80.9%	13.0%	6.2%
(a) Chlorides (Cl-)	0.0%	0.0%	0.0%	6.60E-07	13.9%	2.0%	84.1%
(a) Fluorides (F-)	0.0%	0.0%	0.0%	8.08E-06	97.2%	0.3%	2.6%
(a) Non-methane hydrocarbons (including VOCs)	0.9%	2.6%	33.8%	5.95E-01	11.0%	1.3%	87.7%
(a) Hydrogen Chloride (HCl)	0.0%	0.0%	0.0%	2.05E-06	11.6%	1.6%	86.8%
(a) Hydrogen Fluoride (HF)	0.0%	0.0%	0.0%	3.81E-07	56.7%	3.3%	40.0%
(a) Hydrogen Sulfide (H2S)	0.0%	0.0%	0.0%	2.21E-08	56.6%	5.4%	38.0%
(a) Metals (unspecified)	0.0%	0.0%	0.0%	2.53E-09	53.2%	5.2%	41.6%
(a) Methane (CH4)	0.0%	0.0%	0.3%	5.07E-03	88.9%	4.2%	6.9%
(a) Nitrogen Oxides (NOx as NO2)	1.0%	3.0%	39.0%	6.86E-01	24.3%	3.9%	71.8%
(a) Nitrous Oxide (N2O)	0.0%	0.0%	0.5%	9.54E-03	95.8%	2.3%	1.9%
(a) Organic Matter (unspecified)	0.0%	0.0%	0.1%	1.06E-03	80.2%	4.3%	15.6%
(a) Particulates (unspecified)	0.1%	0.2%	2.4%	4.16E-02	56.4%	8.2%	35.4%
(a) Sulfur Oxides (SOx as SO2)	0.4%	1.3%	17.2%	3.02E-01	10.6%	2.2%	87.1%
(a) Tars (unspecified)	0.0%	0.0%	0.0%	7.69E-07	56.2%	5.4%	38.4%
Isoprene	30.8%	92.3%	0.0%	2.12E+01	100.0%	0.0%	0.0%

Of the twenty-five water emissions tracked, dissolved matter was released in the largest quantity, Table 2-22. Ammonia, COD, and Oils were the next three most emitted pollutants.

Table 2-22: average water emissions per kWh of net electricity produced (Mann and Spath 1997)

	% of Total in this Table	Total (g/kWh)	% of Total from Feedstock	% of Total from Transportation	% of Total from Power Plant
(w) Acids (H+)	0.0%	1.36E-05	99.3%	0.1%	0.6%
(w) Ammonia (NH4+)	12.2%	7.45E-03	100.0%	0.0%	0.0%
(w) Ammonia (NH4+, NH3, as N)	0.0%	6.92E-06	90.8%	1.4%	7.8%
(w) BOD5 (Biochemical Oxygen Demand)	0.5%	3.05E-04	98.4%	1.5%	0.1%
(w) Chlorides (Cl-)	0.0%	4.90E-06	30.7%	3.8%	65.5%
(w) COD (Chemical Oxygen Demand)	1.5%	9.12E-04	98.3%	1.5%	0.2%
(w) Cyanides (CN-)	0.0%	4.37E-08	84.3%	2.8%	13.0%
(w) Dissolved Matter (unspecified)	83.1%	5.09E-02	79.2%	18.6%	2.2%
(w) Fluorides (F-)	0.0%	6.74E-06	80.7%	2.9%	16.4%
(w) Hydrocarbons	0.0%	5.22E-08	100.0%	0.0%	0.0%
(w) Inorganic Dissolved Matter (unspecified)	0.0%	1.11E-06	56.4%	5.4%	38.2%
(w) Iron (Fe++, Fe3+)	0.0%	1.56E-09	55.4%	3.6%	41.0%
(w) Metals (unspecified)	0.0%	6.73E-07	56.2%	5.4%	38.5%
(w) Nitrates (NO3-)	0.0%	1.91E-07	55.4%	3.6%	41.0%
(w) Nitric acid	0.7%	4.13E-04	100.0%	0.0%	0.0%
(w) Nitrogenous Matter (unspecified, as N)	0.0%	2.21E-08	56.6%	5.4%	38.0%
(w) Oils	1.6%	9.80E-04	75.8%	13.9%	10.3%
(w) Organic Dissolved Matter (unspecified)	0.0%	4.41E-08	56.6%	5.4%	38.0%
(w) Phenol (C6H6O)	0.0%	1.33E-07	83.8%	2.8%	13.4%
(w) Sodium (Na+)	0.0%	8.08E-07	34.2%	3.7%	62.0%
(w) Sulfates (SO4--)	0.0%	8.13E-07	35.4%	3.7%	60.9%
(w) Sulfides (S--)	0.0%	8.73E-08	84.3%	2.8%	13.0%
(w) Suspended Matter (unspecified)	0.4%	2.40E-04	71.8%	5.7%	22.5%
(w) Tars (unspecified)	0.0%	1.10E-08	56.2%	5.4%	38.4%
(w) Water: Chemically Polluted	0.0%	3.80E-08	18.1%	2.5%	79.4%

This study, in addition to thoroughly tracking the facility emissions, tracked the emissions from upstream processes and feedstock production with much detail. Of the feedstock production emissions, the soil carbon sequestration rate has one of the largest impacts. Depending on the soil sequestration rate assumed, the GHG emissions can vary drastically. Figure 2-17 shows the CO_2 emissions for various carbon sequestration rates.

As previously mentioned, this study is somewhat unique as it tracked all emissions from the beginning of plant construction to the end of decommissioning. For the CO_2 emissions from year to year, the biomass production has the largest effect. This can be seen in

Figure 2-18.

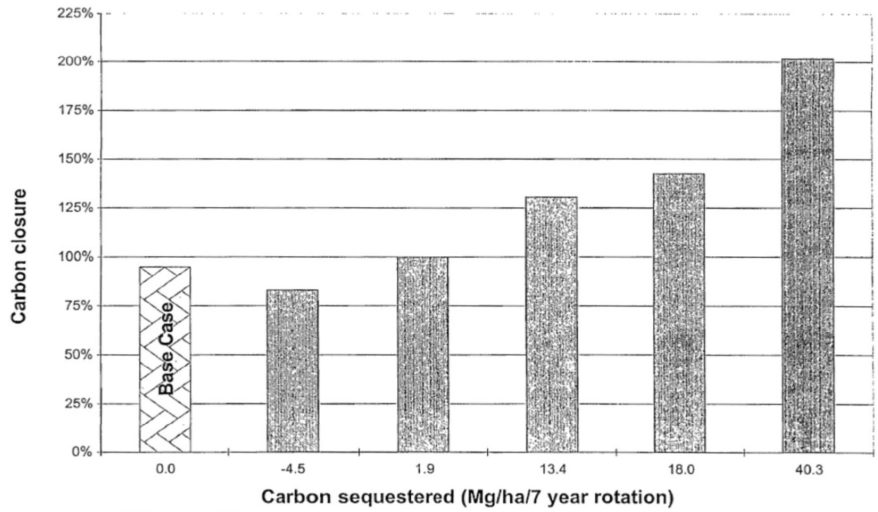

Figure 2-17: Effects of soil carbon sequestration rates on carbon closure (Mann and Spath 1997)

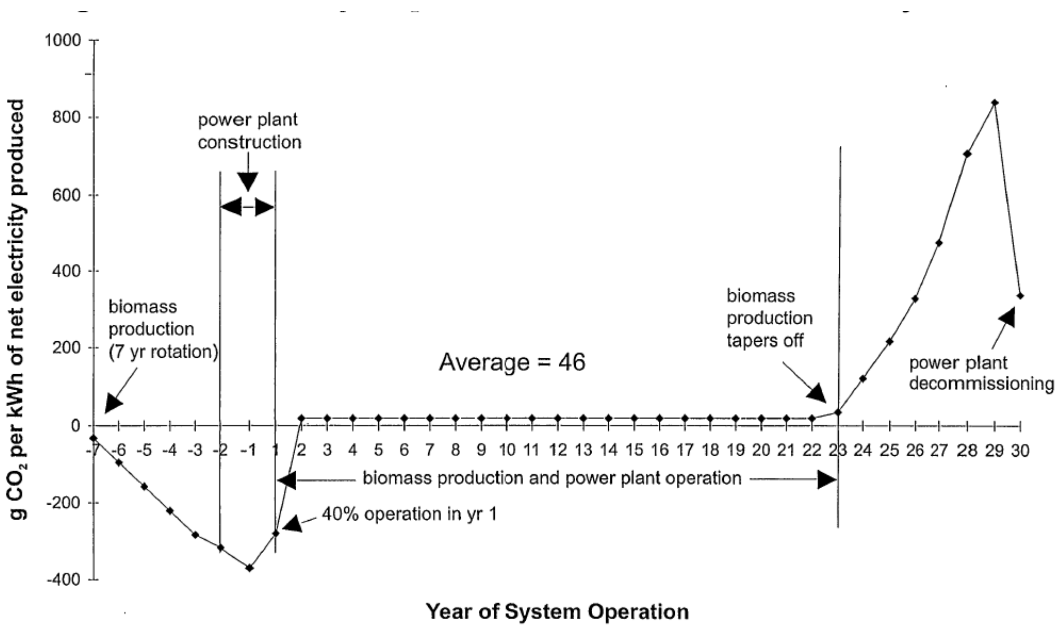

Figure 2-18: Net yearly CO_2 emission (Mann and Spath 1997)

With biomass production and harvesting at a steady state, the overall emissions were below 46 g CO_2 per kWh. The CO_2 emission value from year 2 until year 23 indicates the non-biogenic carbon releases.

The production facility released many emissions, however, the feedstock production has a significant effect utilizing much fossil fuel. Within feedstock production, the study grouped energy users in to five categories, Figure 2-19. Of all the energy consumed in upstream operations and feedstock production, fossil fuels used in farming operations are more than 85% of the total energy usage. This results from use of heavy equipment required to plant and harvest the feedstocks.

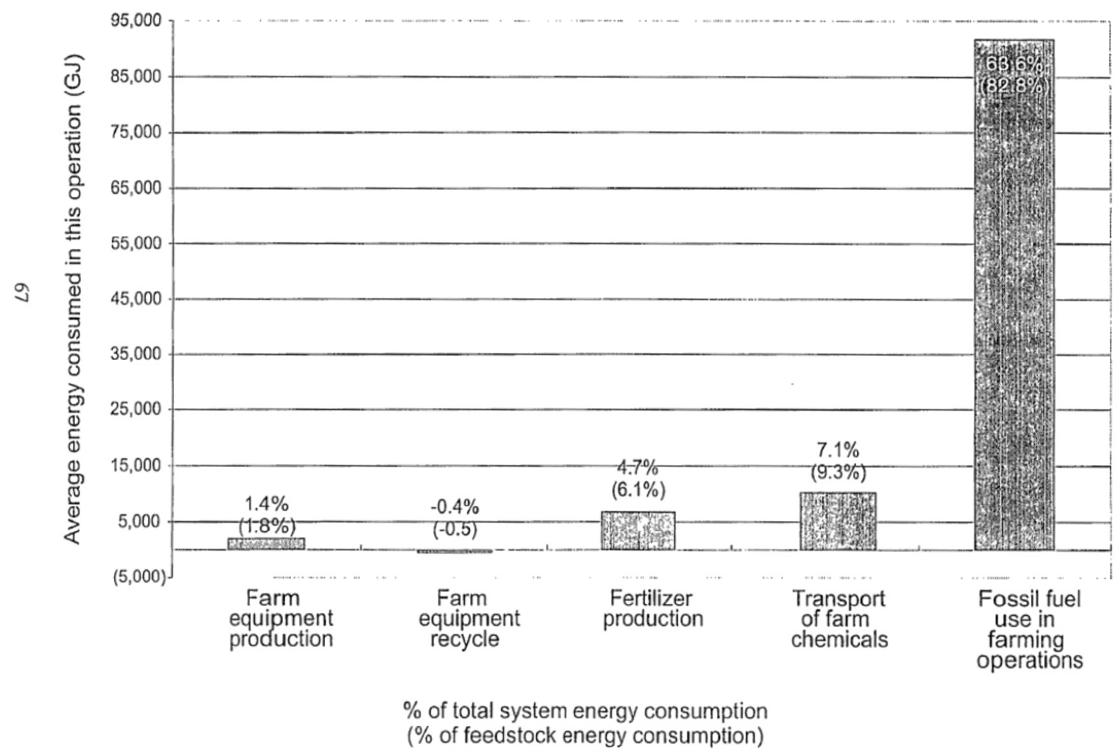

Figure 2-19: Energy consumption in feedstock production (Mann and Spath 1997)

As sediment is becoming one of the most common water pollutants, this study analyzed the effects of sediment loss due to feedstock production. Very few articles analyzed this aspect of feedstock production, making it worthy of discussion here. Sediment losses for several plots and feedstocks were measured the first two years. Results from this study and data used within the LCA are shown in Table 2-22. Both low and high values were found and all values were averaged and reported in kg/ha/three months. The high values came from the rainy months while the low values came from the dyer months. This data supports that nitrogen and phosphorus movement is minimal due to the low sediment losses.

Table 2-23: Sediment loss data from two-year field trials (Mann and Spath 1997)

	Tree	Sediment Loss (kg/ha/three months)		
		Low value	High value	Average
Alabama A&M, with cover	Sweetgum	20	250	111
Alabama A&M, without cover	Sweetgum	280	1300	749
Ames Plantation, TN	Sycamore	10	105	30
Stoneville, MS	Cottonwood	0	250	91

This study also examined the construction and decommissioning environmental effects of ethanol production. This area is not well covered within many other articles. Most studies assume that the plant will be in production long enough to produce enough product that the impacts due to construction will be distributed in a negligible amount. Of the emissions due to construction, cement accounted for 83% CO_2 emissions while steel accounted for 10%,Figure 2-20. These results were expected, as both cement and steel were the two most used materials in plant construction. The author, however, point out that these emissions are seen by the environment in the years that they occur, but they become negligible when averaged over the lifetime of the plant.

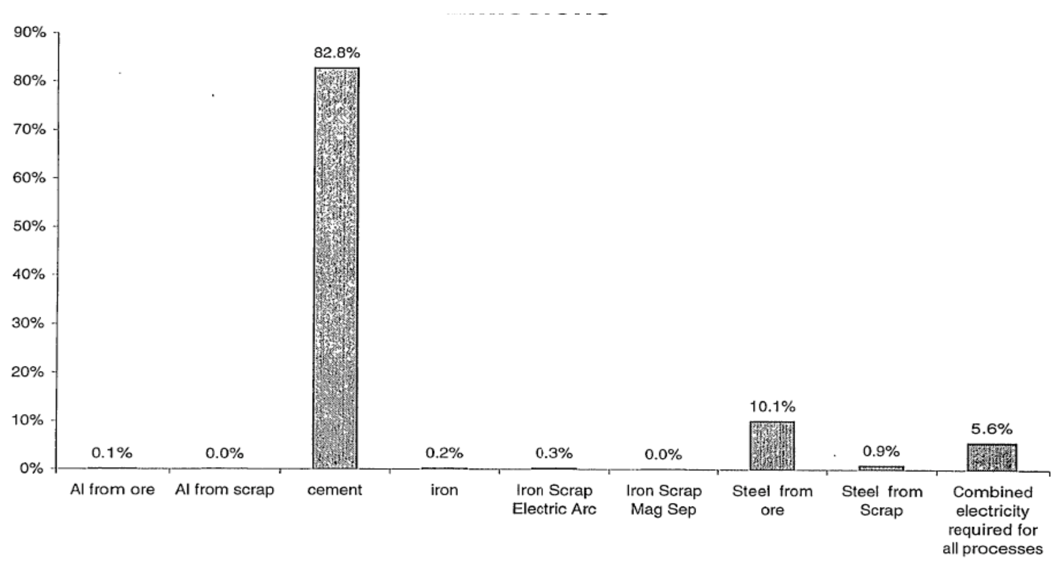

Figure 2-20: CO2 air emissions from plant construction (Mann and Spath 1997)

To determine the factors having the largest effect on the overall emissions, this study considered 19 different scenarios listed in Table 2-24. Both low and high values were run for each scenario. Results from this analysis are in Figure 2-21.

Table 2-24: Sensitivity analysis abbreviations (Mann and Spath 1997)

CASE LETTER	SENSITIVITY CASE
A	Yield of 9 Dry Tonnes / Hectare / Year (4 tons/acre/yr)
B	Yield of 15.7 Dry Tonnes / Hectare / Year (7 tons/acre/yr)
C	Nitrogen Fertilizer Low Case
D	Nitrogen Fertilizer High Case
E	Phosphorous Fertilizer Low Case
F	Phosphorous Fertilizer High Case
G	Potassium Fertilizer Low Case
H	Potassium Fertilizer High Case
I	Ammonium Nitrate as Sole Nitrogen Fertilizer
J	Urea as Sole Nitrogen Fertilizer
K	Herbicide Application High Case
L	Construction Materials Low Case
M	Biomass Transportation Distance Increased by 46%
N	Decrease in Recycle of Materials by 1/3
O	Decrease in Feedstock Fuel Use by 50%
P	Increase in Feedstock Fuel Use by 40%
Q	Decrease plant efficiency by 5 points
R	Increase plant efficiency by 5 points
S	Plant operating capcity factor = 65% in normal years
T	Plant operating capcity factor = 85% in normal years

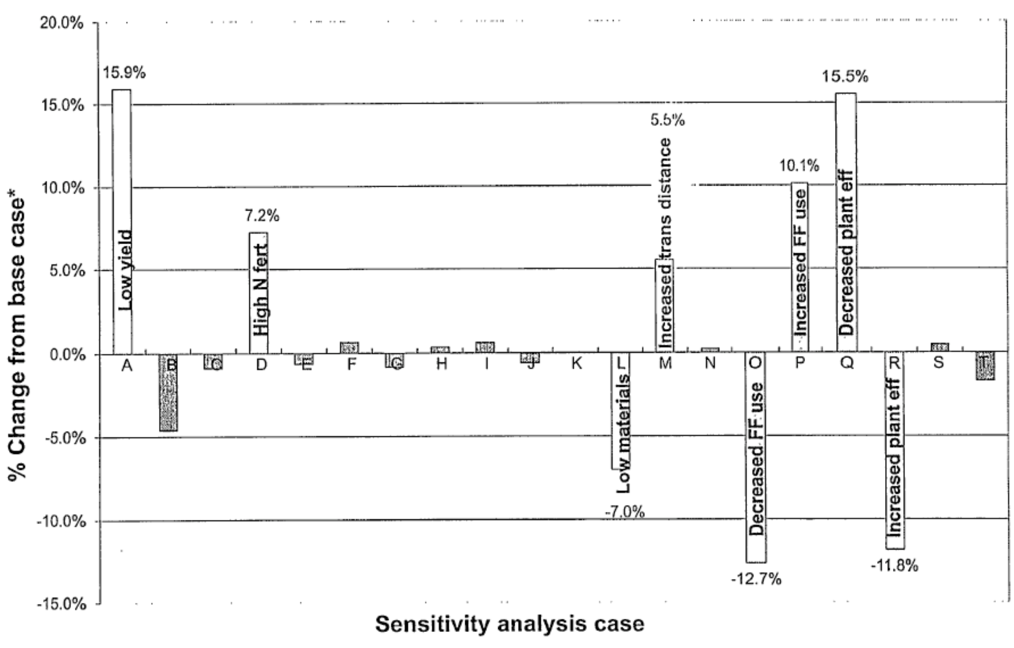

Figure 2-21: Sensitivity analysis: CO2 emissions (Mann and Spath 1997)

The parameters having the largest effect on CO_2 emissions are fully labeled, while others are only labeled by the assigned letter. Yield and conversion efficiency, as found within many studies, have the largest effect on CO_2 emissions. These parameters could increase CO_2 emissions by more than 15%. Fossil fuel usage and fertilizer efficiency also have large effects on the overall environmental impacts. Due to the extreme global warming potential of NO_X, being more than 300 times more potent than CO_2, efficient fertilizer usage is critical.

This sensitivity analysis also indicates which parameters, when improved, can reduce the emissions the most. Increased plant efficiency, decreased fossil fuel usage, and low material usage for construction are the parameters that have the largest potential to reduce the CO_2 emissions. Based on these findings, these said parameters should be further investigated to decrease the overall burdens.

In conclusion, this study analyzed the impacts of electricity production from biomass gasification. The study was performed on a cradle-to-grave basis examining all emissions from electricity production while particularly focusing on CO_2 emissions and energy consumption/production. A rudimentary impact analysis was performed, but was not reviewed here as it was based on past analysis guidelines which have since been improved. This study, however, does not compare emissions from electricity produced from biomass to electricity produced from other fossil fuels. The authors indicate that this is an area that should be investigated further. Other areas warranting further analysis include LCA of coal and biomass co-fired boilers as well as retrofitting old boilers to accommodate biomass feedstocks.

Mann and Spath describe the environmental impacts of cofiring biomass in A life cycle ***assessment of biomass cofiring in a coal-fired power plant*** (Mann and Spath 2001) Cofiring biomass refers to the use of biomass as a supplemental feedstock in an existing coal power plant. This may be done for reasons including economics, to meet emissions standards, and to diversify an energy portfolio (EPRI 1997a). This method of environmental process improvement is considered more attractive than other more capital intensive process improvements such as increasing boiler efficiency and flue gas carbon sequestration systems (Mann and Spath 2001). At lower biomass feed rates, little process modification was needed to accommodate the biomass feedstocks.

To analyze the full environmental impacts of the potentially economically attractive cofiring biomass scenario, a cradle-to-grave analysis was performed. The boundaries include the production and decommissioning equipment, direct emissions, waste displacement and associated end of life emissions. Tools for Environmental Analysis and Management (TEAM), by Ecobalance, was used to analyze the system. Within this analysis, ISO 1400 standards were followed to assure creditability. A minimal impact assessment was performed and justified by "a less is better approach" (Mann, Spath 2001). According to accepted ISO standards, impact assessment is an optional step and is not required for all analyses. In the place of a more in depth impact assessment, this study focuses more on the inventory analysis quantifying all energy usages and material flows.

Within this study, residual wood was considered as a biomass feedstock. It was fired at rates of 5% and 15%. The biomass feedstock parameters are described Table 2-25. This feedstock is assumed to come from thinnings, urban wastes and mill residues.

Table 2-25: Cofired biomass composition (Mann and Spath 2001)

	Carbon	Oxygen	Hydrogen	Nitrogen	Sulfur	Chlorine	Ash
Weight%, dry basis	50.62	41.40	5.76	0.25	0.03	0.00	1.94
Moisture, as received: 50 wt%							
Lower heating value: 18,295 kJ/kg (7,873 Btu/lb)							

The biomass composition is important for several reasons. Not only does it affect the energy production process, it will affect the emissions due to decomposition in alternative scenarios. More specifically, this study considers the fate of the biomass when it is not used for energy production. The typical end of life for this biomass type would include landfilling and mulch production. Both these process create emissions that can be avoided through energy production. These emissions savings are counted as a credit for the two biomass scenarios. However, there is no penalty for the decomposition emissions for coal only scenario. Figure 2-22 shows the typical end of life and associated emissions for this type of biomass.

