Life Cycle Assessment of Biofuels Produced from Short Rotation Woody Crops

Erik Budsberg

A thesis

submitted in partial fulfillment of the

requirements for the degree of

Masters of Science

University of Washington

2013

Committee:

Rick Gustafson

Renata Bura

Maureen Puettmann

Program Authorized to Offer Degree:

School of Environmental and Forest Sciences

©Copyright 2013

Erik Budsberg

University of Washington

Abstract

Life Cycle Assessment of Biofuels produced from Short Rotation Woody Crops

Erik Budsberg

Chair of the Supervisory Committee:

Dr. Rick Gustafson

Denman Professor of Bioresource Science and Engineering

School of Environmental and Forest Sciences

In an effort to find a substitute for petroleum based liquid transportation fuels many countries are turning to biofuels. The newest form of these biofuels, also known as the second generation or cellulosic biofuels, have received considerable attention. Short rotation woody crops (SRWC) such as willow and poplar have been proposed as possible sources of biomass to produce these biofuels via biochemical conversion. Before moving to commercial scale, the impacts these biofuels could place on environment must be investigated. In this thesis two research projects to assess environmental performance of SRWC biofuels using Life Cycle Assessment (LCA) are presented.

In the first project an LCA of ethanol production via bioconversion of willow biomass crop feedstock is investigated. Willow crop data are used to assess feedstock production impacts. The bioconversion process is modeled with an Aspen simulation that predicts an overall conversion yield of 310 liters of ethanol per tonne of feedstock (74 gal per US short ton). Vehicle combustion impacts are assessed using greenhouse gases, regulated emissions, and energy use in transportation (GREET) model. The impacts of bioconversion produced ethanol are compared with those of gasoline on an equivalent energy basis. Results of the LCA show that the life-cycle global warming potential of ethanol is slightly negative. Carbon emissions from ethanol production and use are balanced by carbon absorption in the growing willow feedstock and the displacement of fossil fuel produced electricity with renewable electricity produced in the bioconversion process. The fossil fuel input required for producing 1 MJ of energy from ethanol is 141 percent less than that from gasoline. More water is needed, however, to produce 1 MJ of ethanol fuel than 1 MJ of gasoline. The life-cycle water use for ethanol is 169 percent greater than that for gasoline. The largest contributors to water use are the conversion process itself and the production of chemicals and materials used in the process, such as enzymes and sulfuric acid.

In the second project, LCA for two lignocellulosic bioethanol production pathways are simulated using hybrid poplar as a feedstock are developed and compared. Both processes use a dilute acid pretreatment followed by enzymatic hydrolysis. The processes differ in the fermentation process. In the first pathway an ethanologen is used to produce ethanol. The second pathway is fermented with an acetogen to produce acetic acid. Acetic acid undergoes hydrogenation to produce ethanol. Both bioconversion pathways are modeled in ASPEN-plus simulations. In both processes lignin is recovered and burned onsite to produce electricity. The critical difference between the two processes is that the acetic acid pathway has a higher product yield but requires hydrogen for the process. Steam methane reforming is assumed to be the source of hydrogen. Greenhouse gases, regulated emissions, and energy use in transportation (GREET) is used to model combustion of ethanol from each scenario in a flex fuel vehicle. All necessary chemicals, transportation, and processes required by each production pathway are included within the LCAs. Each pathway is assessed to determine the global warming potential (GWP), fossil fuel use, and freshwater use. Compared to gasoline the ethanologen pathway has a GWP that is 97 percent lower, uses 97 percent less fossil fuels, and 180 percent more water. The acetogen pathway has a GWP 53 percent lower than gasoline, reduces fossil fuel use by 55 percent, and increases water use by 81 percent. In regards to the GWP and fossil fuel use the ethanologen pathway achieves larger reductions compared to gasoline. However, the acetogen pathway will produce more ethanol per unit of land and this may play a crucial role in choosing a lignocellulosic ethanol production method if land is a limited resource.

Contents

1. Thesis Introduction

Global warming is becoming a very real threat to Earth and the life it supports. From melting ice caps, rising sea levels, and shifts in ocean currents and weather patterns the effects of the climate changing are varied and wide ranging. A primary cause of global warming is increased concentrations of greenhouse gases (GHGs) in the atmosphere, with carbon dioxide emissions being of largest concern. CO_2 is a naturally occurring gas, but also is a byproduct from the combustion of fossil fuels. Since the industrial revolution CO_2 concentrations in the atmosphere have increased by 36% (Environmental Protection Agency (EPA), 2007). This increase of CO_2 is largely responsible for 0.8°C degrees of warming since 1900 and if left unchecked could cause 1.1 to 6.4°C of warming by the end of this century (Solomon et al. 2007). In an attempt to reduce fossil fuel CO_2 emissions, much emphasis has been placed in developing alternative and sustainable energy.