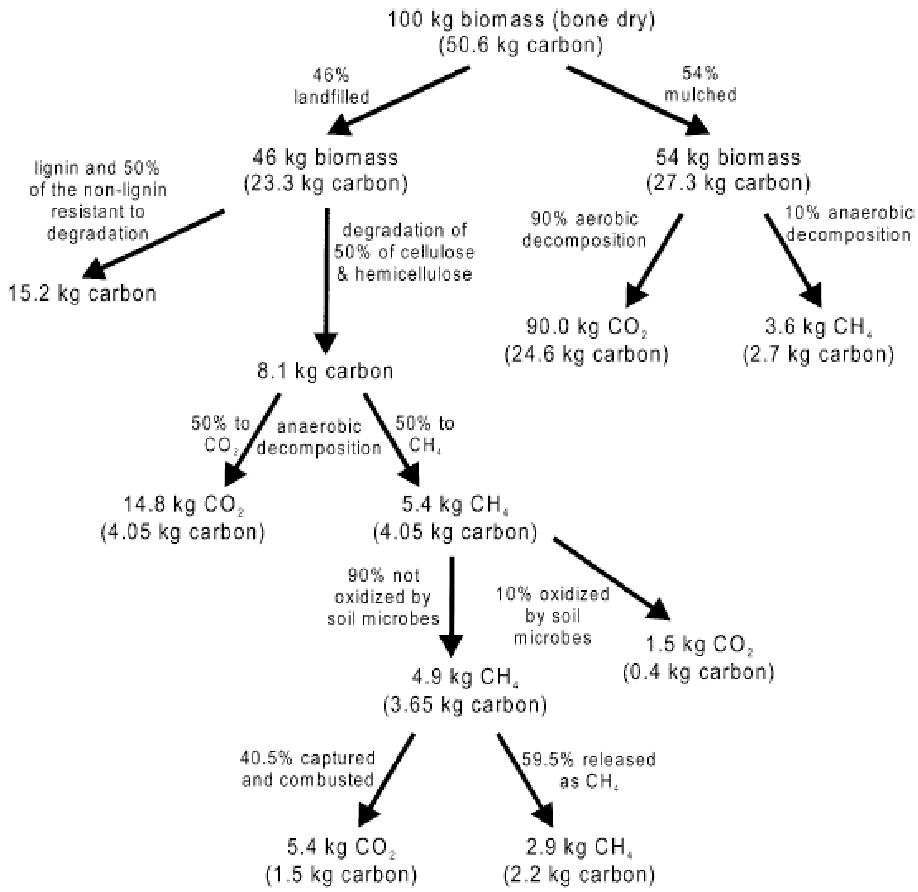

Figure 2-22: Avoided biomass fate (Mann and Spath 2001)

Mann and Spath cover avoided biomass emissions in more detail than most other studies. Within this study, these emissions prove to be a significant factor supporting that they should be analyzed in further studies.

Within the conversion process, cofiring biomass has a significant effect on the overall boiler efficiency. The efficiency is decreased due to increased fuel moisture content and lower heating value. The efficiency loss for the two cases were assumed to be 0.5% and 0.9% for the 5% and 15% cases, respectfully. Facility operating parameters are given Table 2-26. As seen in the table, the plant capacity decreases with increased biomass use. This results from the decreasing plant efficiency previously mentioned. Depending on plant capacity, additional biomass could be fed to maintain the previous power production.

Table 2-26: Cofiring operating parameters (Mann and Spath 2001)

Design parameter	No cofiring	15% cofiring	5% cofiring
Plant capacity (MW)	360	350	354
Average operating capacity factor (%)	60	60	60
Coal feed rate at 100% operating capacity (Mg/day) (as-received basis)	3,872	3,291	3,679
Biomass feed rate at 100% operating capacity (Mg/day) (as-received basis – 50% moisture)	0	1,498	499
Power plant efficiency (%)	32	31.1	31.5

Non-renewable resource depletion was also analyzed within this study. Both scenarios resulted in less non-renewable resource use in every category considered, Table 2-27. As to be expected, coal as a non-renewable was reduced the most.

Table 2-27: Cofiring resource depletion (Mann and Spath 2001)

	15% cofiring			5% cofiring			No cofiring	
	% by wt[a]	g/kWh	% change[b]	% by wt[a]	g/kWh	% change[b]	% by wt[a]	g/kWh
Coal	80	395	−13	80	436	−4	80	452
Limestone	18	90	−12	18	99	−3	18	103
Oil	2	10	−10	2	11	−3	2	11
Natural gas	0.2	1.1	−12	0.2	1.2	−4	0.2	1.2

[a]Percent of total resource consumption. Not all resources consumed by the system are shown; therefore the numbers do not add up to 100%
[b]Percent of reduction due to cofiring, based on the amount consumed in each case per kWh produced

Solid wastes production was also considered within this study. It was found that there are three main sources of solid wastes resulting from coal energy (Mann, Spath 2001):

1. Flue gas cleanup waste,
2. Boiler ash
3. Miscellaneous non-hazardous process waste

When cofiring biomass, these wastes decreased by 27.6% and 85.6% for the 5% and 15% cofiring rates, respectfully.

Water emissions were considered small when compared to other emissions and resulting primarily from coal production. These water emissions decreased when biomass was used. Ground water contamination from landfills was recognized but not included within this study. This omission results from the highly sight specific nature of these contaminations.

The modeled facility produced 8 major air emissions. For both biomass feed scenarios, all 8 of the emissions decreased, Table 2-28. In addition to air emission reductions, a negative methane emission was recorded. Since emissions that typically occur during biomass decomposition were prevented by energy production, a credit is given resulting in a negative methane emission.

Table 2-28: Cofiring air emissions (Mann and Spath 2001)

	15% cofiring		5% cofiring		No cofiring Emissions (g/kWh)
	Emissions (g/kWh)	% change from no cofiring	Emissions (g/kWh)	% change from no cofiring	
Carbon dioxide	954	−6	1,003	−2	1,018
Carbon monoxide	0.2	−5	0.3	−1	0.3
Non-methane hydrocarbons	0.2	−11	0.2	−4	0.2
Methane	−5.0	−652	−1.0	−214	0.9
Nitrogen oxides (NO_x)	3.1	−8	3.3	−2	3.3
Nitrous oxide (N_2O)	0.0	−19	0.0	−6	0.0
Particulates	8.1	−12	8.9	−3	9.2
Sulfur oxides (as SO_2)	5.9	−12	6.5	−3	6.7

Mann and Spath also indicated that reduced SO_2 and NO_x emission result from less sulfur and bound nitrogen within the feedstocks. These values, however, change with the quality of coal and types of biomass used.

A global warming potential sensitivity analysis was performed analyzing 18 parameters. Parameters that resulted in less carbon sequestration and methane recovery reduced the GWP savings to less than the base case. All but one scenario, all residual biomass carbon sequestered in landfill, resulted in GWP savings when compared to coal only. These savings were recorded as high as 0.28 %

In conclusion, cofiring waste biomass resulted in environmental benefits. The extent to which savings were experienced depends highly on the assumptions around the biomass alternative scenario. Much of the overall emission savings result from preventing anaerobic biomass decomposition that occurs in landfills and mulch piles.

Renewable Energy from Willow biomass Cops: Life Cycle energy, environmental and economic performance*,* by Keoleian and Volk (Keoleian and Volk 2005), examines environmental benefits of energy produced from biomass feedstocks of willow and wood residues. TEAM was used for process chemical and transportation emissions data. The conversion model from Mann & Spath 2001 was also used to generate inventory data. However, the impacts of additional feedstocks were examined along with gasification and other conversion technologies.

A large review of willow as an energy crop was performed providing useful data and background information. Willow feedstocks will not be covered extensively within this review; rather a paraphrasing of LCA approach/findings will be presented. From this, the reader should gain a better understanding of the environmental impacts of feedstock cultivation and emissions related to energy production.

This study was performed on a cradle-to-grave basis with boundaries as seen in Figure 2-23. The following operations are included within the study: willow biomass production, coal mining and processing, coal and biomass transportation, manufacturing of co-firing retrofit equipment, and avoided operations of wood residue in landfill disposal (Keoleian, Volk 2005). However, the environmental burdens associated with the construction of the original co-fired coal boiler were not considered within the study. Alternative fuel emissions were compared to average emissions from the Dunkirk Unit #1 over the years of 96, 97 and 98.

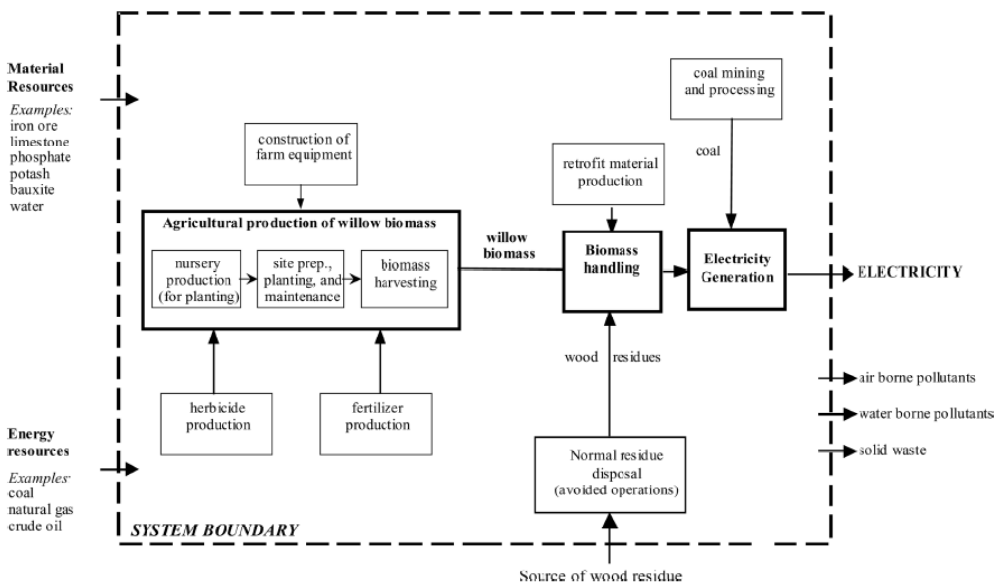

Figure 2-23: energy system boundaries for power generation via co-firing with coal and/or wood residue or gasification (Keoleian and Volk 2005)

For the purposes of this study, willow was assumed to grow on a seven year rotation. Biomass production emissions were reported on a seven year basis. Some greenhouse gasses are produced through the biomass cultivation and harvesting, however, the carbon sequestration within the tree is more than a magnitude greater, Table 2-19. As within many studies, the N_2O emissions from the forest show some variability or uncertainty. Not including the harvested biomass, the net emissions of biomass production were found to be 3.77 kg CO_2 per hectare of harvested biomass.

	CO_2	Other GHG Mg CO_2 eq. ha^{-1}	Totals
Diesel fuel	3.12	0.06	3.18
Ag. inputs[b]	2.97	0.4	3.37
N_2O from applied N		+3.97 (±3.17)[c]	3.97
N_2O from leaf litter		+7.28 (±5.83)[c]	7.28
C sequestration			−14.1
Below-ground biomass	−14.1		
Soil carbon	0		0
Net total	−8.01	+11.7 (±9.0)[c]	3.7
Harvested biomass	−499.2		−499.2

[a]Positive values indicate additions (releases) to the atmosphere.
[b]Includes fertilizer and herbicide manufacturing and transport, machinery manufacturing, and nursery operations.
[c]Bracketed numbers represent the N_2O emission range presented by the IPCC (1997) estimate.

Table 2-29: Base case GHG emissions per hectare on seven year rotation basis (from Keolin, Volk 2005)

Keolin and Volk not only examined co-firing willow, they also examined several other process conversion technologies, Table 2-30. When biomass was co-fired with coal, emissions savings were experienced in all categories. There was little change between residues/willow blend and the willow only scenarios. The NO_x emission for these two scenarios varied the most at 4.5%.

Electricity production from gasification was examined using models from NREL (National Renewable Energy Lab) and EPRI (Electric Power Research Institute). The emissions from these technologies were compared to emissions standards from the national energy grid. Both the NREL and EPRI gasifiers resulted in CO_2 emission savings while the EPRI direct gasifier emitted 324% more CO_2 than the standard grid electricity. Emissions from non-methane hydrocarbons, often produced in feedstock drying, were significantly different between the three gasifier models. The NREL model produced the most with an emission 1089% higher than grid electricity while the EPRI models ranged from 139%-434% increase in emissions. Other emissions from the gasifier models all showed emissions savings. The varying results from EPRI and NREL models may be from the poorly understood and hard to model gasification process. The models used are often based on limited range of gasification data and may not accurately calculate emissions for all biomass types.

Data from Keoleian & Lewis 2003 and Schleisner were used for wind and photovoltaic electricity emissions. When these types of electricity are compared to the grid average, savings are experienced in all categories except in the non-methane hydrocarbons category. When wind and solar energy are compared to biomass energy, solar power produces more CO_2 emissions then all three biomass electricity producing processes. The rest of the emissions are similar to those of biomass based electricity systems. Wind electricity only reported emissions for SO_2, NO_2 and global warming potential. When compared to grid energy, savings were realized. Biomass energy emissions compared to wind emissions are reported to be similar. Overall, the biomass feedstocks, wind, and solar energies produced global warming potential savings of around 95% when compared to grid electricity. Co-fired biomass at a rate of 10% produced global warming potential savings of 5%-9%.

When considering biomass based electricity and ethanol produced in large scales, land becomes a limiting factor. As more uses for biomass arise and begin to compete with current biomass consumers, biomass value will increase resulting in higher biomass production. As land is a finite resource, there will be a maximum biomass production given the current growth rates and land area that will be met. This may not be a factor in the early stages of biomass energy uses, but may become an issue as ethanol production processes mature and the ESIA renewable fuels standards are met through commercial cellulosic ethanol production.

Table 2-30: Air emissions and energy ratios for biomass based electricity compared to other alternative sources (Keolin, Volk 2005)

	CO (g CO/ MWh_{elec})	NO_x (g NO_2/ MWh_{elec})	SO_2 (g SO_2/ MWh_{elec})	Non-methane hydrocarbons (g/MWh_{elec})	Particulates (unspecified size) (g/MWh_{elec})	Global warming potential (kg CO_2 eq./MWh_{elec})	Net energy ratio
10% co-fire, residue & willow blend[a]	152.4 (−3.2%)	1868 (9.7%)	13670 (−9.6%)	84.1 (−10.1%)[b]	707.6 (−6.3%)	905.7 (−7.4%)	0.341
10% co-fire, all willow[a]	160.1 (1.7%)	1614 (−5.2%)	13675 (−9.5%)	86.4 (−7.6%)[b]	705.8 (−6.6%)	882.7 (−9.9%)	0.342
Average US grid[c]	416.8	3329.9	3207.5	44.1	2136.0	989.1	0.257
Willow production & transport with...[d]							
NREL gasifier	69.9 (−83.2%)	645.0 (−80.6%)	373.9 (−88.3%)	524.6 (1089%)	34.0 (−98.4%)	38.9 (−96.1%)	13.3
EPRI gasifier	277.3 (−33.5%)	816.6 (−75.5%)	941.9 (−70.6%)	105.5 (139.1%)	>31.4 (−98.5%)[e]	40.2 (−96.0%)	12.9
EPRI direct-fired	1769.2 (324.4%)	278.9 (−91.6%)	>161.0 (−95.0%)[e]	235.9 (434.6%)	>40.8 (−98.1%)[e]	52.3 (−94.7%)	9.9
BIPV[d,f]	43.3 (−89.6%)	247.6 (−92.6%)	512.2 (−84.0%)	67.5 (53.0%)	574.8 (−73.1%)	59.4[g] (−94.0%)	4.3
Wind[d,h]	na	30 (−99.1%)	20 (−99.4%)	na	na	9.7[g] (−99.0%)	30.3

[a]Parentheses are percent change relative to coal-only (no co-fire) operation.
[b]Biomass contribution to stack emissions.
[c]TEAM database, version 3.0 (Ecobalance).
[d]Parentheses are percent change relative to average US grid.
[e]Power plant stack emissions not specified; values shown are from feedstock production and transportation only.
[f]BIPV = building integrated photovoltaic. Reference: (Keoleian and Lewis, 2003).
[g]Global warming potential contains CO_2 contributions only.
[h]Schleisner (2000).

Each energy source requires some amount of land to be produced. Intrinsically, biomass based energy requires more land as most biomass needs access to the sun and nutrient rich soils. Natural gas, however, requires very little land to extract and convert to electricity. Land requirements are shown for different energy production scenarios in Figure 2-24. Electricity produced through direct firing gasification of willow biomass required the most land. The variation between the gasification systems land use results from varying yield and efficiencies levels. The direct fire gasification system required more biomass than the other gasification systems to produce the same amount of electricity. As a result of this lower conversion efficiency, more land is required to produce a unit of electricity.

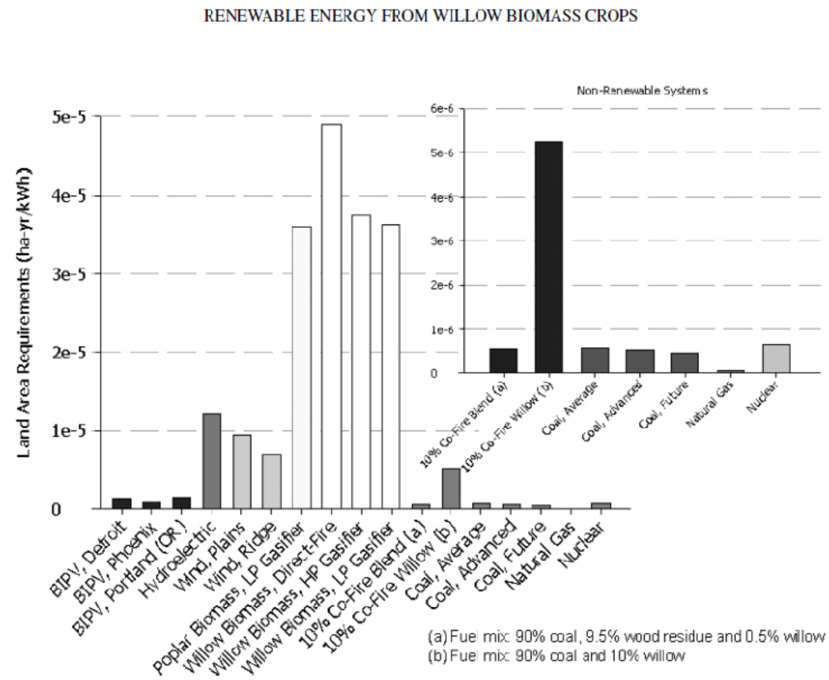

Figure 2-24: Land requirements for various energy production pathways (Keoleian and Volk 2005)

Within this article, several energy producing methods were studied examining emissions and land use requirements. As a closer to near term option, co-fired biomass was examined. Electricity emissions from co-fired biomass systems resulted in a 5%-9% decrease in global warming potential. Other production methods such as gasification using 100% biomass feedstocks were able to achieve global warming potential savings of 90%-99%. These higher savings are due to the carbon sequestered in biomass growth, which is assumed to offset the biogenic carbon released through combustion/ gasification. In addition to comparing biomass-based electricity to coal fired and grid average energy, this study considered wind and solar power. Overall, the global warming potential for solar and wind were similar to biomass based electricity. However, the land use for these energy sources were much less than biomass based energy.

2.3.3.3 Bioenergy Literature Summary

Consistently throughout the bioenergy LCA and GHG analysis publications, GHG and global warming potential savings were reported. Despite the savings in GHG and global warming potential, some environmental impacts increased. Eutrophication effects, resulting from feedstock cultivation, were generally found to increase with biomass based energy. Additionally, non-methane hydrocarbon emissions were reported to increase with the use bio-based energy. The environmental benefits of the systems are highly sensitive to conversion efficiency, feedstock yields, and decomposition emissions abatement due to wood waste use.

Given the state of the technology, co-firing coal power plants present a low cost and efficient approach to decrease GHG emissions. Man and Spath found that firing 10% waste biomass could decrease total GHG emissions by as much as 9% with little process modifications and no modifications at firing rates of 2% or less. This GHG abatement strategy for many facilities could be more economically attractive than investing in emissions control equipment and produce a higher rate of return while diversifying the facility's energy portfolio.

Of the three main types of biomass to electricity conversion pathways considered, 1. combustion, 2. co-firing combustion, and 3. gasification, gasification is the most efficient method to produce electricity. This higher efficiency results in better biomass utilization and lower overall emissions in most categories. The limited knowledge surrounding biomass gasification and the risk involved in investing large amounts of capital into new gasification systems are the main hurtles for this technology.

2.3.3.4 Knowledge Gaps

Within the literature reviewed, several knowledge gaps were identified. Others were identified through observing the lack of publications covering a specific topic area. These knowledge gaps represent future research topics that should be considered. Knowledge gaps are listed below:

- Full LCAs of energy systems with thorough impact assessments
- Ethanol and energy facility integration
- Retrofitting paper mill for energy production
- Effects of production scale on the environmental aspects of bioenergy
- The environmental effects of various feedstocks for

    - Gasification
    - Combustion
    - Co-firing
- Environmental impact comparison between bioenergy and biofuels as transportation fuels
- N_2O emission rates due to feedstock production

As with biofuel research, to date, more emphasis has been placed on the technical and financial aspects of bioenergy production. As more research supports that bioenergy technology is financially and technically feasible, more environmental analyses will be required to evaluate the impacts of different bioenergy conversion pathways. Government mandates will likely require these analyses to quantify the environmental impact reductions into the future.

2.4 Overall summary

2.4.1 Literature reviewed

Within this analysis, publications evaluating the environmental impact of biofuels/energy were analyzed and reviewed. A select number of these articles were reviewed in detail to provide the reader with a platform of knowledge and understanding of the current LCA methodology. The reviewed articles were selected based on the overall quality and to expose the reader to range of topic areas within LCA of biofuels/energy. In total, six biofuel and three bioenergy LCA articles were reviewed to educate the reader in the different aspects of the environmental impacts of bioenergy/fuels as well as provide a general overview of the findings within the literature. In addition to educating the reader, knowledge gaps were identified through analyzing the literature knowledge base and through identifying knowledge gaps found in other studies.

Table 2-2-31: lists LCA papers performing LCA or GHG analyses around biofuels and energy. Publications found but are not listed here did not perform actual system analyses but covered other LCA related topics. Within this table, articles are listed by author and year with a description of conversion technology, boundaries, software used, impact assessment methods, study/publication regions, and the GHG emissions findings.

Table 2-2-31: LCA publication review table

Authors and year	Conversion Pathway	Feedstocks	PRODUCT	Assessment Boundaries			Software			Methodology			Impact Assessment Method			Publication Data		Findings compared to gasoline		
				Cradle-to-gate	Cradle-to-grave	Gate-to-gate	SimaPro	Aspen	Other	Full LCA	LCI	GHG inventory	Global warming potential	Ecoindicator 99	Other Impact method	Year	Region/Country	GHG reduction	GHG increases	assumption dependent
Marano&Ciferno_2001	Thermochem	mass coal natural g	fishertropic fuel		x				X		X				X	04	USA	X		
Kikuchi_etal_2008	biochem (D.A.)	corn, wood waste	ethanol		x				x		x	x				08	Portugal	x (20-30%)		
Kemppainen&Shonnard_2005	biochem (D.A.)	paper/ Poplar	ethanol		x			x	x	x					x	05	USA	X		
Sheehan_etal_2004	biochem (D.A.)	corn stover	ethanol		x				x	x					x	04	USA	100%		
MacLean&Spatari_2009	biochem (various)	various	ethanol	x	x				x		x	x				09	USA			X
Lynd&Wang_2004	biorefinery	corn stover	ethanol		x				GREET			x				04	USA			X
Davis_etal_2008	multiple pathways	multiple feedstocks	ethanol	x	x											08	USA	x	x	x
Fu_etal_2003	biochem	Candian timber	ethanol				x			x	x				x	03	Canada			
Foust_etal_2009	bio vs thermochem	poplar/ corn stover	ethanol			x		x			x	x				09	USA			
Bright_etal_2009	bio/thermochem	forest biomass	ethanol		x		x			x						09	Norway	x		
Malkki&Virtanen_2003	combust/gasify	forest chips	electricity						x			x				03	Finland			
Ren_etal_2009	various	biomas, petrol	ethanol, petrol		x							x				09	USA			
Holmberg&Gustavsson_2007	biomass energy	pulpwood/paper	electricity													07				
Reijnders_2008	biomass energy	crop residues	electricity													08	USA			
Prasad_etal_2007	multiple pathways	wastes	ethanol													07	Canada			
Stichnothe&Azapagic_2009		waste paper	ethanol		x				GaBi, WRATE							09	England			
Yu&Tao_2009		corn	ethanol		x				GREET							09	China			
Reijnders&Huijbregts_2007					x											07	Europe			
Graham_2003	biomass energy	poplar/chips	electricity	x												03	Canada			
Kim_etal_2006			ethanol		x				GREET						x	06	USA			
Cherubini&Jungmeier_2009	biorefinery	switchgrass	ethanol + other		x		x									09				
Bai_etal_2010	biochem (ammonia ex)	switchgrass	ethanol		x				x	x						10	Nether.	65%		
Roedl_2010	CHP and Thermochem	poplar chips	CHP and FT diesel		x				x	x			x			10	Germany	88% GWP		
Persson_etal_2010	biochem	wheat	ethanol		x				GREET+other			x				10	SE USA	43 - 62%		

2.4.2 Annotated bibliography and database

In addition to reviewing a select number of LCA publications, an annotated bibliography and Microsoft Access database were created. The annotated bibliography includes all the publications found within the literature survey. The publication descriptions found in the annotated bibliography provide a brief description of the study and findings. The database, however, the same data as the annotated bibliography in a searchable electronic version as well as in further detail for many studies.

2.4.3 Final remarks

Through a literature review, annotated bibliography and an Access database, a vast knowledge base is presented. This work is not only informative, but it provides a tool to identify future research topics while providing the user with a searchable electronic publication database focusing on LCA of biofuels and energy. This tool provides the user with a vast amount of knowledge within a powerful searchable database. This database could be used into the future to contain the most recent publications and research in the areas of LCA of forest biofuels. This would require periodic updates and literature searches, however, it would prove to be an invaluable asset to anyone learning and writing about LCA of biofuels.

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3 Bioethanol from lignocellulosic feedstocks: A life cycle assessment of the thermochemical conversion pathway

3.1 Abstract

Due to the Energy Independence and Security Act (EISA) mandated biofuels production, many production pathways are being examined on a technical and economic basis. However, to be considered a 2nd generation biofuel, certain greenhouse gas (GHG) reductions are required under the Renewable Fuel Standard (RFS). These threshold standards are in response to the threat of global climate change and the EPA's classification of CO_2 and other green house gasses as harmful to human health. As a result of this, it is critical to examine and quantify the GHG emissions as well as the overall sustainability of these production processes. Only biofuel production processes proving to be economically feasible and reducing GHG emissions will be successful into the future.

Biomass gasification is widely known as a promising 2nd generation biofuels production pathway due to high alcohol yields and flexible feedstock requirements. Unlike the biochemical route, the thermochemical process can successfully utilize a wider range of feedstocks. However, each biomass depending on the composition will produce different alcohol yields and GHG emissions. The purpose of this work was to examine the yields and GHG emissions from the conversion process for six feedstocks on a gate-to-gate basis. These feedstocks included: 1. Natural hardwood, 2. Loblolly pine, 3. Eucalyptus, 4. Miscanthus, 5. Corn stover, and 6. Switchgrass. Using the NREL thermochemical model (Aden et al. 2007) and SimaPro, a GHG analysis and life cycle assessment were performed.

The NREL model was used for the baseline material of hybrid poplar, resulting in a yield and GHG emission of 105 441 l/tonne and 2.8 kg CO_2 eq. per liter, respectively. When compared to the NREL base model using hybrid poplar as a feedstock, loblolly pine produced the highest alcohol yields, 8.5% increase, and the lowest GHG emissions per liter of ethanol, 9.1% decrease. Corn stover, due to the high ash content, had the lowest yields and the highest GHG emissions per liter of ethanol. Additionally, the results were impacted by ash and water, respectively.

Results from environmental studies combined with technical and economic analyses should be used to determine the most favorable feedstocks for biofuel production processes. However, further

analysis examining feedstock production is needed and will be critical to understanding the overall carbon balance surrounding these feedstocks.

Keywords: biofuel, alcohol, thermochemical, gasification, ethanol, LCA, GHG, pine, hardwood, corn stover, switchgrass, miscanthus.

3.2 Introduction

3.2.1 GHG analysis motivation

"The evidence of human-induced climate change goes beyond observed increases in average surface temperatures; it includes melting ice in the Arctic, melting glaciers around the world, increasing ocean temperatures, rising sea levels, acidification of the oceans due to excess carbon dioxide, changing precipitation patterns, and changing patterns of ecosystems and wildlife" (Jackson). This quote from Lisa Jackson's (the EPA administrator) announcement of *Greenhouse Gases Threaten Public Health and the Environment* outlines a few of the impacts of global warming. These and unanticipated impacts to the world are the motivating force behind greenhouse gas (GHG) monitoring/regulations and renewable fuels initiatives. Responding to the current and potential impacts of global warming, the EPA has determined that GHG are harmful to human health and will be regulated under the Clean Air Act (CAA).

The U.S. is the largest producer of bioethanol in the world with 34 billion liters, as of 2009 (RFA 2010). However, controversy around first generation biofuels, based on the conversion of corn grain (USA) and sugar cane (Brazil) (Runge, Senauer et al. 2007; Mitchell 2008; Gonzalez, Treasure et al. 2011), have prompted research and investments in 2nd generation biofuels produced from non-food based lignocellulosic feedstocks. Lignocellulosic biomass has also been identified as a key player to other forms of energy. Studies suggest the use lignocellulosic feedstock (as agriculture residues and forest feedstocks) have clear benefits in the mitigation of GHG emissions (Schneider and McCarl 2003; Hill 2009; Zhang, McKechnie et al. 2009).

The Energy Independence and Security act of 2007 (EISA) outlined a set of goals to increase energy security as well as reduce GHG emissions. As biofuels are seen as a key component of energy security and GHG reduction(Sims, Mabee et al. 2010), the Renewable Fuels Standard (RFS) requires production of approximately 136 billion liters of blended renewable transportation fuels by 2022. However, there is much controversy over the GHG reductions due to first generation biofuels production and use (Davis, Anderson-Teixeira et al. 2009); EISA also required the EPA to apply life cycle GHG threshold standards to ensure reductions through the use of renewable fuels. Through following these threshold requirements, 60% GHG reduction for cellulosic ethanol and 20% for other biofuels, the use of biofuels will decrease anthropogenic GHG emissions and create a more sustainable path forward.

3.2.2 Previous biofuels GHG analysis

For the CAA and EISA requirements to be successful, research must be performed developing tools and knowledge to assist industry in reducing GHG emissions while maintaining economic feasibility. Wang and Argonne National Laboratory for example, developed the Greenhouse Gases, Regulated Emissions, and Energy use in Transportation Model (GREET) to analyze the GHG emissions from biofuels, utilizing many different production pathways and blending options (Wang 2001). This tool has been the backbone for a large part of the knowledgebase surrounding biofuel GHG emissions resulting in many publications.

In addition, there have been many publications studying the GHG balance of various ethanol conversion processes and feedstocks. The two most common second generation biofuels processes studied are alcohol syntheses through i) gasification and ii) biochemical pathways. Both of these processes, despite the lack of commercial production facilities, are considered to emit less GHGs than first generation biofuel pathways. Due to the potential GHG reduction through the production and use of second generation biofuels, EISA has required that approximately 79 billion liters of biofuels be produced solely from non-starch feedstocks. This drastic production increase from no commercial second generation biofuels to 79 billion liters by 2022 will have many unknown environmental impacts. GHG analysis and life cycle assessment studies have been the means to predict the environmental outcomes of such production in order to make process and feedstock decisions to minimize future environmental impacts.

Davis et al 2009 performed a comprehensive biofuel GHG emissions literature review examining first and second-generation biofuels. GHG emissions from many feedstocks, primarily using a biochemical conversion pathway, were tabulated and ranked from the most GHG reductions to the least GHG reductions, Table 3-1, corn based biofuel was reported from two different studies to either have an 86% GHG savings or 93% GHG burden.

These vastly varying results illustrate the inconsistency between studies and the mishandling of the following factors (Cherubini et al 2008):

- Recognition of biomass carbon cycle
- Including carbon stock changes in biomass and soil over time
- Inclusion of nitrous oxide and methane emissions from agriculture activities,
- Selection of appropriate fossil reference system
- Homogeneity of the input parameters in life cycle inventories
- Influence of the allocation procedure when multiple products are involved

These mishandlings and inconsistency are not exclusive to GHG analysis. LCA studies offer an even larger spectrum and opportunity for inconsistent handling of these factors, however, when done transparently with appropriate assumptions, can offer a more encompassing environmental assessment.

Despite these the inconsistency of the results, some trends can be observed from this review. Nine out of the eleven cellulosic feedstock options report GHG savings with an average savings of 59%. Corn, however, only had five out of the seven reports indicating GHG savings with an average of 2.42% GHG displacement. These findings are in line with other GHG review studies such as (Cherubini, Bird et al. 2009).

Table 3-1: GHG emissions from varying feedstocks (biochemical conversion except as noted)

Feedstock	GHG Displacement %	S	Feedstock	GHG Displacement %	S
Switchgrass	-114	1	Corn	-86	9
Switchgrass combustion compared with coal combustion	-109	2	Corn-soy	-38	10
Miscanthus (gasification)	-98	3	Corn (starch)	-25	11
Switchgrass	-93	4	Corn (starch)	-24	12
Switchgrass	-73	5	Corn	-3	13
Switchgrass	-11	6	Corn (starch)	66	14
Switchgrass	43	7	Corn (starch)	93	15
Switchgrass	50	8			

Source: [1](Adler, Grosso et al. 2007), [2](Ney and Schnoor 2002), [3](Lettens, Muys et al. 2003), [4](Schmer, Vogel et al. 2008), [5](Wu, Wu et al. 2006), [6](Lemus and Lal 2005), [7](Delucchi 2006), [8](Searchinger, Heimlich et al. 2008), [9](Delucchi, 2006), [10](Adler, Grosso et al. 2007) [11](DiPardo 2004), [12](Wu, Wu et al. 2006), [13](Niven 2005), [14](Delucchi, 2006), [15](Searchinger, Heimlich et al. 2008)

3.2.3 Process technology overview

Bioethanol production process technologies can be broken down into two categories: biochemical and thermochemical. The biochemical conversion pathway is defined by the utilization of microorganisms to convert cellulosic monomeric sugars into ethanol. The thermochemical pathway utilizes high temperature and catalytic reactions to convert feedstocks to fuels.

To provide a basis of comparison for future process technologies, NREL performed technical and economic evaluations for both of these process technologies. The biochemical technology utilized dilute acid pretreatment followed by enzymatic hydrolysis and fermentation, as reported in (Aden et al. 2002). For the thermochemical technology, indirect gasification and catalyzed mixed alcohol production was examined in (Phillips 2007) and was the basis for this study. For both processes, advantages, disadvantages and major barriers have been identified around biomass cost and availability, (Gonzalez, Saloni et al. 2008; Gonzalez, Treasure et al. 2010; Wu, McLaren et al. 2010), pretreatment costs, high capital expenditure (CAPEX), equipments scale up and overall production costs (Aden, Ruth et al. 2002; Mosier, Hendrickson et al. 2003; Mosier, Wyman et al. 2005; Wyman 2007; Wyman 2008; Tao and Aden 2009; Gonzalez, Treasure et al. 2010; Wu, McLaren et al. 2010). As the most heavily supported production route, biochemical conversion relies mainly on hydrolysis (acid and/or enzymatic hydrolysis) to reduce polymeric carbohydrate chains into fermentable monomeric sugars. The other and less understood approach is thermochemical conversion, with numerous versions and hybrid designs. The major concept behind thermochemical processes is the production of synthetic gas (syngas) from cellulosic biomass; gasses are then reformed and passed through catalytic reactors to produce alcohol species (Mosier, Wyman et al. 2005; Phillips, Eggeman et al. 2007; Mu, Seager et al. 2010). Economic and life cycle analysis studies made to compare biochemical and thermochemical pathways do not clearly identify a winner technology for conversion (Foust, Aden et al. 2009; Mu, Seager et al. 2010; Sims, Mabee et al. 2010), in fact there is a general and logic agreement that market place economics would be used to decide which conversion approach should be used (Blaschek and Boateng 2009; Mu, Seager et al. 2010), this is based on type of biomass available and delivered costs. Biochemical technologies seem to be more feasible in regions where large volumes of consistent biomass are available, while thermochemical pathways are more accepting of variations in feedstock variables (Schuetzle et al. 2007; Foust et al. 2009; Mu et al. 2010). Moreover, some studies suggest that hardwood and herbaceous feedstock are more suitable for biochemical pathways, while more recalcitrant raw materials as softwood feedstock are better suited for the thermochemical processes (Foust et al. 2009; Gonzalez et al. 2010). Conversion pathways capable of processing several types of biomass, such as the thermochemical process, present a strategic advantage to the economy of the biorefinery as it can use feedstocks with the lowest delivered cost across the year.

The objective of this research was to determine how the alcohol yields and GHG emissions from the NREL thermochemical ethanol production model vary with incoming feedstock characteristics. Six feedstocks were examined and used as input to the NREL process simulation in AspenPlus. On a gate-to-gate basis, GHG emissions varied with incoming feedstock composition and moisture content.

3.3 Methods

3.3.1 Gasification process simulation

In order to perform a life cycle assessment of a production process, material and energy balance data are needed to build a life cycle inventory (LCI). Since there are no commercial cellulosic ethanol production processes currently in operation, process simulation was used to generate these values. A thermochemical ethanol conversion process simulation developed by NREL (Aden et al. 2007) was used. This model performs energy and material balances based on the incoming biomass feed rate and composition. These balances are based on correlations and data obtained from the Battelle coal gasifier (van der Drift et al. 2001). The simulation was operated in Aspen Plus version 2004.1, as newer versions of Aspen Plus were unable to run the model.

3.3.1.1 Major unit process description

The thermochemical process is broken down into seven major process areas, Figure 3-1. Each area is comprised of multiple unit operations such as reactors, separations, heat exchangers, and many other operations that alter the matter within the process. The hundreds of unit processes are grouped into seven hierarchy groupings within the Aspen Plus simulation. The following describes the unit processes within Figure 3-1.

A100 Feedstock Handling and drying: The incoming feedstock is dried and screened to remove unusable biomass and contaminants. Flue gas from the char combustor and syngas boiler is the primary source of heat for drying. Biomass moisture content is reduced to around 5%.

A200 Gasification: Incoming biomass is further heated by olivine, sand like substance, circulated from the char combustor. Endothermic reactions release syngas, primarily CO and H_2 in the gasifier.

A300 Gas cleanup and conditioning: tars and other hydrocarbons are reformed into CO and H_2, syngas is cooled/quenched, and acid gas is removed and reduced to sulfur. Syngas contaminants or “Acid gases” such as CO2 and H2S are removed in a monoethanoamine-based scrubbing system. Finally, H2S is further catalytically reduced to sulfur. These cleanup steps are critical to preventing both catalyst fouling and poisoning in the subsequent alcohol synthesis steps.

A400Alcohol synthesis: Once the syngas is cleaned, it can then be converted to alcohols using a fixed bed reactor. In the NREL process, this is accomplished with a sulfur tolerant molybdenum disulfide catalyst. Unconverted syngas is primarily recycled back to the tar reformer for additional cycles through alcohol synthesis. A purge stream of unreacted syngas is sent to the tar reformer catalyst regenerator as fuel.

A500 Alcohol separation: Within this process area, the mixed alcohol stream is depressurized in preparation for dehydration using a molecular sieve. Once water is removed from the alcohol stream, a distillation column is used to separate methanol and ethanol from higher alcohols. A second distillation column separates the methanol from the ethanol final product. The higher alcohols are sold as a co-product, while most of the methanol is first recycled back to molecular sieve to flush adsorbed water, and then returned to the input of the synthesis reactor to help maximize ethanol production.

A600 Power and steam: Steam for process heating and shaft work is generated from the highly integrated reuse of process energy. Heat exchanging both boiler feed water and steam with high temperature flue and syngas streams is used in conjunction with heat recovered from alcohol synthesis to created superheated steam for power generation. Turbo generators then generate electricity as well as extract lower pressure steam to meet any remaining process energy requirements. The tar reformer catalyst regenerator is configured to burn raw syngas to provide any additional process energy, and allow the model biorefinery to be energy independent.

A700 Utilities: Low quality steam from power production and other unit processes are condensed using cooling towers fed by well water. The condensate is recycled back to the process for further use.

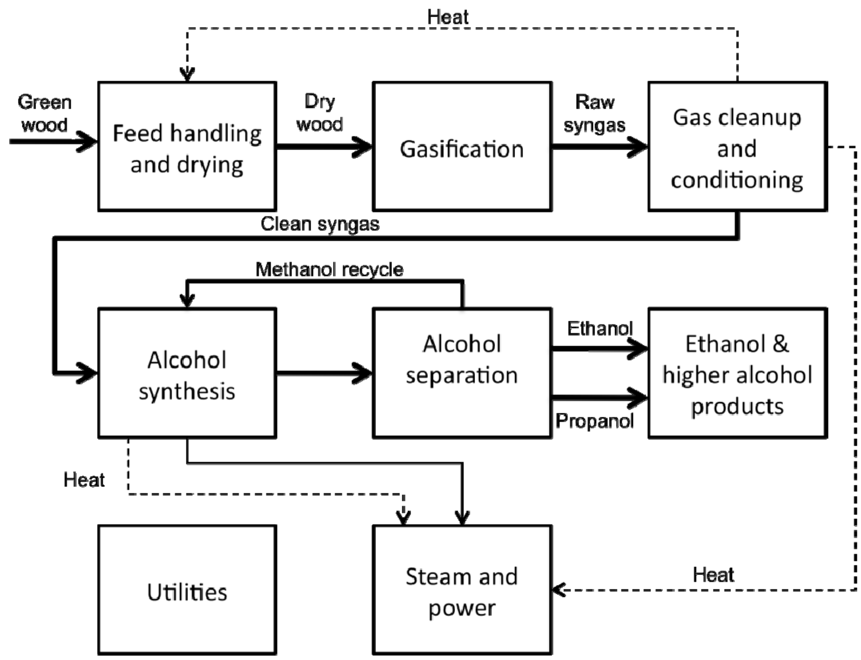

Figure 3-1: Major unit process for NREL thermochemical alcohol conversion process (Phillips 2007)

This process description presents the basic unit processes of the thermochemical conversion pathway. A detailed process description is included in (Phillips 2007) technical feasibility study.

3.3.1.2 Model version and supporting files

The Aspen Plus simulation model was downloaded from the NREL Biorefinery Analysis Process Models website. To run the simulation five files were downloaded from NREL: Aspen file sp0612M.bkp, two Fortran files contained in "Fortran Mixed Alcohols.zip", aspen tool kit files in "AspenToolKit.zip", and a simulation analysis file SP0612.xls. The Aspen, Fortran, and toolkit files are required to run the simulation while the excel analysis file assisted in the analysis of results.

To fully utilize the simulation and analysis spreadsheet, several additional pieces of software were required and downloaded from other sources. As the Aspen model used correlations calculated in Fortran, a compiler was needed to operate the model. Newer Fortran compilers were run with the model but were unsuccessful. As a result of this, the original version FORTRAN 2004.1 was used. Finding this Fortran compiler was difficult as it is no longer produced or supported by the company. However, it can be bought from some select software vendors.

After installing all the original programs and software used to create the simulation, the model ran and computed results correctly. Without any component of the software, the model would not run or compute results. Therefore, anyone attempting to use this program must pay particular attention to attaining the correct software and program versions.

3.3.1.3 Simulation modification

To meet the needs of this study, several modifications were made to the NREL thermochemical model. Several aspects of the model were not activated as received from the NREL website. One of these deactivated features was the input parameter calculator "SETFEED". The Fortran code was updated and the calculator was modified to write the input parameters into the incoming biomass stream.

Depending on the incoming feedstock flow rate, composition, and moisture content, the power production was adjusted to meet the needs of the process. This was done through manually changing the design specification "REFTEMP". The temperature was adjusted in the positive direction to create more energy and negative direction to produce less energy. The model was run multiple times until the WNET stream (net energy production or use) was within the range of -50 to +50 horsepower. This range was chosen as hp variation at this level did not significantly affect the results (less than 0.7% of alcohol yield). The manual iteration process was time consuming but unavoidable as the model would not converge using a traditional controller for this parameter.

3.3.1.4 Operation parameters

To demonstrate model characteristics, multiple input parameters were manipulated. The original feed rate of 700,000 tonnes per year of dry biomass was maintained while changing the biomass type and moisture content, Table 3-2.

In total, six biomass types were examined in addition to the original hybrid poplar feedstock, these feedstocks were selected based on extensive literature review to identify potential feedstock for energy conversion in Southern U.S. (Gonzalez, Phillips et al. 2010; Gonzalez, Treasure et al. 2011). However, the moisture content of the hybrid poplar was changed to 45% to match the other forest-based feedstocks. The moisture content of the energy crops and agricultural residue were set at 16%. Both the ultimate and proximate analyses for each biomass type are included in Table 3-2. A sensitivity analysis around moisture and ash content was performed and described in further detail in the sensitivity analysis section.

Table 3-2: Biomass composition of studied lignocellulosic materials (Johnson, Adam et al. 1994; Adebayo, Wang et al. 2009; Yan, Acharjee et al. 2009; Heo, Park et al. 2010)

	Ultimate Analysis						Proximate Analysis			
Feedstock type	% C	% H	% N	% O	% S	% Ash	% Fixed Carbon	% Volatile Matter	% Ash	% Moisture Content
Eucalyptus salina (1)	49.74	5.95	0.20	42.59	0.02	0.98	18.19	81.06	0.98	45
Mixed hardwoods (2)	50.43	6.54	0	42.48	0	0.6	18.94	80.39	0.67	45
Loblolly (3)	51.85	6.45	0	41.3	0	0.45	14.21	85.34	0.45	45
Corn stover (4)	46.6	5.7	0.7	39.4	0.1	11.9	21.1	72.5	11.9	16
Switch grass (5)	47.26	5.60	0.58	40.63	0.08	5.84	20.57	74.25	5.84	16
Miscanthus (6)	48	6	0.1	45.9	0	1.4	15.7	74.9	1.4	16

3.4 LCA methodology

3.4.1 Goal & scope

The goal of this study was to determine how various feedstocks impact the GHG emissions from the thermochemical ethanol pathway. By examining the process on a gate-to-gate basis, the dependence of GHG emissions on feedstock composition was explored. The results from this study will be used to help select appropriate biomass sources for the thermochemical conversion process.