Alternative energy improves upon the use of fossil fuels by greatly reducing emissions of CO_2 as well as other GHGs. Many types of alternative energies are needed to meet the vast energy demands of the world's populations and development is limited by the resources available in a given region. The last couple decades have seen great improvements in utilizing solar power, wind, tidal, and geothermal energy. While these technologies are a good way to sustainably produce electricity they do not help in replacing liquid transportation fuels such as gasoline and diesel. Biofuels made from various types of biomass have been identified as a replacement option of these fossil fuels.

The underlying benefit of biofuels is the idea that they are part of a carbon cycle, not just a one way source of carbon emissions like fossil fuels. The biofuels carbon cycle begins with growing biomass. As the plants grow they remove CO_2 from the air through photosynthesis. Through chemical reactions, carbon in the CO_2 is separated and stored within the plants biomass in various polymers. It is this carbon that gives plants much of their mass. The plant will eventually be harvested and transported to a biorefinery where the carbon will be converted into biofuel. When that biofuel is combusted it releases the carbon back into the air in the form of CO_2, thereby completing the cycle. When petroleum and other fossil fuels are combusted they also release CO_2 into atmosphere. It takes millions of years for CO_2 to be removed from the atmosphere and turned back into petroleum or coal. In regards to anthropogenic timescales the carbon cycle of petroleum and coal are one way sources of CO_2. In the simplest terms biofuels are sustainable and fossil fuels are not.

Life Cycle Assessment

A major goal of biofuels is to reduce environmental impacts relative to the fuel source they are displacing, namely gasoline. A common way to determine if these biofuels, or any type of fuel, reduce environmental impacts is to use Life Cycle Assessment (LCA). This technique is useful in studying the entire life of a biofuel, called a cradle to grave assessment, or just part of it, such as cradle to gate or gate to grave assessment. The structure of how to perform an LCA is set by ISO standards 14040 and 14044 (ISO, 2006a & 2006b) and is broken up into four main sections: goal and scope, life cycle inventory (LCI), life cycle inventory assessment (LCIA), and interpretation of the results. The following descriptions are summarized from ISO 14040 (2006a).

Goal and Scope

The goal of an LCA will depend on the purpose of the research. The author will state why the research is being conducted, who and what is it intended for, and the intended use of the results. For corn to biofuel LCA the goal could be to identify processes that contribute the most to global warming and to compare these results to gasoline. If publishing this LCA, the intended audience is the general public.

The scope involves stating the details of analysis of an LCA. The product or system studied and the system boundaries used are included in the scope. System boundaries refer to where the study begins and ends. It also identifies what processes are considered in the production of the main product or system (Figure 1.1). Processes within the system boundaries are those that contribute to production, use, and disposal. These processes, referred to as unit processes, require technological inputs (technosphere flows). Flows that cross the system boundaries are the natural resources or emissions required to produce, use, or dispose of something (environmental flows). Sometimes it is not possible to include all unit processes and it is important to note what is and isn't included in the scope along with all other assumptions. A functional unit is set which will be used as the reference point for the LCI and LCIA. Using the biofuel example, this could be one MJ of energy in the fuel, one ton of biomass, or one mile driven using the fuel produced.