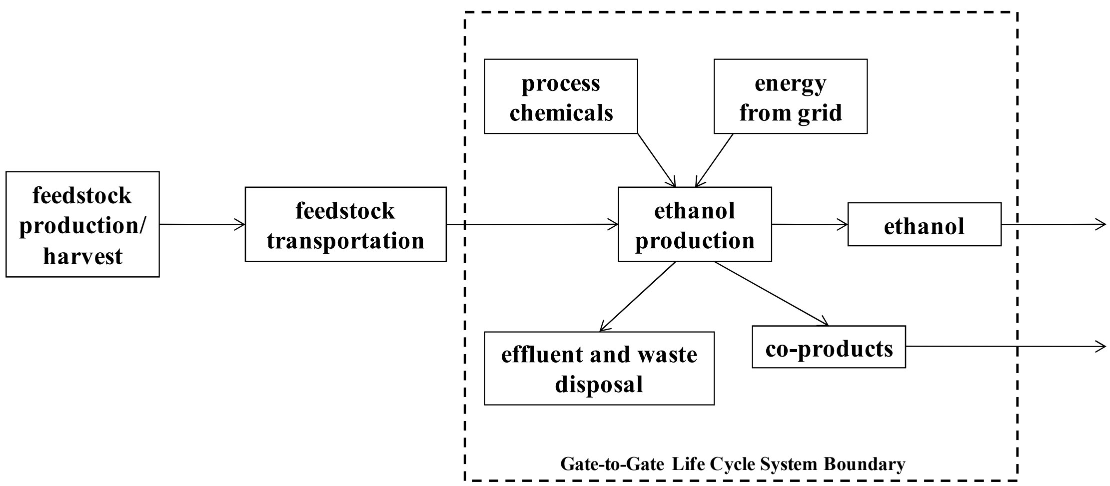

Figure 3-2: Life cycle inventory analysis system boundaries (gate-to-gate analysis)

3.4.2 Data sources

To do a complete gate-to-gate analysis of the described process, several different data sources were used. The process simulation was the major source for process data and related emissions. However, the simulation and design were based on numerous studies and extensive work done by NREL. More information pertaining to the simulation data sources are documented (Phillips et al. 2007).

For emissions related to process chemicals and production wastes, a variety of data sources were used. GHG emission data from the United States Life Cycle Inventory (USLCI) were used whenever available. To track all the GHG emissions related to these substances and all the sub-processes, SimaPro was used.

To calculate the emissions from the magnesium oxide (MgO) required preventing glass buildup within the gasifier, the USLCI database was not helpful and a literature review was required. A report from the European Commission (IPPC.Bureau 2009) described the MgO production process providing converting emissions and energy usages. Data from the IPCC 2006 report and the USLCI database were used to convert fuel requirements to GHG emissions for petroleum coke, fuel oil, and natural gas. In addition to these fuels, the process required electricity, which was converted to GHG emissions using emissions factors for North America, provided by the Energy Information Administration (EIA).

3.4.3 Parameters examined

Due to the mandated GHG reduction thresholds for cellulosic ethanol, GHGs were the primary focus of this study. These gases include carbon dioxide, methane and nitrous oxide. However, as nitrous oxide and methane are stronger GHGs, global warming potentials (GWP) from the IPPC were used to calculate GHGs in CO_2 equivalents. These GWP have been updated several times since 1996 to the most recent in 2006, Table 3-3. Data from the most recent report in 2006 were used for this analysis.

Table 3-3: Global warming potential of methane and nitrous oxide (IPCC 2006)

CO_2 equivalents Revision Year	CH_4	N_2O
1996	21	310
2001	23	296
2006	25	298

3.5 Results and discussion

3.5.1 Life cycle inventory

As this study was concerned primarily with the variation of GHG emission from different feedstocks, the life cycle inventory was done on a gate-to-gate basis. However, upstream emissions from process chemicals were included while emissions from feedstock procurement and production were not. Emissions from the process chemicals were calculated using data from several sources and reported in kg of CO_2 equivalents per kg of chemical usage, Table 3-4. As the process chemicals contributed minimally, Table 3-5, to the overall emissions, some simplifying assumptions were taken when calculating the emissions factors. Additionally, emissions due to clear water chemical use were not included as they do not vary with feedstock type and were less than one kg per hour.

Table 3-4: GHG emission factors for process chemicals and non-wood inputs (2,3,4,5,6: (National Renewable Energy Laboratory 2010), 1: (WRI and WBCSD 2004; " 2009; Bureau.IPPC 2009; IPPC 2009; IPPC.Bureau 2009)

Material/process	Units	Emissions factor	Source
MgO	kg $CO_{2\ eq.}$/kg	3.77E+00	1
Olivine	kg $CO_{2\ eq.}$/kg	3.92E-02	2
Molydbenum	kg $CO_{2\ eq.}$/kg	1.08E+01	3
Waste treatment	kg $CO_{2\ eq.}$/kg	6.37E-07	4
Landfill transportation	kg $CO_{2\ eq.}$/tonne*km	1.42E-01	5
Landfill	kg $CO_{2\ eq.}$/kg	2.45E-03	6

Table 3-5: Variation in GHG emission from process chemicals and wastes

Feedstock	Hybrid poplar	Mixed hardwood	Loblolly pine	Eucalyptus	Corn stover	Switchgrass	Miscanthus
kg CO_2 eq. hour	27	22.70	20.89	27.76	167.56	89.08	32.89
% of total process GHGs	0.03%	0.02%	0.02%	0.03%	0.17%	0.09%	0.03%

3.5.2 Gasification process

3.5.2.1 Material balance

The Aspen process simulation generated results for each feedstock scenario. However, to ensure proper operation, a material balance was manually performed and compared to results from Phillips 2007. All inputs, outputs and system closure are reported in Table 3-6 for the base case scenario of hybrid poplar. These data are organized by actual streams that exit the system and are organized from least to greatest within the table. The overall system closure was 98.5%.

This level of closure is generally accepted, especially with process models of this size and detail. Additionally, these results were comparable to the results reported in Philips et al. 2007.

Table 3-6: Hybrid poplar material balance and major input and output stream flows

Input Stream	kg/hr	Ouput Stream	kg/hr
Clear water chemicals	3.70E-01	Catalyst purge	4.84E-01
Make up catalyst	4.84E-01	Vent to atmosphere	8.63E-01
MgO	3.16E+00	Solid waste	3.60E+01
Char combuster water	1.10E+02	Sulfur storage	5.11E+01
Lo-Cat oxidizer air	1.24E+02	Air to atmosphere	1.27E+02
Make up olivine	2.44E+02	Water to treatment plant	5.49E+02
Steam make up water	1.48E+04	Sand fly ash	1.10E+03
Cooling make up water	3.90E+04	Windage to atmosphere	3.70E+03
Combustion air	1.19E+05	Higher alcohols	4.15E+03
Feedstock	1.52E+05	Blow turbine blow down	7.71E+03
Combustion air	1.95E+05	Ethanol product	2.30E+04
Condensor water	1.85E+06	CO2 vent	2.48E+04
		Flue gas stack	4.24E+05
		Evaporated to atmosphere	1.92E+06
Total in	2.37E+06	Total out	2.41E+06
% System closure	98.5%		

After determining the convergence (more than 97% closure) of the model, six additional feedstock compositions were used as input for additional simulations. The results from the various feedstocks were compared to the results from hybrid poplar or the “base case”. These results are reported in percent change calculated.

3.5.2.2 Alcohol yield

When comparing ethanol yields from various feedstocks, three numbers are of particular importance: liters of ethanol, liters of propanol, and total liters of ethanol equivalents. The propanol was converted to ethanol equivalents by energy content ratio. This ratio, energy content of ethanol divided by energy content of propanol, was approximately 0.68 (Design Institute for Physical Properties 2011). When compared to hybrid poplar, loblolly pine produced the highest yields while corn stover produced the lowest, Table 3-7. Overall, the forest based feedstocks all produced higher yields than the other energy crops or residues; although, eucalyptus was slightly lower than hybrid poplar. The corn stover yield was the lowest, with a 13.0% decrease relative to hybrid poplar followed by switchgrass and miscanthus.

Alcohol yields are highly influenced by two parameters: moisture and ash content. It is worth noting that the forest-based biomass was processed at a moisture content of 45% while the non-wood feedstocks were processed at 16%. The lower moisture content of the non-wood feedstocks offset the negative effects of the higher ash content. When comparing feedstocks with equal moisture content, lower ash contents consistently produced higher alcohol yields. The model behaves in this way for several reasons. First, with lower ash content, there is more available carbon to convert to alcohols at the same feed rate. Second, with higher ash contents, the energy requirements of the electrostatic precipitators are greater. Third, biomass of higher moisture content requires additional process heat to achieve the required moisture content for the gasifier. This energy is created through burning raw un-cleaned syngas in a boiler. As a result of less clean syngas production, the alcohol yield decreased.

Table 3-7: Alcohol yield variation for various feedstocks expressed in percent change from hybrid poplar

Feedstock	Hybrid poplar	Mixed hwd	Loblolly	Eucalyptus	Corn stover	Switch grass	Miscanthus
Units	(l/OD tonne)	Δ %	Δ %	Δ %	Δ %	Δ %	Δ %
Ethanol	350	1.8%	5.6%	-3.5%	-13.0%	-5.3%	-5.5%
Propanol	62	1.8%	5.6%	-3.5%	-12.8%	-5.1%	-5.3%
Total alcohol	441	1.8%	5.6%	-3.5%	-13.0%	-5.3%	-5.4%

3.5.2.3 Greenhouse gas emissions

Emissions from this ethanol conversion pathway include many air pollutants, liquid pollutants and solid waste. However, the purpose of this paper was to focus primarily on GHG emissions variation due to feedstock compositions and only the GHG emissions resulting from non-air emissions were calculated.

There are 14 streams exiting the conversion process, however, only two significantly contribute to GHG emissions. The flue gas stream released approximately 77% of the GHGs while the CO_2 vent released 23%. The total GHG emissions from the process utilizing hybrid poplar were approximately $1.03X10^5$ kg per hour, or 2.8 kg CO_2 equivalents per liter of ethanol produced. Compared to hybrid poplar, the loblolly pine produced the lowest GHG emission with a -5.4% change.

The non-wood biomass types produced similar or reduced GHG emissions compared to hybrid poplar ranging from -2.5% to -0.3% change in kg CO_2 eq. per liter, Table 3-8. Despite higher ash content of the non-wood species, the GHG emissions were decreased. This reduction was due to the low incoming moisture content, 16%, of the non-wood species compared to the 45% moisture content of hybrid poplar. With lower heating requirements in the feedstock preparation area (A100), more syngas was available for alcohol syntheses. Clearly, the effect of moisture content is significant and can be more influential than even the ash content.

Table 3-8: GHG emission variation for various feedstocks expressed in percent change from hybrid poplar

GHG Emissios	Hybrid poplar (NREL)	Mixed hardwood	Loblolly pine	Eucalyptus	Corn stover	Switchgrass	Miscanthus
Units	-	Δ %	Δ %	Δ %	Δ %	Δ %	Δ %
kg CO2 Eq. per OD tonne	1235	-2.34%	-0.06%	-0.81%	-12.55%	-7.95%	-7.79%
kg CO2 eq. per l ethanol	2.8	-4.08%	-5.36%	2.80%	-0.35%	-2.84%	-2.50%

Since the gasification process is powered entirely by biomass, there are not direct fossil fuel emissions from the process. However, raw materials used in the process have fossil fuel based emissions associated with them. The process chemicals previously discussed are the source of fossil fuel based emissions within this study. However, it is should be noted that the feedstock production would be the major source of fossil fuel emissions if it were within the scope of the study. Despite this, the fossil fuel based emissions were magnitudes smaller than the biogenic CO_2 GHG emissions.

Table 9: Biogenic and fossil fuel based GHG emissions

Feedstock	Hybrid poplar	Mixed hardwood	Loblolly pine	Eucalyptus	Corn stover	Switchgrass	Miscanthus
Fossil kg CO2 eq. hr	2.68E+01	2.27E+01	2.09E+01	2.78E+01	1.68E+02	8.91E+01	3.29E+01
Biogenic kg CO_2 eq. hr	1.03E+05	1.00E+05	1.03E+05	1.02E+05	9.67E+04	1.01E+05	9.49E+04

3.5.3 Sensitivity analysis

As the moisture (van der Drift et al. 2001) and ash (Phillips 2007) content are the major influencers of process efficiencies and GHG emissions and are expected to vary, further analysis was performed define the correlations between these two variables and the total yield and GHG emissions. Loblolly pine, the most promising feedstock based on yield and GHG emissions, was chosen for the sensitivity analysis.

The moisture content manipulation was straight forward, requiring only an input change within the Aspen simulation. Moisture contents (weight of oven dried wood/total weight of wet wood) examined included 35%, 45%, and 55%. This range covers most moisture contents expected for loblolly pine. To examine the effects of moisture content, alcohol yield and kilograms CO_2 per liter were plotted against moisture content, Figure 3-3. The alcohol yield was negatively correlated with moisture content varying approximately 15%. However, a positive correlation was observed between the moisture content and the GHG emissions.

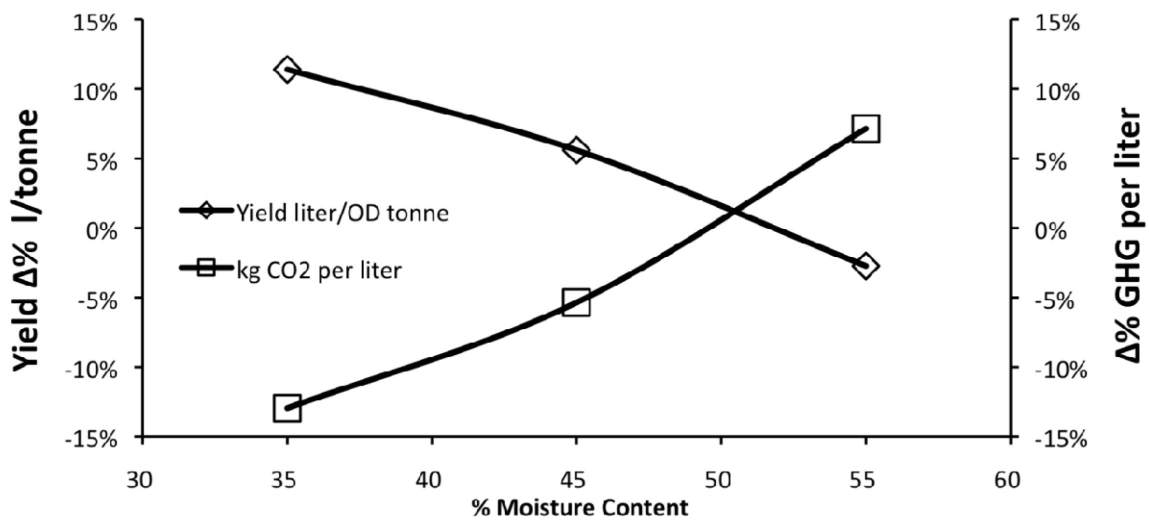

Figure 3-3: Effects of moisture content on GHG emissions and alcohol yield (lines for visual appearance only)

Biomass ash content heavily influenced both the yield and GHG emissions for all six biomass types. Due to the importance of this parameter, a sensitivity analysis was performed for loblolly pine varying the ash content from 0.4% to 15%. The ash content was increased and oxygen, carbon and hydrogen were decreased proportionally to maintain a balance of 100%. Keeping the oxygen, carbon and hydrogen ratios constant was critical to isolate and understand the effects of higher ash content. The volatile and fixed carbon were also adjusted proportionally to compensate for the increased ash and to maintain the 100% balance. However, pine ash content does not vary drastically from species to species and the range of ash contents examined would never be observed in real pine species.

Despite this, this analysis showed the significance of ash disregarding the other variables. All compositions used for this sensitivity are listed in Table 3-9. Additionally, the moisture content was held constant at 45%.

Table 3-9: Biomass composition used for ash sensitivity analysis

	Ultimate Analysis						Proximate Analysis			
Loblolly pine	% C	% H	% N	% O	% S	% Ash	% Fixed Carbon	% Volatile Matter	% Ash	% Moisture Content
A1	51.85	6.45	0	41.3	0	0.4	14.21	85.34	0.45	45
A2	49.45	6.15	0	39.39	0	5	13.56	81.44	5	45
A3	46.85	5.82	0	37.32	0	10	12.84	77.15	10	45
A4	44.25	5.05	0	33.25	0	15	12.13	72.87	15	45

For this analysis, the simulation results for feedstocks, listed in Table 3-9, were plotted as yield and GHG emissions per liter as a function of ash content, Figure 3-4. As ash content increased, the yield decreased from around 5% to negative 16%. However, the GHG emissions per liter only experienced an increase from around negative 6% to 14%. Less usable carbon to convert to syngas was the primary driver of these trends. With less syngas produced, the alcohol production will decrease. This sensitivity analysis further supports the previous conclusion of the negative correlation between ash content and alcohol yields and the positive correlation between ash content and GHG emissions.

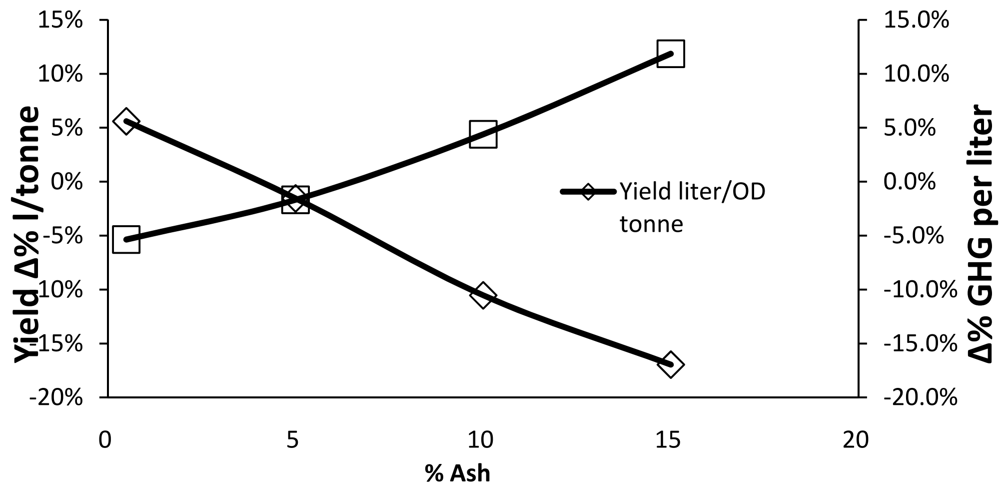

Figure 3-4: Effects of ash content on alcohol yields and GHG emissions (lines for visual appearance only)

3.6 Cradle-to-grave analysis

To understand the broader impacts of cellulosic ethanol, a cradle-to-grave analysis accounting for all inputs and outputs from feedstock production to end use was performed. Loblolly pine was the chosen feedstock due to the availability in the southeast and the lower GHG emissions discussed in the previous sections. Through analyzing ethanol in this manner, an overall impact of its production and use can be compared to gasoline. This type of analysis is required by the EPA to determine the overall GHG reductions and the fuel classification under the Renewable Fuels Standard.

3.6.1 Cradle-to-grave methods

The thermochemical simulation previously discussed provided emissions data for the production process while SimaPro and GREET provided feedstock production and fuel use emissions. This study focused on global warming potential (GWP) however, the impacts of acidification, carcinogens, non carcinogens, respiratory effects, eutrophication, ozone depletion, ecotoxicity, and smog impact categories were significant. The environmental impacts were calculated using the TRACI2 V3.01 impact assessment method in SimaPro. The LCA model incorporated data from both the United States Life Cycle Assessment Inventory (USLCI) and Ecoinvent database. The overall impacts were calculated for 1 MJ fuel used in a passenger vehicle.

3.6.2 Product stages

3.6.2.1 Feedstock production and harvest

The total feedstock emissions were calculated using the "Pulp chips, at saw mill, US SE/kg/US" record within SimaPro. This feedstock production model utilizes data from the USLCI database to account for all emissions from reforesting, forest management, wood harvesting and transportation. This record was slightly modified to account for the carbon sequestered during tree growth. This value was calculated by assuming the wood was approximately half carbon, sequestered from the atmosphere, which was then converted to CO_2 equivalents by molecular weight ratios.

3.6.2.2 Feedstock transport

A conservative transportation distance of 50 miles was used for this analysis. Ronalds, 2009 indicates biomass collection radii at this production level to be 40 miles at standard production levels. As vehicles must follow roads that do not travel straight lines, the real transportation distance is greater than the radius.

3.6.2.3 Conversion technology

The ethanol production process analyzed in the cradle-to-grave analysis was the same as described within the gate-to-gate analysis. For more details refer to section 3.3.1.

Gasoline production emissions were calculated using SimaPro and the USLCI database. The LCA record "Gasoline, at refinery/l/US" provided cradle-to-gate emissions for gasoline production. This process accounts for the extraction all conversion processes required to produce gasoline.

3.6.2.4 Fuel distribution

A combination truck using diesel fuel was used to transport ethanol from the production facility to blending cite. Trucks carrying fuel to the blending site were assumed to travel 50 miles to the blending site with a 50 mile empty return trip (Wonjor, 2010).

3.6.2.5 End use

End use data was based on light duty passenger vehicles attained from the GREET model (Wang, 2008). To facilitate a direct comparison, emissions from a 100% ethanol fuel were considered, however, blends of this purity would not be practical with the current infrastructure and vehicles. The 100% ethanol comparison to gasoline will show the direct GHG savings due to biofuel production and use. These emission savings will be used to classify the biofuel under EISA biofuel classifications (EISA, 2007).

Default values within greet were used to generate GHG emissions for the gasoline comparison. Additionally, the gasoline for comparison was assumed to be 50% / 50% reformulated and conventional gasoline. Emission factors for each process are listed in Table 3-10

Table 3-10: Cradle-to-grave emission factors

Process	value	Units	Source
Transportation	0.14	lb CO_2 per ton*mile	USLCI
Combustion gasoline	0.16	lb CO_2 per MJ fuel combusted	GREET
Combustion ethanol	0.17	lb CO_2 per MJ fuel combusted	GREET
Carbon sequestered	1.80	ton CO_2 per ton OD wood	Daystar et al. 2011
Pulp chips production	150	lb CO_2 per OD ton wood	CORRIM

3.6.3 LCA assumptions

- Pine plantations are sustainably managed
- Forest residues are considered to be a waste of timber/pulp wood production
- Below ground carbon and biomass is considered to be at steady state
- Heating value of gasoline assumed to be 132 MJ/gallon (ORNL)
- Heating value of ethanol assumed to be 89 MJ/gallon (ORNL)

3.6.4 Results

Emissions from ethanol were broken down into six categories including sequestered carbon, raw material transport, raw materials, fuel production, fuel transport and fuel combustion. Fuel combustion and fuel production contributed to 98% of the overall emissions, Figure 3-5. However, carbon sequestered in tree growth offset 86.95% of the overall emissions from the process.

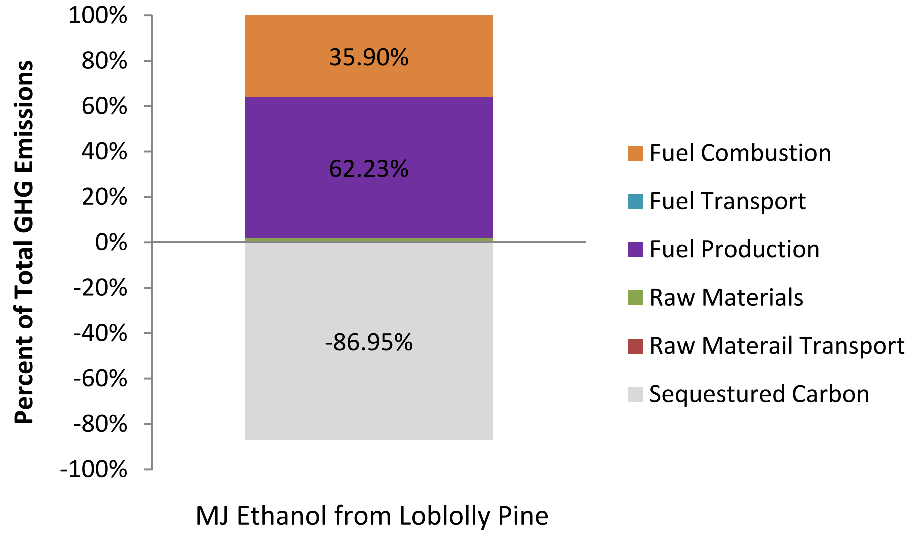

Figure 3-5: GHG emissions from ethanol and gasoline

To gain an understanding of the GHG reductions due to the production and use of cellulosic ethanol, a gasoline reference system is used. Since the energy content of gasoline and ethanol is different, it is critical to compare them on a per energy basis. The emissions from the production and use of 1 MJ of fuel is shown in Figure 3-6.

Gasoline and ethanol have similar emissions in all categories except fuel production and sequestered carbon. Overall, the production and use of ethanol results in a GHG emissions reduction of 68.7%. This emissions reduction level would qualify the fuel under the RFS as "cellulosic biofuel".

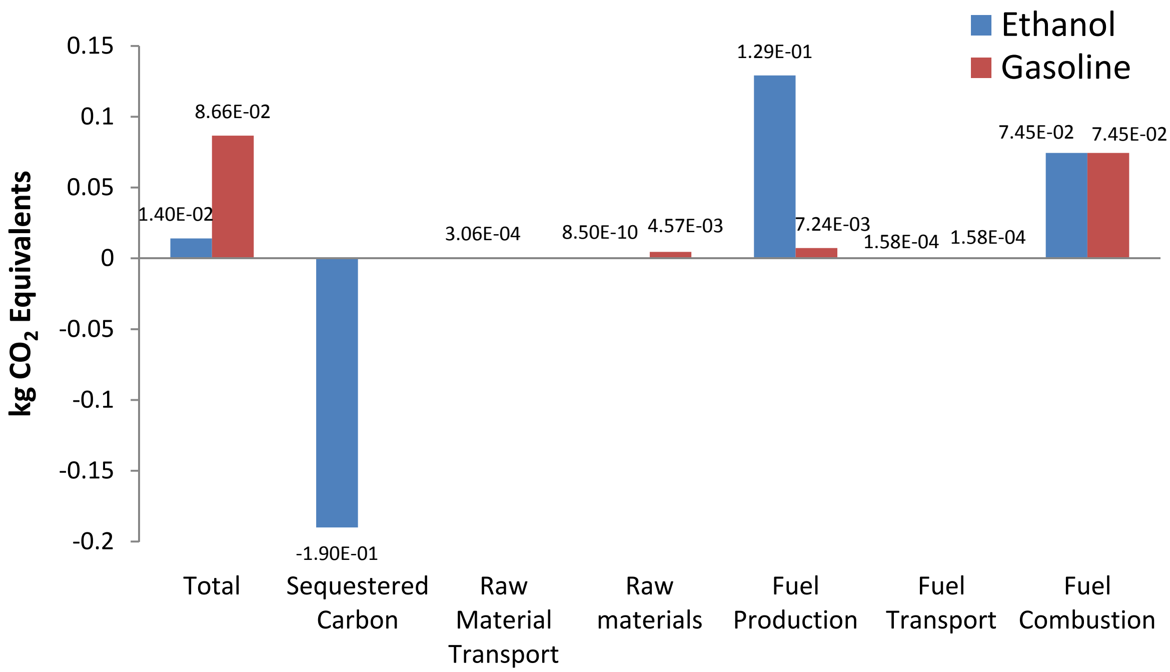

Figure 3-6: GHG emission comparison for gasoline and ethanol

3.7 Summary and conclusions

To understand the potential GHG savings of cellulosic ethanol and the significance of the emissions resulting from the thermochemical ethanol conversion process, a cradle-to-grave analysis was performed utilizing a loblolly pine feedstock. When compared to a gasoline reference, a 68% GHG reduction was realized. The results of this study also indicate that the conversion process contributed 62% of the overall emissions on a cradle-to-grave basis. As the conversion process represents the majority of the overall emissions, further analysis around the conversion was considered critical to the reduction of the overall GHG emissions.

Through process simulation and a life cycle inventory, a gate-to-gate GHG analysis around the thermochemical ethanol production pathway was performed. Six biomass types were compared on a basis of yield and GHG emissions per liter of fuel. Of these six feedstocks, the forest-based biomass including pine, mixed hardwood and eucalyptus performed better than the non-wood biomass types including corn stover, switchgrass and miscanthus. However, when compared to the feedstock originally studied in the NREL report Phillips et al. 2007, hybrid poplar, all six examined feedstocks resulted in a lower GHG emission per liter.

Two major drivers of GHG emissions and yield were identified. First, high ash content decreases alcohol yields and increases GHG emissions per liter of ethanol. When the wood based biomass with moisture contents of 45% are compared, the lower ash biomass resulted in lower GHG emissions and higher alcohol yields. Additionally, when comparing the non-wood biomass types, all having a moisture content of 16%, the same trend was observed. This high sensitivity to ash content was further explored varying pine ash content from 0.4% to 15%. Over this range, the trend of lower yields and higher GHG emissions per liter with increased ash content was confirmed. The yield varied by 21% and the GHG emissions per liter varied by 19%.

Moisture content significantly influenced the simulation results. For wood-based biomass, the examined moisture content was constant, however, the moisture content for the non-wood biomass set at a lower level of 16%. This difference in moisture content inherently improves the performance of the non-wood biomass types despite high ash contents. Moisture content influenced biomass performance by requiring more drying and dirty syngas burning ultimately lowering alcohol yields. To further examine the effects of moisture content, the simulation was run with pine at moisture contents of 35%, 45%, and 55%. From this analysis, it was concluded that moisture content in pine could affect the alcohol yield by approximately 15% and GHG emissions per liter by around 20% over this moisture content range.

In conclusion, the six examined biomass types resulted lower GHG emissions when compared to the NREL hybrid poplar feedstock. However, yields for non-wood biomass types were significantly lower, possibly inhibiting the financial feasibility of these feedstocks. Additionally, biomass with low ash and moisture content is best suited for this conversion process. It may be beneficial to allow biomass additional drying times to improve system performance. However, to gain a full understanding of the overall life cycle emissions of these feedstocks, a detailed feedstock model will be required in addition to this study.

3.8 Acknowledgments

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4 Economics of cellulosic ethanol production in a thermochemical pathway for softwood, hardwood, corn stover and switchgrass.

4.1 Abstract

The economics of producing cellulosic ethanol using loblolly pine, natural mixed hardwood, Eucalyptus, corn stover and switchgrass as feedstock were simulated in Aspen using the thermochemical process via indirect gasification and mixed alcohol synthesis developed by NREL. Outputs from the simulation were linked to an economic analysis spreadsheet to estimate NPV, IRR, payback and to run further sensitivity analysis of the different combinations of feedstocks. Results indicate that forest-based feedstocks including loblolly pine, natural hardwood and eucalyptus may present more attractive financial returns when compared to switchgrass and corn stover, mainly due to their composition (% C, % H, % ash) and alcohol yield. Simulated alcohol yields from forest-based feedstock were significantly higher than from switchgrass and corn stover. Models fed with switchgrass and corn stover, also demonstrated greater sensitivity to changes in ethanol price, alcohol yield, CAPEX and biomass costs. Furthermore, the moisture content of receiving feedstocks greatly affected the economics of the biorefinery. A difference of 10% in the moisture content of the receiving feedstock affected the NPV of the simulated project by US$66 + million.

Keywords: Gasification, thermochemical, eucalyptus, hardwood, pine, corn stover, swtichgrass, ethanol, bioenergy.

4.2 Introduction

Brazil and the United States are the major producers of bioethanol (mainly from sugar cane and corn starch respectively), with a combined production representing ~86% of world's total output for 2009 at approximately 75,571 thousand million liters of ethanol in total (Goldemberg, 2007; RFA, 2010). The United States alone has dramatically increased bioethanol production by 210% since 2005 (RFA, 2010). Despite successes in first generation bioethanol production, there has been special interest around bringing the production of cellulosic ethanol and biodiesel (second generation biofuels) to industrially relevant levels, using cellulosic feedstocks such as grasses (switchgrass, miscanthus) and forest biomass (forest residues, sawdust and industrial waste) as raw materials. The emphasis on increasing the production of second generation biofuels comes from issues particular to 1st generation bioethanol production, as reduced food supply and rising prices have been frequently attributed to the use of corn to produce fuel (Foust et al., 2009; Mitchell, 2008). This debate, often referred to as "food versus fuel," is further exacerbated by estimates that current corn supplies would be insufficient to meet liquid biofuel production targets as mandated by U.S. federal government standards. In response to these issues, pressure to alleviate U.S. commerce imbalances, potential to enhance national security, and establish the basis for a clean energy industry, the Environmental Protection Agency (EPA) has set ambitious cellulosic biofuel production targets of 0.25 billion gallons (bil gal) for 2011, 1 bil gal for 2013 and 16 bil gal for 2022 (EPA, 2010). These mandates have come with unprecedented research and demonstration plant funding. Government-funded examples include three USDOE funded centers (US$ 125 million each), with additional funding for research exceeding US$ 786.5 million not including substantial private interest funding. In the private sector, BP has provided a leading example of biofuels support by funding a bioenergy center for US$500 million (Baker & Keisler, 2009; Schuetzle et al., 2007). Despite extensive efforts of public and private entities to ramp up second generation biofuels, there is not a single commercial facility producing cellulosic ethanol in the U.S. as of 4th quarter 2010. Current barriers to economically feasible cellulosic ethanol production have been widely researched and discussed. Through extensive feasibility studies, several major barriers have been identified, the most important of which are biomass cost and availability (Gonzalez et al., 2008; Gonzalez et al., 2010b; Wu et al., 2010), pretreatment costs, high capital expenditure (CAPEX), equipment scale up and overall production costs (Aden et al., 2002; Gonzalez et al., 2010a; Mosier et al., 2003; Mosier et al., 2005; Tao & Aden, 2009; Wu et al., 2010; Wyman, 2008; Wyman, 2007). Two major pathways have been clearly identified as the most promising routes for cellulosic ethanol production. , Biochemical conversion is the more heavily supported route and relies mainly on hydrolysis (acid and/or enzymatic hydrolysis) to reduce polymeric carbohydrate chains into fermentable monomeric sugars. The other and less understood approach is thermochemical conversion, with numerous versions and hybrid designs. The major steps in the thermochemical pathway are the production of synthetic gas (syngas) from cellulosic biomass, syngas cleanup and reforming, and subsequent catalytic synthesis to produce alcohol species (Mosier et al., 2005; Mu et al., 2010; Phillips et al., 2007). Economic and life cycle analysis studies designed to compare biochemical and thermochemical pathways do not clearly identify a winning technology for conversion (Foust et al., 2009; Mu et al., 2010). There is, however, a general agreement that market place economics will decide which conversion approach is appropriate (Blaschek & Boateng, 2009; Mu et al., 2010), based on type of biomass available and delivered costs. Biochemical technologies seems to be more feasible in regions where large volumes of consistent biomass are available, while thermochemical pathways are less restrictive and can process virtually any type of raw material (Foust et al., 2009; Mu et al., 2010; Schuetzle et al., 2007). Moreover, some studies suggest that hardwood and herbaceous feedstock are more suitable for biochemical pathways, while more recalcitrant raw materials such as softwood feedstock are better suited to thermochemical processes (Foust et al., 2009; Gonzalez et al., 2010a). Conversion pathways capable of processing several types of biomass may bring strategic advantages to the economy of the biorefinery as it can then utilize feedstocks with the lowest delivered cost across the year. Though the number of publications dealing with economic evaluations of cellulosic ethanol production has increased in recent years, a fair economical comparison between various technologies and biomasses remains a difficult task, mainly because of the different assumptions and reaction yields used. Our paper presents an economic evaluation and sensitivity analysis around the production of cellulosic ethanol using the thermochemical process via indirect gasification and mixed alcohol synthesis as developed by NREL (Phillips et al., 2007). This work also includes a revised and more complete estimation of CAPEX and considers the use of five different feedstocks, compared under the same economic conditions: loblolly pine, natural hardwood, Eucalyptus, corn stover and switchgrass. This manuscript should therefore provide practical information for both investors and academics by examining considerations around raw materials, conversion processes, and profitability.

4.3 Methods

4.3.1 Thermochemical process

The conversion process used for this economic evaluation relies on the thermochemical lignocellulosic biomass to ethanol production process via indirect gasification and mixed alcohols synthesis developed by NREL (Phillips et al., 2007). The overall process is illustrated in Figure 4-1

Within the NREL process there are seven major unit processes including biomass handling and drying, biomass gasification, syngas cleanup and conditioning, catalytic alcohol synthesis and alcohol separation, along with supporting utilities/heat and power processes. Detailed process descriptions are presented in the following sections.

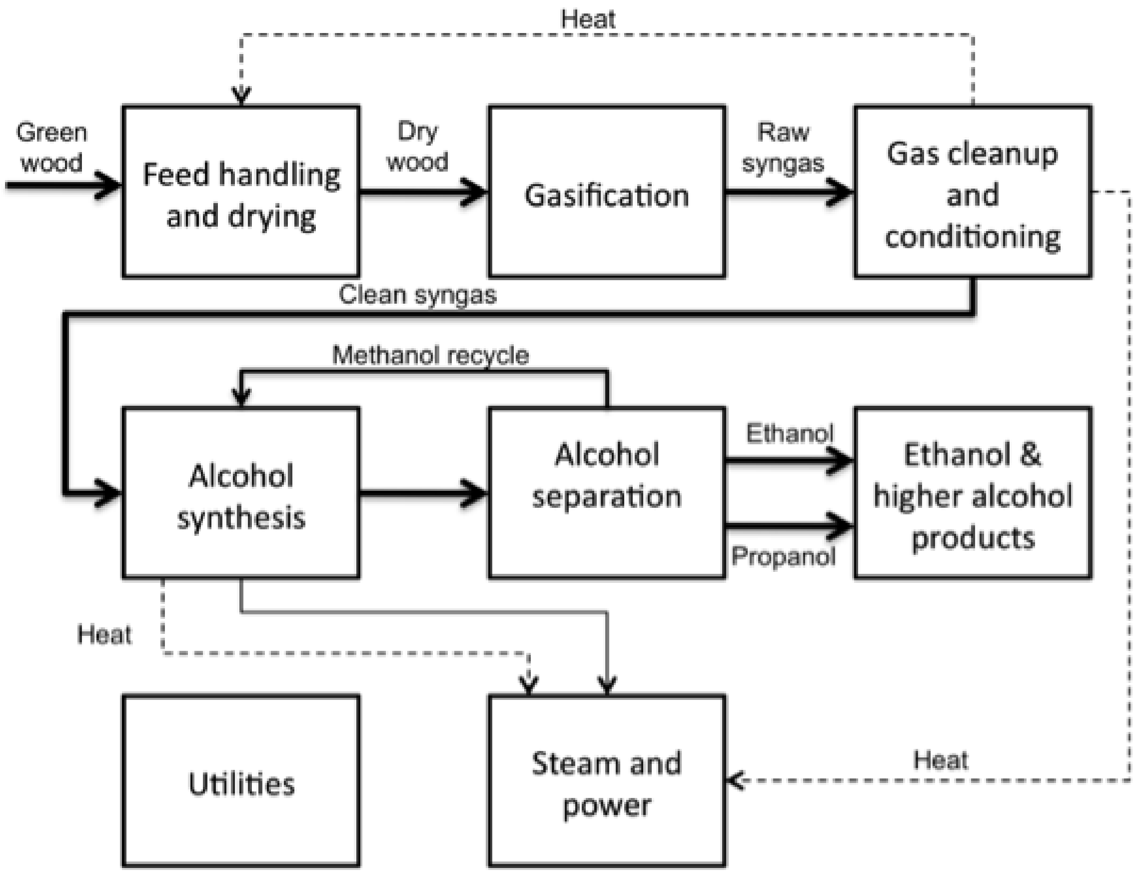

Figure 4-1: Thermochemical ethanol production simplified PFD

4.3.1.1 Major unit process description

Feed preparation

Incoming biomass must be chipped and screened to insure uniform, proper chip size. Additionally, as the gasification step requires low biomass moisture content (~17%) (Phillips et al., 2007), drying is accomplished by direct contact with gasifier char combustor and tar reformer catalyst regenerator flue gas. An immense amount of energy is required to dry this biomass and would be difficult to achieve without using recovered process energy.

Gasification

An indirect gasification process such as the dual-bed design utilized in the NREL system is based on indirect heating of the feedstock. This is achieved by circulating heated olivine between the gasifier and a separate char combustor unit. Char and olivine from the gasifier are burned in the combustor unit, heating the olivine to around 1800˚F. Once recirculated back to the gasifier, the olivine, heats the biomass to a temperature of 1600˚F, supplying the energy for the endothermic gasification reactions. The products of these reactions include CO, H_2, CO_2, CH4, tars, and solid char. This solid char, resulting from fixed carbon deposited on the olivine, is then separated using cyclone filters and sent to the char combustor to close the feedback loop.

Gas cleanup and conditioning

Within this process area, ammonia, tars and other hydrocarbons are reformed into N_2, CO and H_2 respectively in a fluidized bed catalytic reactor. The syngas is cooled/quenched to further reduce particulate loading, by indirect heat exchange and venture scrubbing. Syngas contaminants or "Acid gases" such as CO_2 and H_2S are removed in a monoethanoamine-based scrubbing system. Finally, H_2S is further catalytically reduced to sulfur. These cleanup steps are critical to preventing both catalyst fouling and poisoning in the subsequent alcohol synthesis steps.

Alcohol Synthesis

Once the syngas is clean, it can then be converted to alcohols using a fixed bed reactor. In the NREL process, this is accomplished with a sulfur tolerant molybdenum disulfide catalyst. Unconverted syngas is primarily recycled back to the tar reformer for additional cycles through alcohol synthesis. A purge stream of unreacted syngas is sent to the tar reformer catalyst regenerator as fuel.

Alcohol Separation

Within this process area, the mixed alcohol stream is depressurized in preparation for dehydration using a molecular sieve. Once water is removed from the alcohol stream, a distillation column is used to separate methanol and ethanol from higher alcohols. A second distillation column separates the methanol from the ethanol final product. The higher alcohols are sold as a co-product, while most of the methanol is first recycled back to molecular sieve to flush adsorbed water, and then returned to the input of the synthesis reactor to help maximize ethanol production.

Heat and Power

Steam for process heating and shaft work is generated from the highly integrated reuse of process energy. Heat exchanging both boiler feed water and steam with high temperature flue and syngas streams is used in conjunction with heat recovered from alcohol synthesis to created superheated steam for power generation. Turbo-generators then generate electricity as well as extract lower pressure steam to meet any remaining process energy requirements. The tar reformer catalyst regenerator is configured to burn raw syngas to provide any additional process energy, and allow the model biorefinery to be energy independent.

4.3.2 Feedstock

Within this study five feedstocks were considered, including loblolly pine, southern mixed natural hardwood, Eucalyptus, corn stover and switchgrass. Major assumptions used to estimate biomass delivered costs are listed in

Table 4-1. Annual supply was estimated for 453,567 dry tons (metric tons) or 500,000 BDT (bone dry short tons). Loblolly pine and Eucalyptus biomass delivered cost was estimated assuming a 6% IRR for the forestland owner (stumpage), and assuming 8% IRR to the harvesting contractor and freight cost at market values. These assumptions are similar to 2010 market values and the methodology to estimate delivered cost is similar to the one used by Gonzalez et al 2010 (Gonzalez et al., 2010b). For natural hardwood, all values including stumpage, harvesting, and freight costs were estimated using market values. The estimating approach for switchgrass considers biomass cost including 6% IRR to the farmer, harvesting cost assuming 8% IRR to the harvesting contractor and freight cost using market values. Corn stover cost was estimated based on reported market values and more recent published information. Chemical composition, %C, %H, %O, %N, % fixed carbon, % volatile mater, and % ash assumed for each of the biomass is presented in Table 4-2.

Table 4-1: Biomass delivered cost, rotation length, productivity, moisture content and annual supply

Biomass	Loblolly pine	N. hardwood	Eucalyptus	Corn stover	Switchgrass
$/dry ton	69.4	71.0	69.4	80.3	79.3
Rotation length (years)	11	-	4	-	10
Productivity (dry ton/ha/yr)	17.0	2.2	20.2	4.5	15.7
Moisture content (%)	45%	45%	45%	16%	16%
Covered area (%)	5%	5%	5%	5%	5%
Supply (dry ton/year)	453,597	453,597	453,597	453,597	453,597

Table 4-2: Biomass chemical composition

Feedstock type	% C	% H	% N	% O	% S	% Ash	% Fixed Carbon	% Volatile Matter	% Ash	Source #
Loblolly pine	51.9	6.5	0.0	41.3	0.0	0.4	14.2	85.3	0.5	*1*
N. hardwood	50.4	6.5	0.0	42.5	0.0	0.6	18.9	80.4	0.7	*2*
Eucalyptus	49.7	5.9	0.2	42.6	0.0	1.0	18.2	81.1	1.0	*3*
Corn stover	46.6	5.7	0.7	39.4	0.1	11.9	21.1	72.5	11.9	*3*
Switch grass	47.3	5.6	0.6	40.6	0.1	5.8	20.6	74.2	5.8	*3*

Source: 1= (Yan et al., 2009), 2 = (Adebayo et al., 2009), 3= (DOE, 2010)

4.3.3 Gasification process simulation and financial modeling

Since there are no commercial cellulosic ethanol production processes currently in operation as of the fourth quarter of 2010, process simulation was used to generate values used in the economic analysis. The thermochemical ethanol conversion process model developed by NREL (Phillips et al., 2007) was used as the simulation basis. The NREL model performs energy and a material balances across a simulated integrated biorefinery facility, and is responsive to variations in feedstock biomass feed rate and composition. Gasifier conversion yields for syngas components are based on correlations and data obtained from a pilot-scale gasifier at the Battelle-Columbus Laboratory. (Feldmann, Paisley et al. 1988) The simulations were run in Aspen Plus version 2004.1 (Aspen-Tech, 2004) and accompanying Compaq Visual FORTRAN compiler version 6.6, as newer versions of Aspen Plus were unable to run the model.