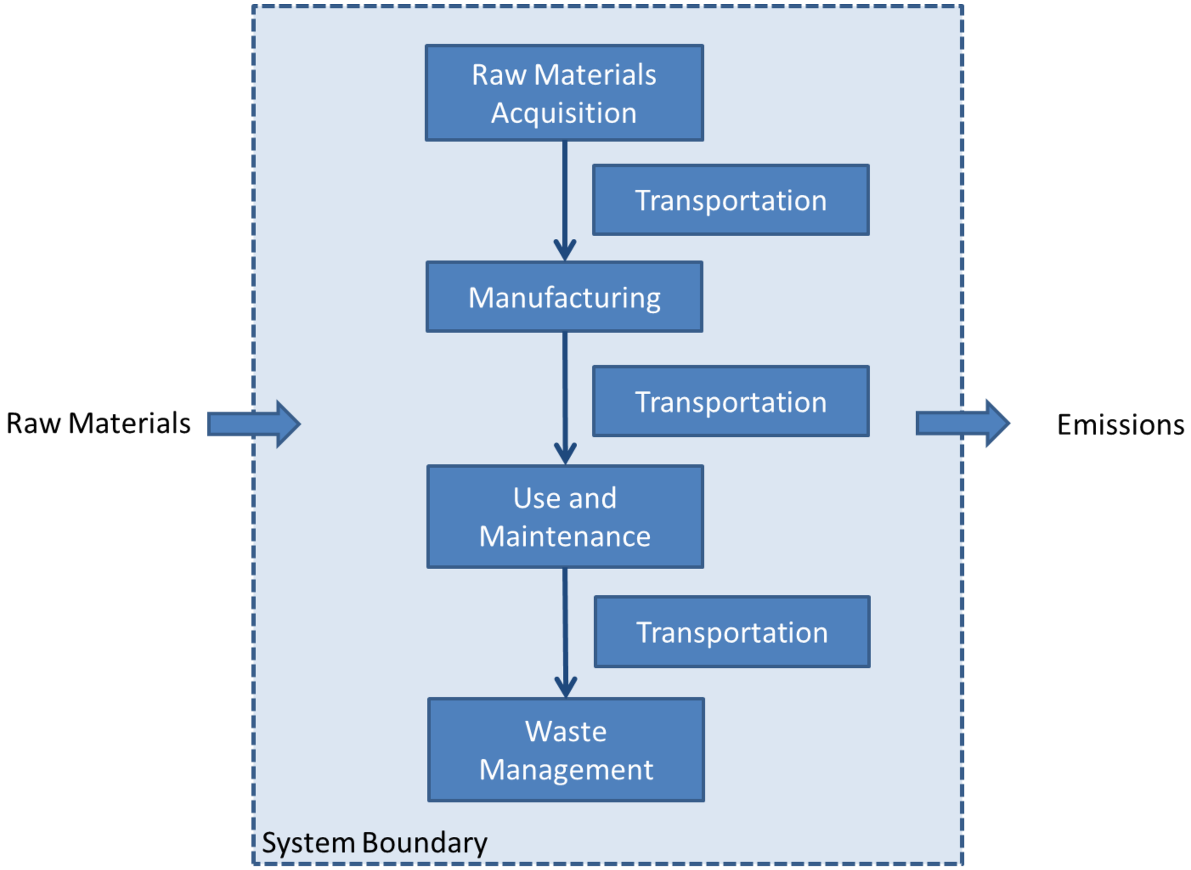

Figure 1.1: - Stages within life cycle assessment (adapted from SAIC 2006). Flows within the system boundaries (grey box) are technosphere flows. Raw materials and emissions that cross the system boundaries are environmental flows.

The process being studied may produce more than one product. In this case how the resource use and emissions will be allocated between the multiple products must be stated. For example a common co-product in biofuel production is electricity. Allocation between the fuel and electricity could be based on energy content or economics. If possible ISO 14044 (2006b) states that system expansion should be used in dealing with co-products. For the biofuel example this means the electricity produced would displace a corresponding amount of electricity elsewhere, thereby expanding the system boundaries to include the avoided production of electricity.

How the environmental impacts will be calculated is based on the impact methodology chosen. There are multiple impact calculation methods and the one that will be used should be stated. In the U.S. the Environmental Protection Agency has put out the Tools for the Reduction and Assessment of Chemical Impacts (TRACI) (Bare 2002). The TRACI methodology is used in this thesis.

Life Cycle Inventory

When preparing an LCA, the LCI is the most time intensive step. Data on all unit processes that contribute to the product or service are collected. Included in a unit process will be environmental and technosphere flows tied to production, use, or disposal of that processes. The quality of the data used to produce unit flows is critical. Errors or inaccuracies in unit processes will propagate throughout the results. Data sources should be thoroughly analyzed for completeness and accuracy to produce the most useful LCAs. Data sources used for unit process information should also be disclosed to ensure transparency in the LCA. Transparency is key to creating reproducible LCA results (Borrion et al. 2012).

Life Cycle Impact Assessment

The environmental impact of a product and the processes within it are calculated using LCI data. As mentioned above, an impact assessment methodology can be used to relate data in the LCI to given environmental impacts. For example, the Global Warming Potential (GWP) is based on the amount of GHG emissions produced during the products life. It ignores emissions and natural resources use that don't contribute to atmospheric warming. Other impacts TRACI calculates include ozone depletion, smog, acidification, eutrophication, carcinogenics, non-carcinogenics, respiratory effects, ecotoxicity, and fossil fuel depletion. How an emission contributes to a given impact is calculated using a characterization factor. Characterization factors assign point values to each emission or resource use based on their observed contribution to an impact. In the case of the 100 year GWP, CO_2 is given a score of one. All other GHGs are given values based on their atmospheric radiative forcing and decay rate relative to CO_2 (Solomon et al. 2007). The unit for GWP is known as CO_2 equivalence. The CO_2 eq. of CH_4 and N_2O, common GHGs, are 25 and 298 respectively. Other environmental impact characterization factors are calculated in a similar format.

Interpretation

The end product of the LCIA will be scores for the impact categories considered in the LCA. These scores can be used to compare to other products and environmental performance can be assessed. Within the LCA impact categories are broken up to determine which processes or systems contribute to a given environmental impact. This is used to identify areas for improved environmental performance. The interpretation provides a summary of the LCA work and suggestions for future work regarding the environmental impacts of the product.

Corn Ethanol

There are different types of biofuels, with varying methods to produce them. Currently the most common form of biofuel is bioethanol. It is already in commercial production today and in the tanks of many vehicles. In the U.S. bioethanol is mixed into gasoline at a 10% concentration (E10) to serve as an anti-knocking agent and fuel oxygenate, replacing the environmentally toxic methyltributylether (MTBE) (The Royal Society, 2008). A majority of vehicles in the U.S. cannot run on ethanol-gasoline fuel blends with more than 10% ethanol (E10) (The Royal Society, 2008). A vehicles inability to run on higher ethanol concentrations is a result of ethanol's chemical properties. It has a much lower energy content compared to gasoline (HHV of 29.6 MJ/kg for ethanol and 47.9 MJ/kg for gasoline (Oak Ridge National Laboratory, 2012)). Ethanol is also hydrophilic, corrosive to some engine parts, and has a lower vapor pressure (The Royal Society, 2008). Lowering the vapor pressure in fuels can cause ignition problems in colder environments (The Royal Society, 2008). Vehicles with engines designed to operate with a higher oxygenate content are known as Flex Fuel Vehicles (FFVs). These FFV are capable of using fuel blends that contain more ethanol and some can operate on pure ethanol (E100).

In the U.S. nearly all of the ethanol comes from corn. Two processes have been used to produce corn ethanol, dry milling and wet milling. In either process, the goal is to isolate glucose and ferment it to ethanol using yeast. Currently the dry milling method is the most common process (Wang et al. 2011). It produces a high ethanol yield as well an animal feed co-product that helps the process be economically viable (Bothast and Schlicher, 2005). In the U.S. 90% of corn ethanol is derived from dry milling (Wang et al. 2011) and a review of this process follows.

The process begins with milling corn kernels into flour and adding it to water. The milling process exposes the starch in the corn. Starch is a polysaccharide comprised of glucose monomers linked by alpha 1-4 and alpha 1-6 linkages. Yeast cannot digest starch, but can digest glucose. Adding alpha-amylase enzymes to the starch slurry at elevated temperatures hydrolyzes 1-4 alpha bonds and the starch is converted to glucose (Bothast and Schlicher, 2005). Glucose is fermented and ethanol and CO_2 are produced in 1:1 molar ratios. A distillation step purifies the ethanol. Solids remaining after distillation are sold as an animal feed (Bothast and Schlicher, 2005).

LCA and Corn Ethanol

LCA to studies of corn ethanol have raised concerns regarding greenhouse gas (GHG) emissions resulting from land use change. Land use change emissions refer to emissions that result from changing use of a landscape. In most instances biomass, in some form or another, will be growing at a given location. Growing biomass removes carbon from the atmosphere through photosynthesis. The carbon is stored in the leaves, stems, roots, and soil. If the land is converted to a new type of use, the biomass will likely be killed and the soil disturbed in preparation for the new management scheme. Decomposition of the biomass and exposure of new soil to the atmosphere will produce carbon based emissions, such as CO_2 and CH_4. The amount of carbon emissions generated associated with land use change will depend on many site specific factors. Land use change can be classified either as direct or indirect. Direct land use change refers to the effects of converting a piece of land from one use to another. Measuring direct land use change can be difficult (Wang et al. 2011). To fully capture direct land use change, site specific factors must be known to determine potential carbon emissions. If a LCA is not site specific, which most are not, estimates have been proposed for carbon emissions resulting from direct land use change (Solomon et al. 2007, Fargione et al. 2008). Indirect land use change is harder yet to assess. It concerns how changing land to a different use in one location affects land use in another. A common example of indirect land use change illustrates that by converting an acre of land in the U.S. to corn for ethanol, an acre of Brazilian rainforest would be converted to cropland to produce food that the acre of land in the U.S. would have provided. To estimate indirect land use change, economic models have been created that simulate market place responses to changes in supply and demand (Wang et al. 2011). Currently the uncertainty in indirect land use change modelling is large (Wang et al. 2011, Sanchez et al. 2012).

Early assessments of land use change, both direct and indirect, in corn ethanol LCAs indicated that an increasing demand for corn would result in large amounts of land being converted to cropland (Fargione et al. 2008, Searchinger et al. 2008). Large carbon land use change emissions would result as corn would not be able to sequester an equivalent amount of the carbon emitted during land use change. This would create carbon debts that would take decades, if not centuries to pay back (Fargione et al. 2008, Searchinger et al. 2008). In these scenarios, there is no beneficial carbon mitigation and the GWP of corn ethanol is higher than gasoline (Searchinger et al. 2008). The suggestion that using corn to make ethanol could create large carbon debts prompted more detailed analysis of land use change modelling.

Recent models have indicated that land use change will likely not be as large as first suggested (Wang et al. 2011). A land use change modelling tool released by the Argonne National Laboratory in 2011 (Wang et al. 2011), that contains critical parameters not included in previous models, found GHGs related to land use change to be 65% lower than that reported in Searchinger et al. (2008). Using this model the GWP of corn ethanol is 20% lower than gasoline. If land use change is not included for corn ethanol, the GWP reduction compared to gasoline would be about 40% (Wang et al. 2011). This newer estimate greatly reduces the previous model estimates for land use change emissions, but land use change still plays a significant role in producing GHGs. Identifying ways to reduce land use change and related emissions will help improve the GWP of corn ethanol.