4.3.3.1 Simulation modification

To meet the needs of this study, modifications were made to the NREL thermochemical model. Several elements of the model were not functional as received from the NREL website. One inactive feature was the biomass input parameter calculator “SETFEED”. The SETFEED calculator was modified to write the input parameters into the incoming biomass stream as originally intended, allowing for feedstock compositional changes to be made in one central location. The “REFSTM” calculator FORTRAN code was also modified to prevent errors caused by negative calculated tar reformer steam flows.

In addition to repairing the "SETFEED" and "REFSTM" calculators, the tar reformer catalyst regenerator temperature was manipulated to maintain overall model energy equilibrium. Depending on the incoming feedstock flow rate, composition, and moisture content, the energy production was adjusted to meet the needs of the process. This was done by manually changing the target temperature of design specification "R301BTEM".

4.3.3.2 Operation parameters

To demonstrate model characteristics, multiple input parameters were manipulated. The original feed rate of 772,000 dry tons per year (dry metric tons) of biomass was maintained while altering the biomass type and moisture content; for the economic analysis and CAPEX estimation a flow of 453,597 dry metric tons was used (500,000 dry short tons). In total, five biomass types were examined in addition to the original NREL hybrid poplar feedstock (hybrid poplar was not included in the paper). The energy crop and agricultural residue (switchgrass and corn stover respectively) moisture contents were set at 16%. Both the ultimate and proximate analyses for each biomass type are included in Table 4-2

The biomass gasification to biofuels pathway can be very complex and typically requires many unit processes. As a result, the process requires a large capital investment and is generally less well understood than the biochemical process. A revised CAPEX is presented including other potential capital investment not considered initially in the NREL report.

4.3.3.3 CAPEX

Capital expenditure was estimated based on the NREL report (Phillips et al., 2007) and consultation with CAPEX estimation experts (Phillips, 2010). CAPEX was projected for a biorefinery with a capacity to process 453,597 dry tons per year (500,000 BDT). Total CAPEX, excluding land, is estimated at approximately US$ 290 million. Further details in equipment, scale factor, and estimated green field cost and sources are illustrated in Table 4-3.

Table 4-3: Capital expenditure for a green field biorefinery

Description	Scale factor	Green field US$	S	Description	Scale factor	Green field US$	S
Site preparation				*Continuation*			
Land purchase	0.9	923,012	1	Methanol/Ethanol Splitter Reboiler	0.68	162,330	2
Land preparation	0.9	18,328,324	1	Mol Sieve Flush Condenser (air cooled)	1	68,499	2
Biomass handling				Product Cooler / Mol Sieve preheater	0.6	4,649	2
Roundwood/chipping receiving	0.6	19,462,961	1	Ethanol Product Pump	1.79	3,992	2
Bark drying	0.6	16,591,727	2	ETHANOL Product Cooler / Mol Sieve preheater	0.6	11,408	2
Flue Gas Cooler/Steam Generator	0.6	1,280,203	2	Ethanol Product Pump	2.79	196,596	2
Flue Gas Cooler /Boiler Water Preheater	0.6	465,933	2	Ethanol/Propanol Splitter Bottoms Pump	0.79	24,151	2
Flue Gas Cooler / Steam Generator	0.65	233,016	2	Ethanol/Propanol Splitter Reflux Pump	0.79	4,172	2
Rotary Biomass Dryer	0.75	19,357,788	2	Methanol/Ethanol Splitter Bottoms Pump	0.79	38,475	2
A100				Methanol/Ethanol Splitter Reflux Pump	0.79	4,172	2
Indirectly-heated Biomass Gasifier	0.65	12,916,238	2	Mixed Alcohol Product Pump	0.79	6,661	2
A200				Ethanol Product Pump	0.79	25,773	2
Post-tar Reformer Cooler / Steam Generator	0.65	280,793	2	Syngas Separato	0.6	106,310	2
Reformer Flue Gas Cooler/Steam superheater	0.6	573,129	2	Molecular Sieve (9 pieces)	0.7	3,445,594	2
Reformed Syngas cooler / Synthesis Reactor Preheat	0.44	254,966	2	Ethanol/Propanol Splitter Reflux Drum	0.93	12,034	2
Water-cooled Aftercooler	0.44	79,254	2	Methanol/Ethanol Splitter Reflux Drum	0.93	12,034	2
LO-CAT Preheater	0.6	4,498	2	Mixed Alcohol Product Storage Tank	0.51	452,976	2
Recycle Syngas Cooler / Steam Generator	0.6	180,778	2	Ethanol Product Storage Tank	0.51	1,084,940	2
Recycle Syngas cooler #2 / Air preheat	0.6	32,214	2	**A500**			
Syngas Compressor	0.8	17,647,662	2	Blowdown Water-cooled Cooler	0.44	94,962	2
Regenerator Combustion Air Blower	0.59	98,824	2	Hot Process Water Softener System	0.82	3,044,885	2
Sludge Pump	0.33	9,795	2	Extraction Steam Turbine/Generator	0.71	11,801,498	2
Tar Reformer Catalyst Regenerator	0.65	9,719,926	2	Startup Boiler	0.6	579,837	2
Tar Reformer	0.65	8,670,224	2	Collection Pump	0.33	21,122	2
LO-CAT Oxidizer Vessel	0.65	2,378,057	2	Condensate Pump	0.33	30,304	2
Pre-compressor Knock-out	0.6	638,432	2	Deaerator Feed Pump	0.33	50,691	2
Post-compressor Knock-out	0.6	170,781	2	Boiler Feed Water Pump	0.33	558,718	2
L.P. Amine System	0.6	12,147,805	2	Blowdown Flash Drum	0.6	43,703	2
Sludge Settling Tank	0.65	759	2	Condensate Collection Tank	0.6	71,468	2
A300				Condensate Surge Drum	0.6	83,371	2
Flue Gas Cool / syngas rxn preheat	0.6	43,705	2	Deaerator	0.72	381,292	2
Air preheat #3 / post Reactor Syngas cooling	0.6	24,862	2	Steam Drum	0.72	27,467	2
Post synthesis cooler #2/Deaerator Water Preheater	0.6	52,558	2	**A600**			
C 1 Post Synthesis cooler	0.6	31,445	2	Plant Air Compressor	0.34	283,936	2
Post Synthesis cooler	0.6	37,295	2	Cooling Tower System	0.78	564,218	2
Post Synthesis Cooler	0.6	8,745	2	Hydraulic Truck Dump with Scale	0.6	237,526	2
Post Mixed Alcohol Cooler	0.44	214,230	2	Flue Gas Stack	1	46,530	2
Mixed Alcohol first Condenser	1	136,649	2	Cooling Water Pump	0.33	807,601	2
Mixed Alcohol Condenser	0.44	281,814	2	Firewater Pump	0.79	110,110	2
Recycle Syngas Heat #2 / Flue gas Cool	0.44	344,070	2	Diesel Pump	0.79	36,504	2
Mixed Alcohol Gas Compressor	0.8	2,262,251	2	Ammonia Pump	0.79	29,921	2
Purge Gas Expander	0.8	13,710,103	2	Hydrazine Pump	0.79	16,457	2
Mixed Alcohol Reactor	0.56	3,218,633	2	Instrument Air Dryer	0.6	48,813	2
Mixed Alcohols Condensation Knock-out	0.6	246,225	2	Plant Air Receiver	0.72	20,472	2
A400				Firewater Storage Tank	0.51	496,991	2
Ethanol/Propanol Splitter	1.32	478,460	2	Diesel Storage Tank	0.51	43,086	2
Methanol/Ethanol Splitter	1.32	531,228	2	Ammonia Storage Tank	0.72	859,635	2
Syngas Cooler #4 / Mol Sieve preheater	0.6	64,211	2	Hydrazine Storage Tank	0.93	37,102	2
Mol Sieve Superheater / reformed syngas cool	0.6	10,842	2	**Others**			
Condenser (air cooled	1	127,442	2	Product storage and shipment	0.6	4,735,574	1
Ethanol/Propanol Splitter Reboiler	0.68	126,830	2	Power	0.6	23,807,177	1
Condenser (air cooled)	1	203,538	2	Water	0.6	5,106,802	1

S = Source; 1 = (Phillips, 2010); 2 = (Phillips et al., 2007)

4.3.3.4 General assumptions

Major assumptions used for the economic analysis are illustrated in Table 4-4. In brief, the startup year is assumed to be 2012, with construction beginning in 2010. All CAPEX and costs were up dated to 2012 dollars. The economic analysis included an evaluation horizon of 15 years. CAPEX spending is illustrated in Table 4-4. Revenue includes ethanol selling price at US$ 2 per gallon, plus a subsidy of US$ 1.01 per gallon (price of US$ 0.53 per liter and subsidy of US$ 0.27 per liter of ethanol). Ethanol selling price alone is assumed to increase at a rate of 2% per year. Biomass and other costs are assumed to increase at 3% per year, while chemicals are assumed to increase at 2% per year. A discount rate of 12% and a terminal value in year 15 of five times EBITDA of the same year was used (Earnings Before Interest, Taxes, Depreciation and Amortization).

Table 4-4: Financial analysis assumptions

Description	Value	Description	Value
Startup year	2012	Tax rate, with tax loss carryforward	35%
Terminal year	2026	Discount rate	12%
CAPEX spending		Terminal value, year 15 EBITDA multiple X	5
% of spending in year -2	30%	Hours per year	8400
% of spending in year -1	50%	Revenue per liter of ethanol	2
% of spending in year -0	20%	Subsidy added to price, $ per liter ethanol	1.01
% of nominal capacity, project year 1	50%	Maintenance expense,including Labor,	2%
% of nominal capacity, project year 2	80%	Other fixed costs, % of sales	3%
Working capital % of direct cost + presubsidy product revenue	10%	Capital reinvestment, % of replacement asset value	1%
Years depreciation schedule, straight line	10	Sales and other overhead, % of sales	3%

4.3.3.5 Ethanol and propanol yield

Ethanol and propanol yield (liters of alcohol per dry ton of biomass) are obtained from the ASPEN process simulation, as presented in the next sections (Figure 4-4 and Figure 4-5). In order to estimate revenues from the production of propanol, the energy content of this higher alcohol was determined based on literature review, with its equivalent ratio to ethanol used to estimate revenue, using the same price assumed for ethanol

4.4 Results and discussion

4.4.1 Production costs

Alcohol production cost was estimated for five different feedstocks using raw material cost and chemical consumption as input to the economic feasibility spreadsheet. Net present value, internal rate of return, and investment payback period were the key financial indicators evaluated in this study.

Figure 4-2 illustrates the ethanol selling price and various components of alcohol production costs in year 2014 using loblolly pine as a feedstock. The bar graph displays the estimated cost (negative values) in US$ per gallon of ethanol equivalent (ethanol plus propanol). Total production cost was estimated at US$ 1.76 per gallon of ethanol, while cash cost (production cost minus non cash costs as depreciation) was around US$ 1.21 per gallon of ethanol equivalent, with biomass and depreciation as the major cost drivers. The inner pie graph illustrates the category cost share of total production cost, with biomass and depreciation representing nearly 67% of total costs.

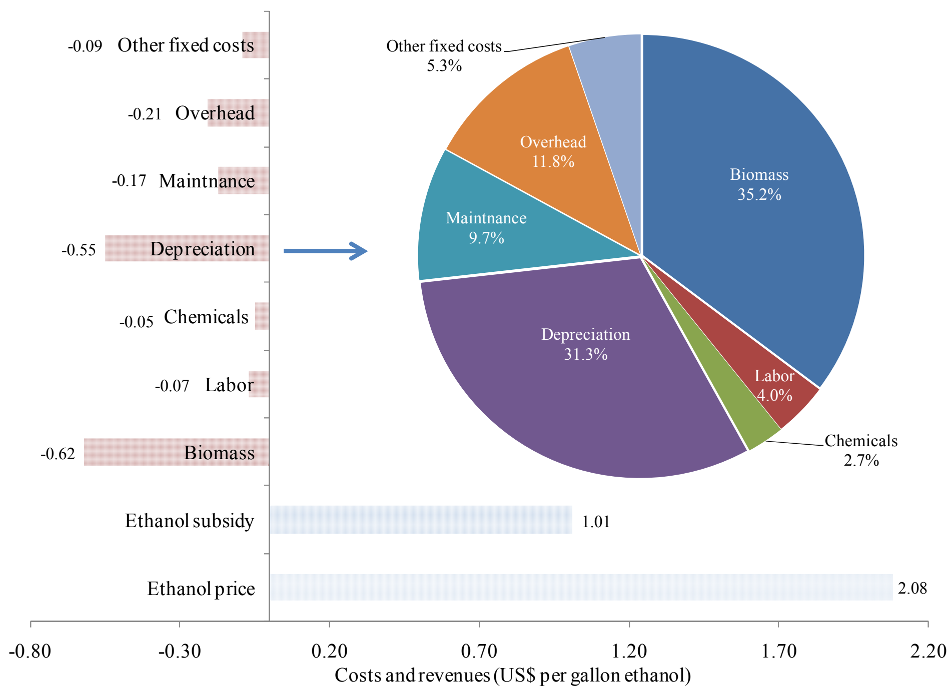

Figure 4-2: Ethanol production cost (US$ per gallon ethanol) and cost share (%), using loblolly pine feedstock (1 gallon =3.78 liters

4.4.2 Feedstock type and profitability

Net present value (NPV) and internal rate of return (IRR) were estimated for each biomass and gasification scenario. Higher NPV and IRR values were observed in forest biomass (softwood and hardwoods), with NPV ranging from US$ 135.5 million to US$ 191.9 million and IRR ranging from 19% to 21.4%. By contrast, lower NPV and IRR were observed for the herbaceous feedstocks corn stover and switch grass. The response of these financial indicators can be explained by a combination of raw material costs (Table 4-2) and alcohol yield (Figure 4-4 and Figure 4-5).

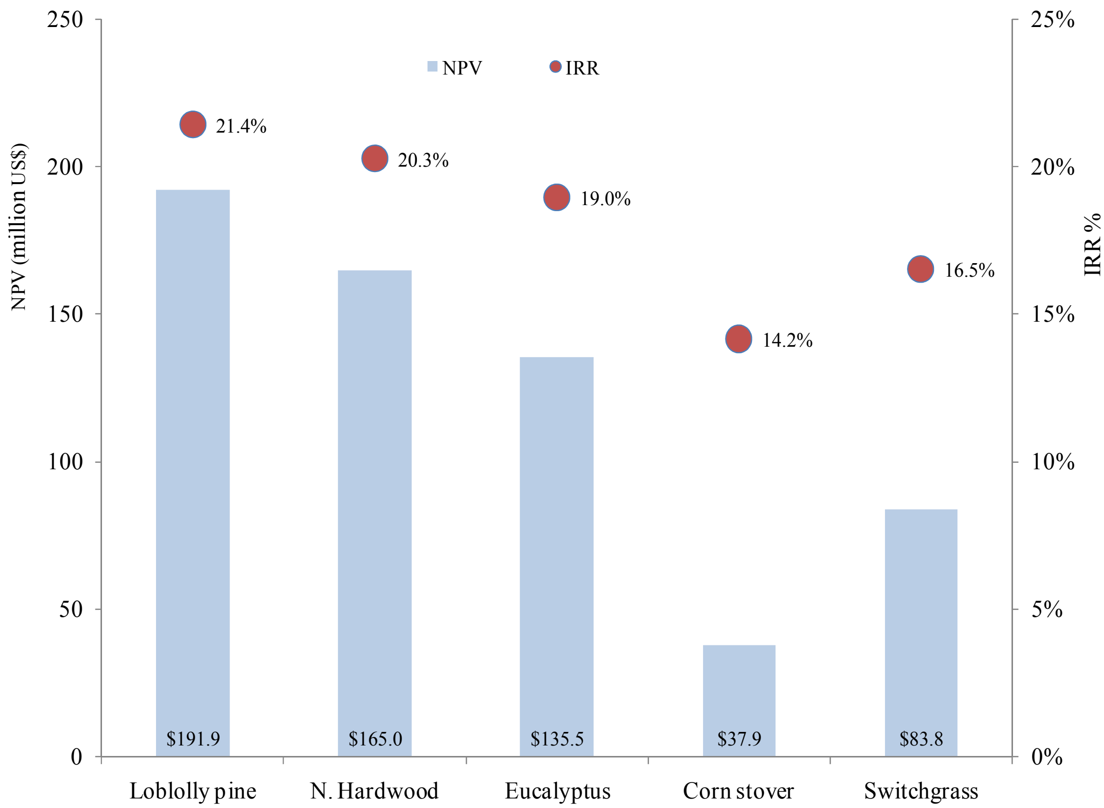

Figure 4-3: NPV and IRR for each feedstock

Alcohol production, IRR, and payback time is presented in Figure 4-4 for each the biomass type. Ethanol production (both ethanol and propanol converted to ethanol equivalents) varies greatly depending on the type of biomass used, with values for herbaceous feedstocks ranging from 169 to 183 million liters of alcohol for corn stover and switchgrass respectively. The evaluation of forest feedstocks yielded a range of 186 to 204 million liters of alcohol for Eucalyptus and loblolly pine, respectively. Payback time, or the number of years required to offset initial investment, was higher for biomass types with lower productivity (Figure 4-4) and ethanol yield (Figure 4-5).

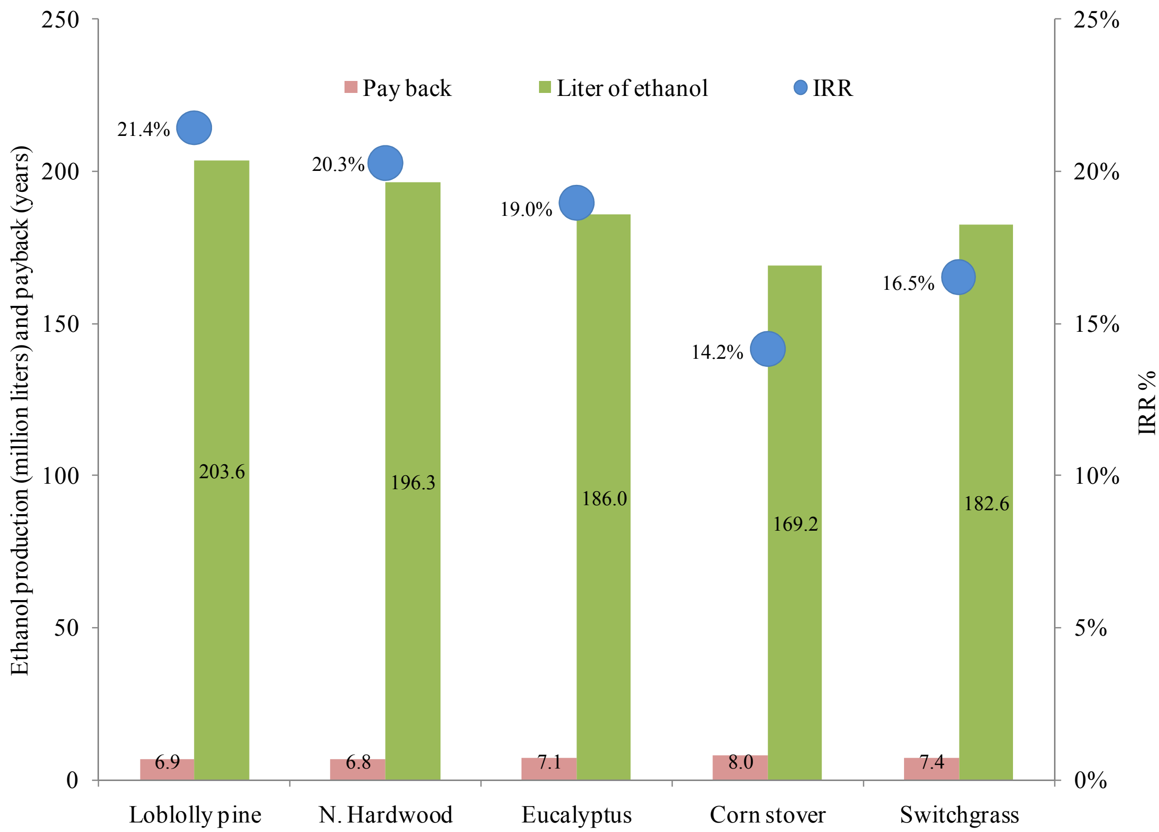

Figure 4-4: IRR, ethanol yield (liter per dry metric ton), and payback (years) for each biomass type

4.4.3 Alcohol yield

Alcohol yield and CAPEX (US$ CAPEX per liter of alcohol) for each biomass type are illustrated in Figure 4-5. As noted in Figure 4-4 and Figure 4-5, higher alcohol yields were found in forest feedstocks (pine, natural hardwood and Eucalyptus), with the highest value of 449 liters of alcohol per dry ton for loblolly pine. This is compared with the lowest alcohol yield of 373 liters alcohol per dry ton where corn stover was utilized as the feedstock. The use of lower yielding biomass types also resulted in greater CAPEX values per liter of alcohol, as the lowest yielding biomass, corn stover, produced the highest CAPEX of US$ 1.8 per liter .

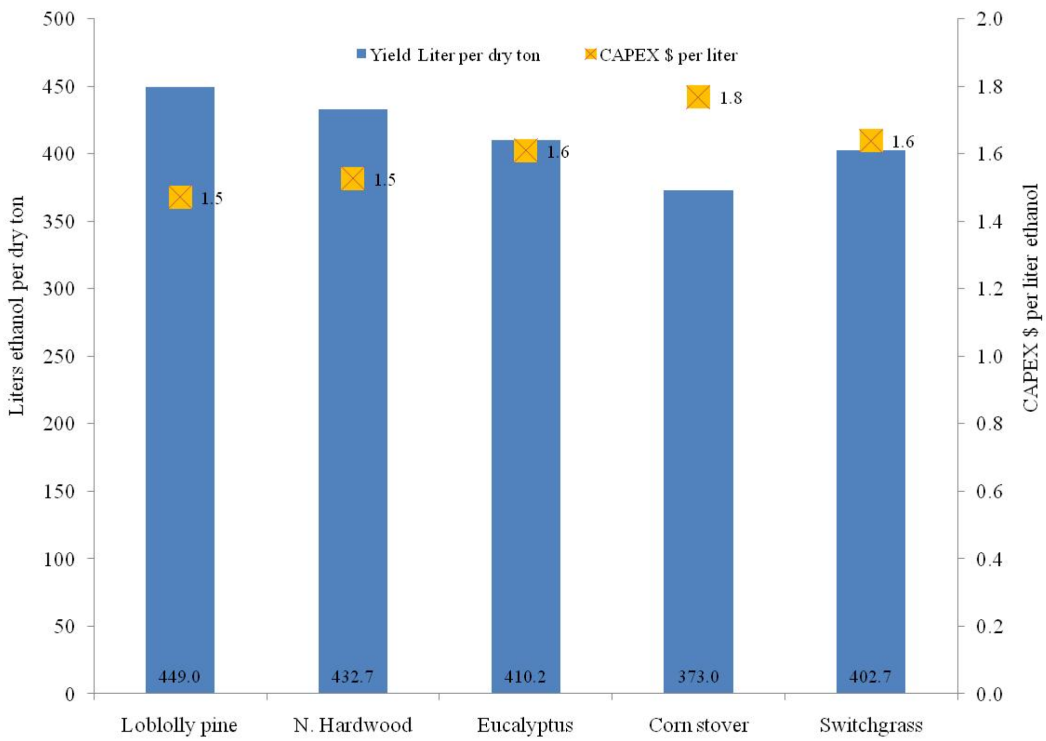

Figure 4-5 Ethanol production and CAPEX per liter of ethanol for each biomass type

4.4.4 Minimum ethanol selling price (MESP):

Minimum ethanol selling price (MESP) can be a useful economic indicator, and is commonly evaluated in alcohol production feasibility studies. MESP is defined as the price (US$ per liter of alcohol) required achieving a specific rate of return, in this case 12% IRR. As might be expected, lower MESP values are found for biomass types with higher alcohol yields (loblolly pine, natural hardwood and Eucalyptus), with MESPs ranging from US$ 0.54 to US$ 0.59 per liter of alcohol. Corn stover produced the highest MESP at US$ 0.71 per liter of alcohol.