LCA and Cellulosic Biofuels

Corn ethanol is not the only way to produce bioethanol. Lignocellulosic biofuels, known as the second generation of biofuels, are currently being researched and developed world wide. Lignocellulosic biofuels are attractive compared to corn ethanol because they can reduce land use change. In addition they use a more diverse range of biomass which allows choosing a feedstock best suited to a given region (Borrion et al. 2012, Wiloso et al. 2012). Potential biofuel feedstocks include corn stover (Aden et al. 2002), switch grass (Cherubini and Jungmeier, 2010), poplar trees (Gonzalez-Garcia et al. 2010), forest residuals, and municipal solid wastes (Schmitt et al. 2011). These potential feedstocks can all be acquired in a way that limits land use change emissions. The corn stover and forest residuals are by-products of current land management practices (agriculture and logging). Using them would not require any land use change (Wang et al. 2011). Switch grass and poplar trees can be grown on marginal lands. Using marginal lands is unlikely to induce large land use change emissions (Fargione et al. 2008, Wiloso et al. 2012). Municipal solid wastes would require no land use change and increasing the demand for solid waste would not displace land elsewhere (Searchinger et al. 2008).

Lignocellulosic ethanol can be produced in three different ways, pyrolysis, gasification, and bioconversion. The work of this thesis focuses solely on the bioconversion approach. Bioconversion of lignocellulosic biomass improves upon the platform used to produce corn ethanol. Like the corn ethanol platform, the goal is to access and ferment sugars contained in biomass. In second generation biofuels the sugar is contained in the cellulose and hemicellulose found in plant cell walls. Cellulose and hemicellulose plus lignin give plants there structural support. The process to produce cellulosic biofuels has been well studied. (Aden et al. 2002, Humbird et al. 2011, Borrion et al. 2012, Wiloso et al. 2012), but producing lignocellulosic biofuels is more challenging than producing corn ethanol. Only now are commercial lignocellulosic biorefineries starting to come online.

Various bioconversion technologies have been proposed and each has limitations on the feedstock that it can covert. For each feedstock, different conversion processes have been proposed that optimize the recovery and fermentation of cellulose and hemicellulose to give the highest ethanol yield possible (Wiloso et al. 2012). These processes require different chemicals and use different unit operations, but the overall bioconversion of lignocellulosic material into ethanol follows the same basic steps. A pretreatment is first required to separate the lignin, cellulose, and hemicellulose. Some form of dilute acid pretreatment is commonly used to separate the lignin, cellulose, and hemicellulose (Humbird et al. 2011). Steam explosion and ammonia fiber explosion are also plausible pretreatment options (Wiloso et al. 2012). In general the cellulose and lignin will remain in the solid stream and the hemicellulose will be hydrolyzed into the liquid stream. The exposed cellulose then undergoes a hydrolysis step to cleave the 1, 4 beta linkage between glucose monomers. The use of enzymes or acid is commonly used to perform the hydrolysis (Wiloso et al. 2012). Sugars in hemicellulose are usually hydrolyzed during the pretreatment step. Glucose and other sugars are then fermented to ethanol and CO_2 in a 1:1 molar ratio using yeast or bacteria. The ethanol will be distilled to 99.5% purity - if it is to be used as a fuel (Humbird et al. 2011) - and then blended into gasoline. The lignin and other unfermentable carbohydrates are burned on site in a boiler to provide process steam and heat (Humbird et al. 2011). It is common to produce excess electricity in this step that can be sold (Huang et al. 2009, Gnansounou and Dauriat, 2010, Stephenson et al. 2010, Gonzalez-Garcia et al. 2012) back on to the power grid. The amount of electricity produced will depend on process demands within the biorefineries.

The environmental impacts of each bioconversion process using each candidate feedstock needs to be thoroughly investigated. Different feedstocks, process chemicals, and ethanol yields will produce unique environmental impacts (Borrion et al. 2012). Overall most lignocellulosic biofuels show GWP reductions compared to gasoline of 11 to 145% (Wiloso et al. 2012). The large ranges in GWP is related to the choice of feedstock (and its management) and assumptions in each LCA (Borrion et al. 2012, Wiloso et al. 2012). This large range underlines the importance of thoroughly investigating the environmental impacts of each proposed system. A one size fits all approach to lignocellulosic biofuels will not work.

Short Rotation Woody Crops (SRWCs) are studied in this research as potential biofuel feedstocks. The SRWCs investigated are willow and poplar trees. These two trees have very similar chemical compositions and are grown using similar practices. They are considered good bioconversion feedstocks because the carbohydrates can be recovered with good yields without extensive pretreatment (Sassner et al. 2005). Other benefits of using willow or poplar as a feedstock include high biomass production, suitability for cultivation on marginal land, ease of vegetative propagation from dormant hardwood cuttings, broad genetic base and ease of breeding, ability to resprout after multiple harvests, and low fertilizer input (Keoleian and Volk 2005, Greenwood Resources, personal communication, 2012). The first project of this thesis work investigated bioconversion of willow feedstock. The second project investigated bioconversion of poplar biomass.