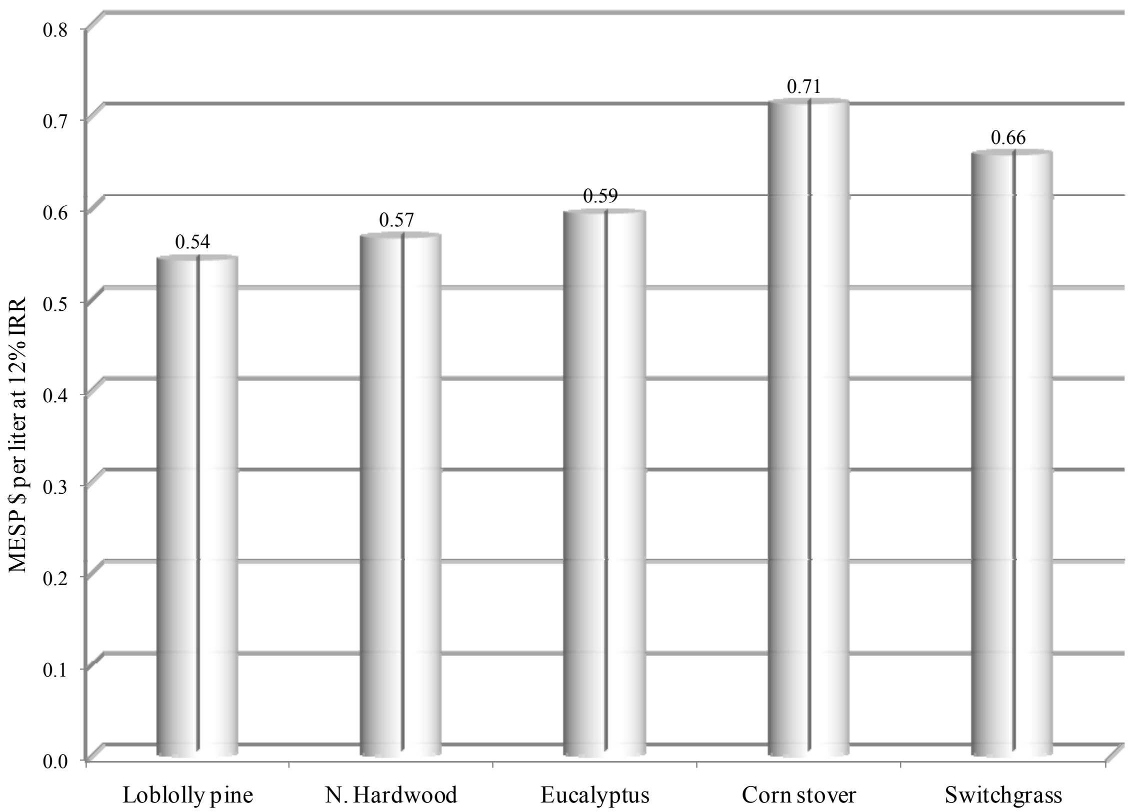

Figure 4-6: Minimum ethanol selling price to achieve 12% IRR for each biomass type

4.4.5 Sensitivity analysis

4.4.5.1 Sensitivity to economic drivers

To understand the impacts of economic driver fluctuations on the key economic indicators, a sensitivity analysis was performed varying alcohol selling price (not including subsidy), alcohol yield (in ethanol equivalents), CAPEX, and delivered biomass feedstock cost. Figure 4-7 outlines the sensitivity results.

These variables were manipulated by +/- 25% for loblolly pine, natural hardwood, corn stover, and switch grass. The economic outlook for all four biomass types was highly sensitive to alcohol yield and selling price. However, only the economics for corn stover and switch grass was influenced substantially by variation in CAPEX and biomass cost. For all sensitivity scenarios, the economics of switch grass and corn stover were impacted the most, mainly due to their lower yield and overall profitability.

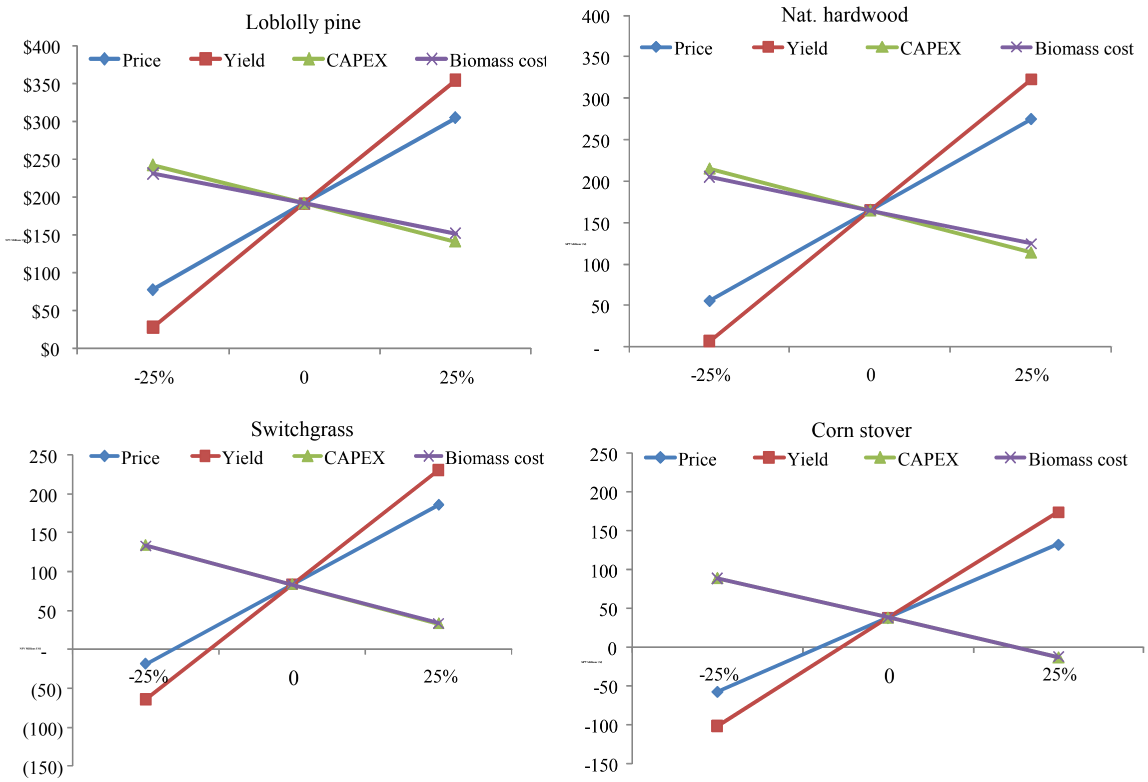

Figure 4-7: Sensitivity analysis +/- 25% in price, ethanol yield, CAPEX and biomass cost for loblolly pine, natural mixed hardwood, switchgrass and corn stover

4.4.5.2 Sensitivity to moisture content variation in feedstock

In order to understand the effect of moisture content on the profitability of the biomass to mixed alcohols thermochemical pathway, loblolly pine feedstocks at 35%, 45%, and 55% moisture content were considered in simulation. The outputs from these analyses were used to calculate alcohol yield, NPV and IRR of the conversion process. Biomass costs were kept constant, as presented in Table 4-2, with no premium or cost reduction associated with moisture content variation. As previously explained in the Methods section, biomass drying is an energy consuming process, energy in the form of syngas that could otherwise be used to produce additional alcohol. Figure 4-8 illustrates this, where an inversely proportional relationship between biomass moisture and each of the main financial indicators (product yield, NPV, and IRR) was noted. The 10% reduction in feedstock moisture content from 45 to 35% increased NPV by US$ 66 million and IRR by 2.8 percentage points.

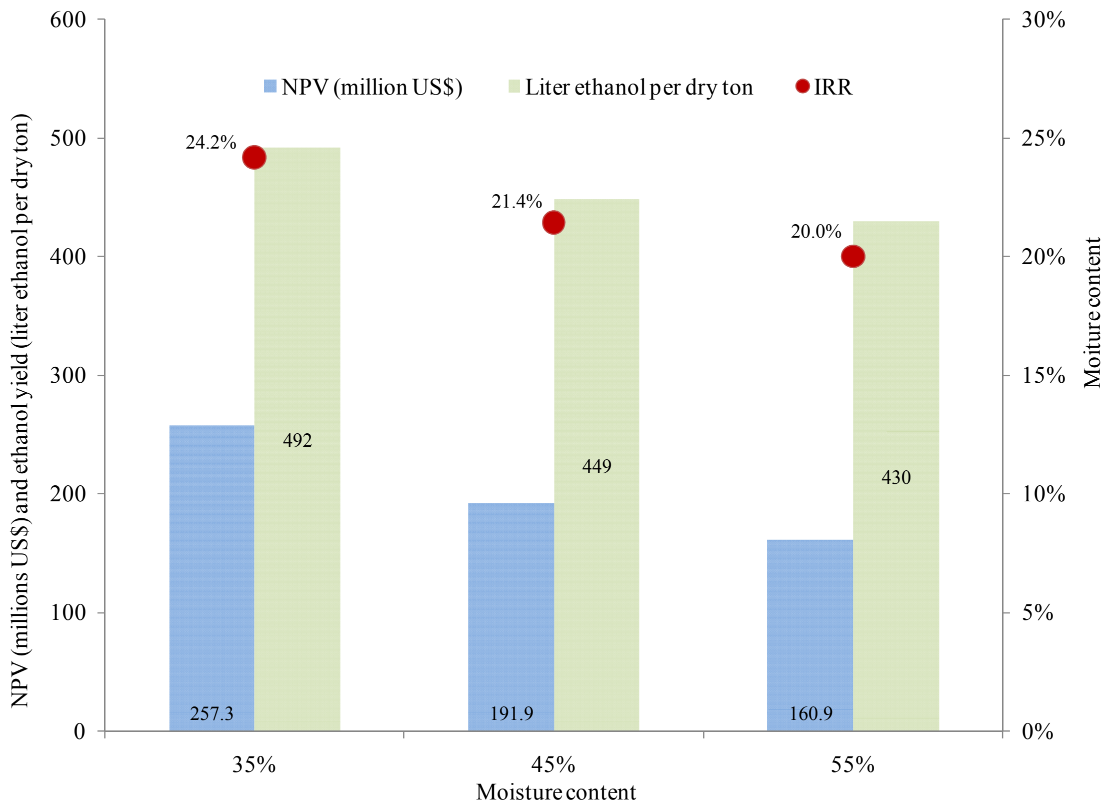

Figure 4-8: Effect of moisture content on biorefinery profitability

4.4.5.3 Effect of raw material on profitability, isolating raw material cost

As presented throughout this document, raw material selection can have a considerable influence on the profitability of a biorefinery due to variations in alcohol yield and biomass cost.

In order to isolate the effect of biomass composition on the process, NPV and IRR were calculated with a fixed biomass cost of US$ 60 per dry short ton (US$ 66.14 per dry metric ton). The results from this analysis indicated significantly higher profitability for forest-based biomass types when compared to corn stover and switchgrass (Figure 4-9). The profitability response was only influenced by biomass composition and moisture content, eliminating feedstock price as a variable.

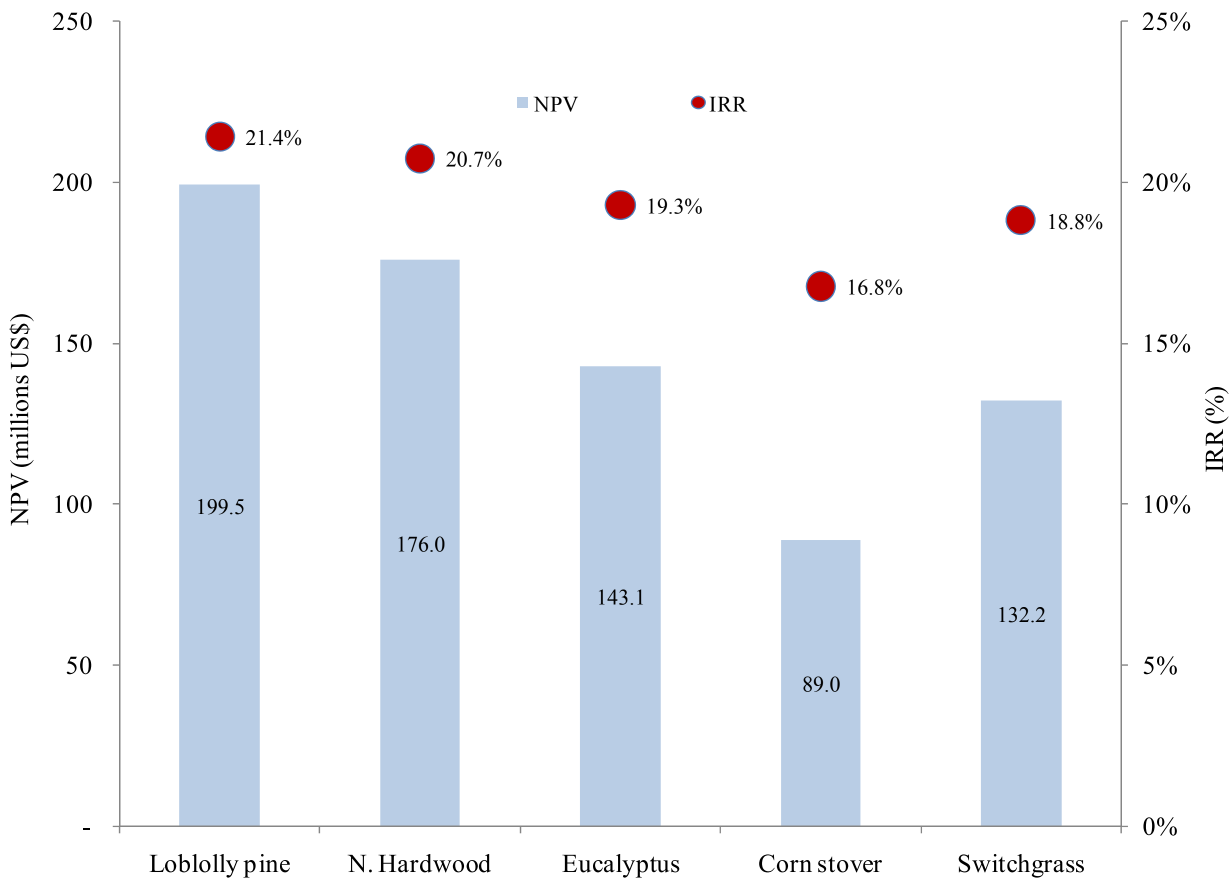

Figure 4-9: Gasification process for ethanol production

4.5 Summary and conclusions

As previously discussed, there are advantages to both the thermochemical and biochemical alcohol productions pathways. However, the thermochemical conversion pathway has been shown to effectively utilize many feedstocks while still resulting in favorable IRR and NPV values. This feedstock flexibility enables a biorefinery to utilize the lowest cost biomass throughout the year in order to maximize profitability. Forest-based feedstocks such as loblolly pine, natural hardwood and Eucalyptus present higher %C and %H content and lower % ash yielding greater alcohol production values. As a result of this high carbon and hydrogen content, forest-based feedstocks produce better financial returns when compared to herbaceous energy crops (such as switchgrass) or agriculture residues (corn stover), even at a constant delivered biomass cost. Additionally, financial success of thermochemical cellulosic ethanol production using switchgrass and corn stover was more sensitive to fluctuations in ethanol price, alcohol yield, biomass cost, and CAPEX than forest-based biomass. For all five biomass types economic success was highly sensitive to changes in alcohol yield and ethanol selling price. Finally, biomass moisture content was an important economic driver; lower moisture content in feedstocks clearly improves the financial performance of the thermochemical ethanol conversion process.

4.6 Acknowledgments

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5 Enviro-economic analysis

As a sustainable biofuels industry is a function of both environmental and economic performance, it is critical to understand the relationship between these. In the previous sections, both these topics have been addressed separately in detail. Within this section, the major findings of the environmental and economic analysis are combined to provide an integrated analysis.

The net present value (NPV) was calculated for each biomass scenario. This economic parameter accounts for the time value of money and determines the overall value of an investment. This economic data is compared to the conversion process GHG emissions for each biomass type, Figure 5-1. This analysis incorporated only GHG emissions from the production process, a dominating factor for overall GHG emissions on a cradle-to-grave basis. For each biomass scenario, as the NPV decreases the GHG emissions increase. This is primarily driven by the yield within the conversion process as yield was found to be a primary economic and environmental driver for this conversion process.

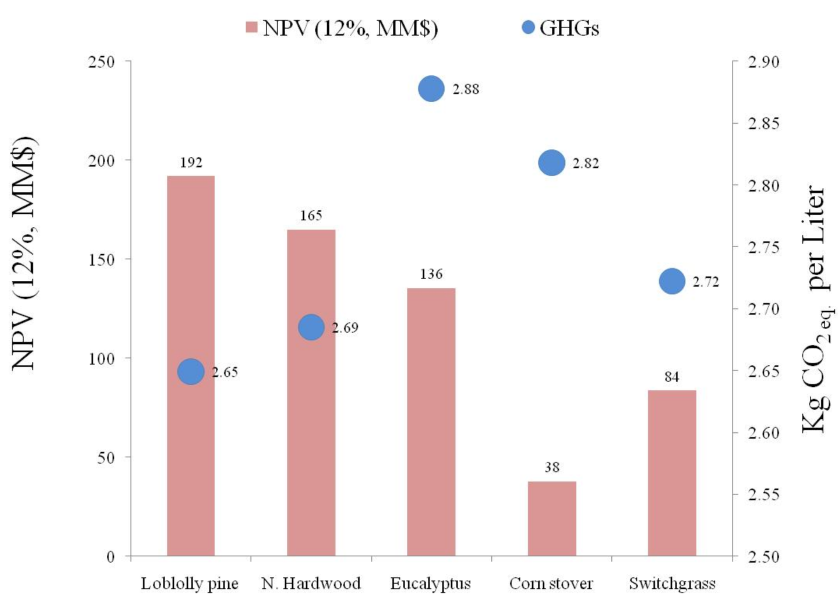

Figure 5-1: NPV and GHG emissions for cellulosic feedstocks

Taking these two environmental and economic results a step further, they can be combined into one number. By dividing the NPV by the GHG emissions, the largest quotient represents the best combined environmental and economic performance, as defined. However, within this process, this value is primarily driven by the economics as the NPV for each feedstock has a significantly larger spread than the GHG emissions values. The combined parameter value was highest for loblolly pine and lowest for corn stover, Figure 5-2.

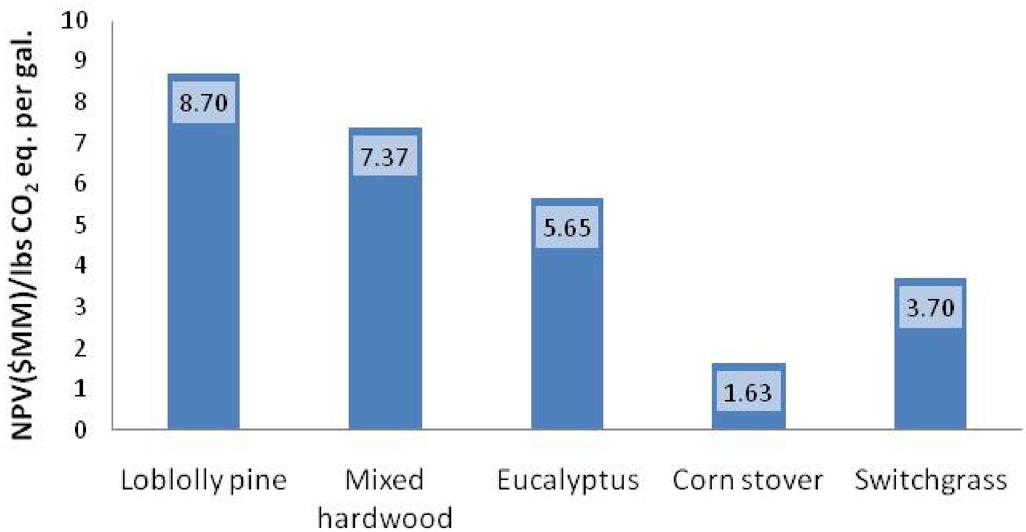

Figure 5-2: Combined environmental and economic performance

6 Thesis summary

A knowledge gap analysis of current biofuel LCA literature was performed identifying many knowledge gaps. From this analysis, the effect of biomass composition on GHG emissions from the ethanol conversion process was explored. Additionally, a background overview of second-generation biofuels production and life cycle assessment methodology was presented. A range of major topics, many major concepts and approaches used to perform LCA and GHG analyses around biofuels and bioenergy were reviewed. In addition, a Microsoft Access database of the reviewed publications and findings was created to further assist in LCA education and knowledge gap identification. A number of knowledge gaps were identified representing topics to be further explored in future research.

Addressing one of the knowledge gaps discovered, a GHG analysis was performed analyzing the effects of biomass composition on GHG emissions. Six cellulosic feedstocks were examined as feedstocks to the NREL thermochemical ethanol production model. Through performing a gate-to-gate analysis ash and moisture content were identified as key biomass compositional factors affecting GHG emissions. These findings should be used as a tool to help select biomass feedstock types for thermochemical ethanol production. However, this study alone does not present an ultimate answer to the most economically feasible and environmentally sustainable feedstock

To determine feedstocks producing the highest financial return on investment, an economic analysis was performed around the thermochemical ethanol production process. Five of the six feedstocks examined in the environmental analysis were considered for the financial analysis. Minimal ethanol selling price, IRR and NPV were the metrics used for quantifying biomass economic performance. The use of forest-based biomass resulted in higher IRR and NPV relative to corn stover and switchgrass. Additionally, return on investment was negatively affected by biomass moisture content. An environmental economic factor was proposed to evaluate biofuel systems, NPV/GHG emissions. Forest based feedstocks resulted in higher values than switchgrass or corn stover.

This work identified many future research topics, characterized emission variations due to biomass type, and differences in economic performance for different cellulosic feedstocks. Only a few of the many factors required for the integration of second generation biofuels into the energy market were explored. Additionally work as identified in the literature knowledge gap analysis is required to help meet the mandated biofuels standards.