Thesis Objectives

Until now no LCA studies have been conducted to investigate the environmental impacts of producing ethanol from willow via a bioconversion route in the United States. Life cycle assessment (LCA) of ethanol produced by bioconversion of willow has been investigated for Europe using the information of feedstock production available in literature from the United Kingdom (Stephenson et al. 2010). This study found a GWP reduction of 90% compared to gasoline. This reduction is a positive sign for use of a willow feedstock, but the results of an LCA will vary between Europe and U.S. Agricultural practices may differ, chemical production methods can differ, and using a U.S. electrical grid instead of a European grid will change the LCA results (Wiloso et al. 2012). The objective of the first project presented in this thesis is to conduct an LCA on the production of bioethanol from a willow biomass crop via biochemical conversion. Feedstock production and harvesting data are provided from operational data for willow crops managed at the Woody Biomass Program at the State University of New York, Syracuse (WBP 2011).

The objective of the second project presented in this thesis is to use LCA to assess environmental impacts of a higher yielding ethanol process. The use of an ethanologen in the fermentation step is potentially an inefficient way to produce ethanol. For every mole of glucose consumed by an ethanologen, CO_2 and ethanol are produced in 1:1 molar ratios. The production of CO_2 limits the maximum theoretical carbon efficiency at 67% (Cherubini and Stromman, 2010). To overcome this inefficiency different fermentation organisms can be used. An acetogen, an organism that ferments acetic acid, can potentially make the bioconversion process more efficient. These organisms will only produce acetic acid as it consumes glucose (and other sugars) and has a theoretical conversion yield of 100% (Verser and Eggeman, 2011). The acetic acid produced can then be converted to ethanol using catalytic hydrogenation. The end result is a much higher yield of ethanol per tonne of biomass (Verser and Eggeman, 2011). In this life cycle assessment a poplar feedstock will be used to supply the necessary biomass. An LCA of a comparable system using a traditional ethanologen fermentation pathway is also simulated using a poplar feedstock. The two LCAs will allow for comparison between the traditional lignocellulosic bioconversion process and the proposed higher yield bioconversion process and a comparison with fuel produced from petroleum.

The results of the two studies presented in this thesis will be published as articles in scientific journals. The first project, an LCA of willow to ethanol via a bioconversion process, has already been published (Budsberg et al. 2012). The LCA of willow to ethanol write up in this thesis includes all work conducted before submission to the Forest Products Journal. The second project, Ethanologens vs. Acetogens: Environmental impacts of two bioethanol fermentation pathways, has been prepared for publication. The format of this thesis includes the introduction, project one in journal publication form, project two in a prepared journal publication form, and a conclusion of work conducted within this thesis.

2. Life-Cycle Assessment for the Production of Bioethanol from Willow Biomass Crops via Biochemical Conversion[1]

Erik Budsberg, Mohit Rastogi, Maureen E. Puettmann, Jesse Caputo, Stephen Balogh, Timothy Volk,
Richard Gustafson ,Leonard Johnson

Abstract

A life cycle assessment (LCA) of ethanol production via bioconversion of willow biomass crop feedstock is conducted. Willow crop data are used to assess feedstock production impacts. The bioconversion process is modeled with an ASPEN simulation that predicts an overall conversion yield of 310 liters of ethanol per tonne of feedstock (74 gallons/ U.S. short ton). Vehicle combustion impacts are assessed using GREET models. The impacts of bioconversion produced ethanol are compared with those of gasoline on an equivalent energy basis. It was found that the life cycle global warming potential (GWP) of ethanol is 120% less than that of gasoline. This reduction in GWP for ethanol is attributable to feedstock CO2 sequestration and displacement of fossil fuel produced electricity with renewable electricity produced in the bioconversion process. The fossil fuel input required for producing one MJ of energy from the ethanol is 141% less than that for gasoline. More water is needed to produce a MJ of ethanol fuel than for gasoline. The life cycle water use for ethanol is 166% greater than gasoline. The largest contributors to water use are the conversion process itself and the production of chemicals and materials used in the process such as enzymes and sulfuric acid.

Introduction

The Energy Independence and Security Act (EISA) mandates that at least 16 billion gallons (61 billion liters) per year of cellulosic fuel be in production by the year 2022 (United States Government, 2007). To meet this ambitious goal, many feedstocks, with appropriate conversion technologies, will be required for fuel production. Woody biomass will play an important role in supplying feedstock for biofuels production. The National Academy of Science (2009) projects that by 2020 124 million dry tons (112 million tonnes) per year of woody biomass will be available for use without compromising the environment. The Consortium for Research on Renewable Industrial Materials (CORRIM) has comprehensively assessed the life cycle impacts of solid wood products. The current work by CORRIM expands that research portfolio to investigate production of fuels from woody biomass. In this project, the production of ethanol using bioconversion is investigated with willow biomass as the feedstock.

---

[1] The version in this thesis is pre-submittal for publication. The published version can be found at: Budsberg, E., Rastogi, M., Puettmann, M. E., Caputo, J., Balogh, S., Volk, T.A., Gustafson, R., and L. Johnson. 2012. Life-Cycle Assessment for the Production of Bioethanol from Willow Biomass Crops via Biochemical Conversion. Forest Products Journal 62(4): 305 – 313.

Willow is considered a good bioconversion feedstock because the carbohydrates can be recovered with good yields without extensive pretreatment (Sassner et al. 2005). The companion CORRIM biofuels investigations reported in this journal use softwood residual feedstock. Softwood residuals were not chosen for this initial study using bioconversion because of the recalcitrance of that material (Mansfield et al. 1999). Other benefits of using willow as a feedstock include high biomass production, suitability for cultivation on marginal land, ease of vegetative propagation from dormant hardwood cuttings, broad genetic base and ease of breeding, and ability to resprout after multiple harvests (Keoleian and Volk 2005).

Life cycle assessment (LCA) of ethanol produced by bioconversion of willow has been investigated for Europe (Stephenson et al. 2010). In this research the information of feedstock production were obtained from available literature from the United Kingdom. The impacts associated with conversion were estimated using the ASPEN model developed by NREL (Aden et al. 2002), and emissions from vehicle use were estimated using CONCAWE and EUCAR (Stephenson et al. 2010). Environmental impacts were calculated using EDIP (Environment Development of Industrial Products) methodology. Stephenson found that ethanol produced using bioconversion reduced lifecycle greenhouse gas (GHG) emissions and fossil energy requirement by 90% and 83%, respectively, when compared to gasoline. There have also been LCA studies for production of ethanol using bioconversion of poplar feedstocks (Gonzalez-Garcia et al. 2010). Poplar is similar to willow in terms of growth and harvesting, and biomass composition. Results from these LCAs should be similar to those using willow. In the Gonzalez-Garcia study feedstock data were obtained from the literature on poplar crops grown and harvested in Spain. They used the NREL model (Aden et al. 2002) to assess the impacts of the bioconversion process and used available literature to estimate emissions associated with vehicle usage. CML was used as the impact characterization method. Gonzalez-Garcia found that life cycle greenhouse gas emissions for bioconversion ethanol (E100) were 80% lower than gasoline and fossil fuel use was decreased by 78%. Gonzalez-Garcia did not account for the impact of excess electricity production on the life cycle impacts, which could explain the smaller lifecycle greenhouse gas emission reduction relative to the results of Stephenson.

In the present work we refine and expand on the previous LCA work by using LCI data bases developed for United States data and by using actual operations data for feedstock production and harvesting. Further, we investigate life cycle water consumption, which may be a significant environmental impact for biorefineries using a bioconversion approach.

Methods

Goal and scope

The goal of this study is to investigate the environmental impacts of using bioethanol that is produced via a bioconversion process with willow as the feedstock. The environmental impact assessed is Global Warming Potential (GWP). In addition, the life cycle fossil fuel and fresh water requirements for bioethanol are assessed. All these impacts and resource demands are compared with gasoline production and use. A functional unit of 1 MJ is used in our analysis to adjust for the different heating values of ethanol and gasoline. In this study we have adhered to the methodology set by the International Standards Organization, ISO 14040 and 14044 (International Organization for Standardization 2006a & 2006b), and those used by CORRIM such that we can compare impact assessments for producing fuels with different conversion technologies and can compare the life cycle carbon impacts of using wood biomass to produce various products, including fuels and solid wood products.

System boundaries

System boundaries for the study are from the establishment of the site for willow crop production to the combustion of the ethanol product. The product stages in this life cycle are feedstock production and harvesting, transport to biorefinery, the conversion process, fuel distribution and use, ancillary chemicals, avoided production, and disposal of solid wastes (Figure 1). Modules were developed in SimaPro v.7.2.4 (Pre Consultants, 2011) using the USLCI (NREL 2011) and EcoInvent (Swiss Center for Life Cycle Inventories 2009) databases for materials and processes that were not user-generated. EcoInvent was used only when no appropriate data were available from the USCLI.