Future work

Many knowledge gaps were identified in Chapter 2. Research presented in Chapter 3 filled the knowledge gap of GHG emission variations due to biomass composition processed by the NREL thermochemical ethanol production model. Additionally, the financial outcomes from these feedstocks were explored. The integration of economics and environmental assessment is a critical area of research deserving further focus. For any forest based material, determining the key process parameters yielding the largest environmental benefits while maintaining economic feasibility will be critical to the success of commercial production and emissions reductions.

To ensure objective environmental comparisons, process configurations for both biochemical and thermochemical routes should be examined utilizing consistent assumptions and system boundaries. As new process conversion pathways are developed, they should also be examined and compared under consistent assumptions and boundaries. However, this may be difficult as many emerging process technologies are proprietary at this point.

Feedstock production was not thoroughly explored within this work, however, it has one of the largest influences over the total emissions. Therefore, detailed emission and LCA models should be created to examine feedstock production. Models enabling the user to input various planting, harvesting, and management practices will be the most robust and will be more capable of capturing the range of results that are experienced in forests.

APPENDIX

Table 8-1: Waste treatment GHG emissions

SimaPro 7.2	Inventory	Date:	1/27/2011
Project	Gasification CORRIM 10 27 09		

			lb CO_2/m^3
Title:	Analysing 1 kg 'Water only (m3) to WWTP size 2 S'	CO_2	3.025E-07
Method:	Eco-indicator 99 (H) V2.06 / Europe EI 99 H/A	Methane	2.854E-08
Compartment:	All compartments	N_2O	3.058E-07
Per sub-compartment:	Yes	Total	6.369E-07

8-2: Landfill emission for ash

SimaPro 7.2	Inventory	Date:	2/1/2011
Project	Gasification CORRIM 10 27 09		

			lb CO_2/lb
Title:	Analysing 1 kg 'Waste (inert) to landfill U'	CO_2	5.32E-04
Method:	Eco-indicator 99 (H) V2.06 / Europe EI 99 H/A	Methane	1.84E-05
Compartment:	All compartments	N_2O	1.90E-03
Per sub-compartment:	Yes	Total	2.45E-03

Table 8-3: emissions for olivine using industrial sand process and olivine mineral from earth

SimaPro 7.2	Inventory	Date:	12/2/2010
Project	Gasification CORRIM 10 27 09		

			lb CO_2/lb
Title:	Analysing 1 kg 'Sand for Industrial Processes'	CO_2	8.46E-03
Method:	Eco-indicator 99 (H) V2.06 / Europe EI 99 H/A	Methane	2.80E-04
Compartment:	All compartments	N_2O	3.05E-02

Table 8-4: transportation emission factors

SimaPro 7.2	Inventory	Date:	1/27/2011
Project	Gasification CORRIM 10 27 09		

Title:	Analysing 1 tkm 'Transport, combination truck, diesel powered/US'		lb CO_2/tkm
Method:	Eco-indicator 99 (H) V2.06 / Europe EI 99 H/A	CO_2	0.1969757
Compartment:	All compartments	Methane	5.91E-03
Per sub-compartment:	Yes	N_2O	8.20E-02
Indicator:	Inventory	Total	2.85E-01

Table 8-5: Hybrid Poplar material balance

Hybrid poplar 45% MC (NREL base case)		MASSFLMX
stream description	stream #	LB/HR
Feedstock in	100	3.34E+05
Combustion air	.200.A200CC.209.	4.30E+05
Char combuster water	A200.A200CC.218	2.43E+02
MgO	A200.220	6.97E+00
Make up olivine	A200.221	5.38E+02
Make up catalyst	A300.A300TR.326	1.07E+00
Combustion air	300.A300TR.32	2.63E+05
Lo-Cat oxidizer air	A300.A300S.322	2.72E+02
Steam make up water	A600.618	3.25E+04
Cooling make up water	A700.710	8.60E+04
Clear water chemicals	A700.711	8.16E-01
Condensor water	A700.718	4.08E+06
output		
Sand fly ash	A200.219	2.43E+03
Catalyst purge	A300.A300TR.329	1.07E+00
Solid waste	A300.A300Q.336	7.94E+01
CO2 vent	A300.A300S.357	5.47E+04
Air to atmosphere	A300.A300S.325	2.80E+02
Sulfur storage	A300.A300S.324	1.13E+02
Ethanol product	A500.592A	5.07E+04
Higher alcohols	A500.590	9.14E+03
Vent to atmosphere	A600.634	1.90E+00
Evaporated to atmosphere	A700.705	4.23E+06
Blow turbine blow down	A700.713	1.70E+04
Windage to atmosphere	A700.704	8.16E+03
Flue gas stack	112	9.35E+05
Water to treatment plant	A300.305	1.21E+03
Hot gasses to feed drying	A100.107	7.94E+05
Dried wood	A100.105	1.93E+05
In		5.22E+06
Out		5.31E+06
Difference		-8.11E+04
Percent closure		-1.5%

Table 8-6: Material balance for loblolly pine 5% ash

Loblolly pine 5% ash **stream description**	stream #	MASSFLMX LB/HR
Feedstock in	100	3.34E+05
Combustion air	A200.A200CC.209A	4.47E+05
water input	A200.A200CC.218	1.08E+03
MgO	A200.220	3.79E+01
Make up olivine	A200.221	5.07E+02
Make up catalyst	A300.A300TR.326	1.03E+00
Combustion air	A300.A300TR.329B	2.57E+05
Lo-Cat oxidizer air	A300.A300S.322	0.00E+00
Make up water preheat	A600.618	3.42E+04
Make up water	A700.710	9.62E+04
Clear water chemicals	A700.711	9.05E-01
Clear water header	A700.718	4.53E+06
output		
Sand fly ash	A200.219	1.08E+04
Catalyst purge	A300.A300TR.329	1.03E+00
Solid waste	A300.A300Q.336	8.04E+01
CO2 vent	A300.A300S.357	5.36E+04
Air to atmosphere	A300.A300S.325	0.00E+00
Sulfur storage	A300.A300S.324	0.00E+00
Ethanol product	A500.592A	4.99E+04
Higher alcohols	A500.590	8.99E+03
Vent to atmosphere	A600.634	3.78E-01
Evaporated to atmosphere	A700.705	4.69E+06
Blow down	A700.713	1.89E+04
Windage to atmosphere	A700.704	9.05E+03
Flue gas stack	112	9.43E+05
Water to treatment plant	A300.305	1.16E+03
Hot gasses to feed drying	A100.107	8.02E+05
Dried wood	A100.105	1.93E+05
In		5.70E+06
Out		5.79E+06
Difference		-9.01E+04
Percent closure		-1.56%

Table 8-7: Material balance for loblolly pine 10% ash

Loblolly pine 10% ash		MASSFLMX
stream description	stream #	LB/HR
Feedstock in	100	3.34E+05
Combustion air	A200.A200CC.209A	4.28E+05
water input	A200.A200CC.218	2.10E+03
MgO	A200.220	7.58E+01
Make up olivine	A200.221	4.69E+02
Make up catalyst	A300.A300TR.326	9.90E-01
Combustion air	A300.A300TR.329B	2.61E+05
Lo-Cat oxidizer air	A300.A300S.322	0.00E+00
Make up water preheat	A600.618	3.43E+04
Make up water	A700.710	1.04E+05
Clear water chemicals	A700.711	9.72E-01
Clear water header	A700.718	4.86E+06
output		
Sand fly ash	A200.219	2.10E+04
Catalyst purge	A300.A300TR.329	9.90E-01
Solid waste	A300.A300Q.336	7.92E+01
CO2 vent	A300.A300S.357	4.92E+04
Air to atmosphere	A300.A300S.325	0.00E+00
Sulfur storage	A300.A300S.324	0.00E+00
Ethanol product	A500.592A	4.53E+04
Higher alcohols	A500.590	8.18E+03
Vent to atmosphere	A600.634	3.65E-01
Evaporated to atmosphere	A700.705	5.04E+06
Blow down	A700.713	2.02E+04
Windage to atmosphere	A700.704	9.72E+03
Flue gas stack	112	9.28E+05
Water to treatment plant	A300.305	1.09E+03
Hot gasses to feed drying	A100.107	7.88E+05
Dried wood	A100.105	1.93E+05
In		6.02E+06
Out		6.12E+06
Difference		-9.67E+04
Percent closure		-1.6%

Table 8-8: Material balance for loblolly pine at 15% ash

Loblolly pine 15% ash **stream description**	stream #	MASSFLMX LB/HR
Feedstock in	100	3.34E+05
Combustion air	A200.A200CC.209A	4.14E+05
water input	A200.A200CC.218	3.12E+03
MgO	A200.220	1.14E+02
Make up olivine	A200.221	4.31E+02
Make up catalyst	A300.A300TR.326	9.40E-01
Combustion air	A300.A300TR.329B	2.64E+05
Lo-Cat oxidizer air	A300.A300S.322	0.00E+00
Make up water preheat	A600.618	3.66E+04
Make up water	A700.710	1.13E+05
Clear water chemicals	A700.711	1.05E+00
Clear water header	A700.718	5.26E+06
output		
Sand fly ash	A200.219	3.12E+04
Catalyst purge	A300.A300TR.329	9.40E-01
Solid waste	A300.A300Q.336	7.84E+01
CO2 vent	A300.A300S.357	4.55E+04
Air to atmosphere	A300.A300S.325	0.00E+00
Sulfur storage	A300.A300S.324	0.00E+00
Ethanol product	A500.592A	4.21E+04
Higher alcohols	A500.590	7.59E+03
Vent to atmosphere	A600.634	3.44E-01
Evaporated to atmosphere	A700.705	5.45E+06
Blow down	A700.713	2.19E+04
Windage to atmosphere	A700.704	1.05E+04
Flue gas stack	112	9.19E+05
Water to treatment plant	A300.305	1.01E+03
Hot gasses to feed drying	A100.107	7.78E+05
Dried wood	A100.105	1.93E+05
In		6.42E+06
Out		6.53E+06
Difference		-1.05E+05
Percent closure		-1.6%

Table 8-9: Material balance for loblolly pine at 55% MC

Loblolly pine 55% MC **stream description**	stream #	MASSFLMX LB/HR
Feedstock in	100	4.08E+05
Combustion air	A200.A200CC.209A	4.62E+05
water input	A200.A200CC.218	1.47E+02
MgO	A200.220	3.41E+00
Make up olivine	A200.221	5.41E+02
Make up catalyst	A300.A300TR.326	1.05E+00
Combustion air	A300.A300TR.329B	3.11E+05
Lo-Cat oxidizer air	A300.A300S.322	0.00E+00
Make up water preheat	A600.618	3.76E+04
Make up water	A700.710	8.29E+04
Clear water chemicals	A700.711	7.87E-01
Clear water header	A700.718	3.94E+06
output		
Sand fly ash	A200.219	1.47E+03
Catalyst purge	A300.A300TR.329	1.05E+00
Solid waste	A300.A300Q.336	7.45E+01
CO2 vent	A300.A300S.357	5.28E+04
Air to atmosphere	A300.A300S.325	0.00E+00
Sulfur storage	A300.A300S.324	0.00E+00
Ethanol product	A500.592A	4.93E+04
Higher alcohols	A500.590	8.88E+03
Vent to atmosphere	A600.634	3.73E-01
Evaporated to atmosphere	A700.705	4.08E+06
Blow down	A700.713	1.64E+04
Windage to atmosphere	A700.704	7.87E+03
Flue gas stack	112	1.10E+06
Water to treatment plant	A300.305	1.15E+03
Hot gasses to feed drying	A100.107	8.84E+05
Dried wood	A100.105	1.93E+05
In		5.24E+06
Out		5.32E+06
Difference		-7.84E+04
Percent closure		-1.5%

Table 8-10: Material balance for loblolly pine at 45% MC

Loblolly pine 45% MC **stream description**	stream #	MASSFLMX LB/HR
Feedstock in	100	3.34E+05
Combustion air	A200.A200CC.209A	4.62E+05
water input	A200.A200CC.218	1.47E+02
MgO	A200.220	3.41E+00
Make up olivine	A200.221	5.41E+02
Make up catalyst	A300.A300TR.326	1.09E+00
Combustion air	A300.A300TR.329B	2.58E+05
Lo-Cat oxidizer air	A300.A300S.322	0.00E+00
Make up water preheat	A600.618	3.44E+04
Make up water	A700.710	8.79E+04
Clear water chemicals	A700.711	8.35E-01
Clear water header	A700.718	4.17E+06
output		
Sand fly ash	A200.219	1.47E+03
Catalyst purge	A300.A300TR.329	1.09E+00
Solid waste	A300.A300Q.336	8.09E+01
CO2 vent	A300.A300S.357	5.73E+04
Air to atmosphere	A300.A300S.325	0.00E+00
Sulfur storage	A300.A300S.324	0.00E+00
Ethanol product	A500.592A	5.35E+04
Higher alcohols	A500.590	9.65E+03
Vent to atmosphere	A600.634	4.05E-01
Evaporated to atmosphere	A700.705	4.33E+06
Blow down	A700.713	1.74E+04
Windage to atmosphere	A700.704	8.35E+03
Flue gas stack	112	9.58E+05
Water to treatment plant	A300.305	1.25E+03
Hot gasses to feed drying	A100.107	8.17E+05
Dried wood	A100.105	1.93E+05
In		5.35E+06
Out		5.43E+06
Difference		-8.30E+04
Percent closure		-1.5%

Table 8-11: Material balance for loblolly pine at 35% MC

Loblolly pine 35% MC **stream description**	stream #	MASSFLMX LB/HR
Feedstock in	100	2.83E+05
Combustion air	A200.A200CC.209A	4.62E+05
water input	A200.A200CC.218	1.47E+02
MgO	A200.220	3.41E+00
Make up olivine	A200.221	5.41E+02
Make up catalyst	A300.A300TR.326	1.12E+00
Combustion air	A300.A300TR.329B	2.21E+05
Lo-Cat oxidizer air	A300.A300S.322	0.00E+00
Make up water preheat	A600.618	3.21E+04
Make up water	A700.710	9.13E+04
Clear water chemicals	A700.711	8.67E-01
Clear water header	A700.718	4.34E+06
output		
Sand fly ash	A200.219	1.47E+03
Catalyst purge	A300.A300TR.329	1.12E+00
Solid waste	A300.A300Q.336	8.53E+01
CO2 vent	A300.A300S.357	6.05E+04
Air to atmosphere	A300.A300S.325	0.00E+00
Sulfur storage	A300.A300S.324	0.00E+00
Ethanol product	A500.592A	5.64E+04
Higher alcohols	A500.590	1.02E+04
Vent to atmosphere	A600.634	4.27E-01
Evaporated to atmosphere	A700.705	4.49E+06
Blow down	A700.713	1.81E+04
Windage to atmosphere	A700.704	8.67E+03
Flue gas stack	112	8.60E+05
Water to treatment plant	A300.305	1.32E+03
Hot gasses to feed drying	A100.107	7.71E+05
Dried wood	A100.105	1.93E+05
In		5.43E+06
Out		5.51E+06
Difference		-8.63E+04
Percent closure		-1.6%

Table 8-12: Material balance for mixed hardwoods at 45% MC

Mixed hardwoods 45% MC **stream description**	stream #	MASSFLMX LB/HR
Feedstock in	100	3.34E+05
Combustion air	A200.A200CC.209A	4.46E+05
water input	A200.A200CC.218	1.77E+02
MgO	A200.220	4.55E+00
Make up olivine	A200.221	5.40E+02
Make up catalyst	A300.A300TR.326	1.07E+00
Combustion air	A300.A300TR.329B	2.57E+05
Lo-Cat oxidizer air	A300.A300S.322	0.00E+00
Make up water preheat	A600.618	3.22E+04
Make up water	A700.710	8.58E+04
Clear water chemicals	A700.711	8.14E-01
Clear water header	A700.718	4.07E+06
output		
Sand fly ash	A200.219	1.77E+03
Catalyst purge	A300.A300TR.329	1.07E+00
Solid waste	A300.A300Q.336	8.02E+01
CO2 vent	A300.A300S.357	5.60E+04
Air to atmosphere	A300.A300S.325	0.00E+00
Sulfur storage	A300.A300S.324	0.00E+00
Ethanol product	A500.592A	5.16E+04
Higher alcohols	A500.590	9.30E+03
Vent to atmosphere	A600.634	3.92E-01
Evaporated to atmosphere	A700.705	4.22E+06
Blow down	A700.713	1.70E+04
Windage to atmosphere	A700.704	8.14E+03
Flue gas stack	112	9.43E+05
Water to treatment plant	A300.305	1.22E+03
Hot gasses to feed drying	A100.107	8.02E+05
Dried wood	A100.105	1.93E+05
In		5.23E+06
Out		5.31E+06
Difference		-8.10E+04
Percent closure		-1.5%

Table 8-13: Material balance for corn stover at 16% MC

Cornstover 16% MC		MASSFLMX
stream description	stream #	LB/HR
Feedstock in	100	2.19E+05
Combustion air	A200.A200CC.209A	3.80E+05
water input	A200.A200CC.218	2.49E+03
MgO	A200.220	9.05E+01
Make up olivine	A200.221	4.54E+02
Make up catalyst	A300.A300TR.326	1.04E+00
Combustion air	A300.A300TR.329B	2.24E+05
Lo-Cat oxidizer air	A300.A300S.322	2.33E+02
Make up water preheat	A600.618	3.06E+04
Make up water	A700.710	1.06E+05
Clear water chemicals	A700.711	9.87E-01
Clear water header	A700.718	4.94E+06
output		
Sand fly ash	A200.219	2.49E+04
Catalyst purge	A300.A300TR.329	1.04E+00
Solid waste	A300.A300Q.336	8.35E+01
CO2 vent	A300.A300S.357	4.78E+04
Air to atmosphere	A300.A300S.325	2.39E+02
Sulfur storage	A300.A300S.324	9.64E+01
Ethanol product	A500.592A	4.41E+04
Higher alcohols	A500.590	7.97E+03
Vent to atmosphere	A600.634	6.26E+00
Evaporated to atmosphere	A700.705	5.12E+06
Blow down	A700.713	2.06E+04
Windage to atmosphere	A700.704	9.87E+03
Flue gas stack	112	7.23E+05
Water to treatment plant	A300.305	1.17E+03
Hot gasses to feed drying	A100.107	6.98E+05
Dried wood	A100.105	1.93E+05
In		5.90E+06
Out		6.00E+06
Difference		-9.82E+04
Percent closure		-1.6%

Table 8-14: Material balance for eucalyptus salina at 45% MC

Eucalyptus Salina 45% MC **stream description**	stream #	MASSFLMX LB/HR
Feedstock in	100	3.34E+05
Combustion air	A200.A200CC.209A	4.12E+05
water input	A200.A200CC.218	2.59E+02
MgO	A200.220	7.58E+00
Make up olivine	A200.221	5.37E+02
Make up catalyst	A300.A300TR.326	1.05E+00
Combustion air	A300.A300TR.329B	2.63E+05
Lo-Cat oxidizer air	A300.A300S.322	0.00E+00
Make up water preheat	A600.618	3.30E+04
Make up water	A700.710	8.12E+04
Clear water chemicals	A700.711	7.71E-01
Clear water header	A700.718	3.85E+06
output		
Sand fly ash	A200.219	2.59E+03
Catalyst purge	A300.A300TR.329	1.05E+00
Solid waste	A300.A300Q.336	7.91E+01
CO2 vent	A300.A300S.357	5.34E+04
Air to atmosphere	A300.A300S.325	0.00E+00
Sulfur storage	A300.A300S.324	0.00E+00
Ethanol product	A500.592A	4.89E+04
Higher alcohols	A500.590	8.82E+03
Vent to atmosphere	A600.634	2.14E+00
Evaporated to atmosphere	A700.705	4.00E+06
Blow down	A700.713	1.61E+04
Windage to atmosphere	A700.704	7.71E+03
Flue gas stack	112	9.22E+05
Water to treatment plant	A300.305	1.19E+03
Hot gasses to feed drying	A100.107	7.81E+05
Dried wood	A100.105	1.93E+05
In		4.98E+06
Out		5.06E+06
Difference		-7.67E+04
Percent closure		-1.5%

Table 8-15: Material balance for miscanthus at 16% MCC

Miscanthus 16% MC **stream description**	stream #	MASSFLMX LB/HR
Feedstock in	100	2.19E+05
Combustion air	A200.A200CC.209A	3.78E+05
water input	A200.A200CC.218	3.41E+02
MgO	A200.220	1.06E+01
Make up olivine	A200.221	5.34E+02
Make up catalyst	A300.A300TR.326	1.05E+00
Combustion air	A300.A300TR.329B	2.18E+05
Lo-Cat oxidizer air	A300.A300S.322	0.00E+00
Make up water preheat	A600.618	3.11E+04
Make up water	A700.710	7.68E+04
Clear water chemicals	A700.711	7.32E-01
Clear water header	A700.718	3.66E+06
output		
Sand fly ash	A200.219	3.41E+03
Catalyst purge	A300.A300TR.329	1.05E+00
Solid waste	A300.A300Q.336	8.47E+01
CO2 vent	A300.A300S.357	5.48E+04
Air to atmosphere	A300.A300S.325	0.00E+00
Sulfur storage	A300.A300S.324	0.00E+00
Ethanol product	A500.592A	4.79E+04
Higher alcohols	A500.590	8.65E+03
Vent to atmosphere	A600.634	1.30E+00
Evaporated to atmosphere	A700.705	3.79E+06
Blow down	A700.713	1.53E+04
Windage to atmosphere	A700.704	7.32E+03
Flue gas stack	112	7.24E+05
Water to treatment plant	A300.305	1.21E+03
Hot gasses to feed drying	A100.107	6.98E+05
Dried wood	A100.105	1.93E+05
In		4.58E+06
Out		4.66E+06
Difference		-7.28E+04
Percent closure		-1.6%

Table 8-16: Material balance for switchgrass at 16% MC

Switchgrass 16% MC **stream description**	stream #	MASSFLMX LB/HR
Feedstock in	100	2.19E+05
Combustion air	A200.A200CC.209A	3.89E+05
water input	A200.A200CC.218	1.24E+03
MgO	A200.220	4.39E+01
Make up olivine	A200.221	5.01E+02
Make up catalyst	A300.A300TR.326	1.08E+00
Combustion air	A300.A300TR.329B	2.24E+05
Lo-Cat oxidizer air	A300.A300S.322	3.13E+02
Make up water preheat	A600.618	3.04E+04
Make up water	A700.710	9.55E+04
Clear water chemicals	A700.711	8.98E-01
Clear water header	A700.718	4.49E+06
output		
Sand fly ash	A200.219	1.24E+04
Catalyst purge	A300.A300TR.329	1.08E+00
Solid waste	A300.A300Q.336	8.39E+01
CO2 vent	A300.A300S.357	5.20E+04
Air to atmosphere	A300.A300S.325	3.21E+02
Sulfur storage	A300.A300S.324	1.29E+02
Ethanol product	A500.592A	4.80E+04
Higher alcohols	A500.590	8.67E+03
Vent to atmosphere	A600.634	5.89E+00
Evaporated to atmosphere	A700.705	4.65E+06
Blow down	A700.713	1.87E+04
Windage to atmosphere	A700.704	8.98E+03
Flue gas stack	112	7.35E+05
Water to treatment plant	A300.305	1.24E+03
Hot gasses to feed drying	A100.107	7.09E+05
Dried wood	A100.105	1.93E+05
In		5.45E+06
Out		5.54E+06
Difference		-8.93E+04
Percent closure		-1.6%