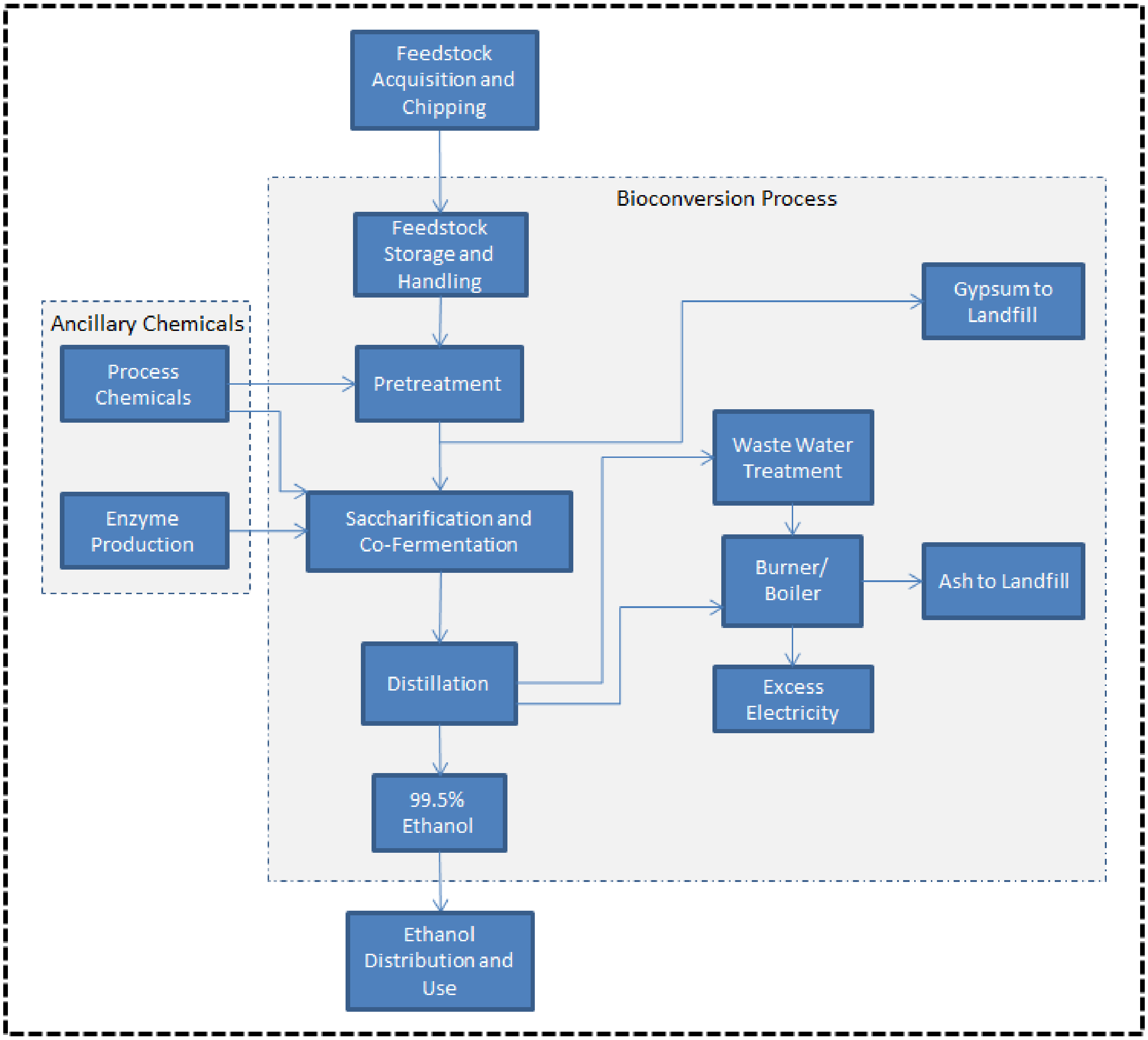

Figure 2.1 – Cradle-to-grave system boundaries. All process inputs and emissions associated with those areas designated in the figure are tracked within the life-cycle assessment.

Most of the data used in the analysis are national averages that are not indicative of site specific conditions for a particular region of the country. All ethanol is assumed to be produced in the continental United States, precluding the need for imports. Electrical energy is a co-product from ethanol production. Two methods are used to analyze the impact of electricity production on global warming. The first is to treat excess electricity as an avoided product employing 'system expansion'. In this case, excess electricity not needed for ethanol production displaces the corresponding amount supplied by the US National Grid. System expansion is commonly employed in LCA studies and is the method of choice when applicable (ISO 14044:2006). The second method is to consider electricity as co-product and perform an allocation based on the ethanol's and electricity's respective energy content.

Allocation was investigated to determine the impact of displaced national grid electricity production on life cycle global warming potential.

Assumptions

- The land used to grow the energy crop had previously been idle cultivated land; the use of such land would not cause any ‘direct’ or ‘indirect’ carbon dioxide emissions. Below ground carbon is assumed to maintain a steady state for the crop’s lifetime. No measurable changes in soil carbon over time to a depth of 45cm in willow plantation sites have been observed (Pacaldo et al. 2010). There may be considerable increases in belowground carbon in willow plantations because of the permanent plant parts – coarse roots and stool – as well as some allocation to fine roots, but how much of that remains as part of the soil matrix over time is not yet clear. The assumption of a neutral belowground carbon pool is believed to be a conservative estimate. Changes in biomass productivity and soil carbon may result from treatments that address nutrient deficiencies or accelerate regeneration, providing potential future alternatives of importance that are not addressed in this study.
- Higher Heating Value for ethanol 29.5 MJ/kg
- Higher Heating Value for gasoline 48.4 MJ/kg

Data collection

Operations data for production and harvesting of willow biomass are combined with bioconversion data generated from an ASPEN-Plus® (Aspen Technology Inc. 2005) simulation. The end use tailpipe emission for ethanol is modeled with Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) (Wang 2010). LCA models were developed using SimaPro® 7 (Pre Consultants, 2011) software. The GWP along with fossil fuels consumption of producing and using ethanol fuel from willow are assessed relative to that of a gasoline product system available in the USLCI (NREL 2011) database covering all primary products. The Life Cycle Impact Assessments (LCIA) were performed using the Tool for the Reduction and Assessment of Chemical and other environmental Impacts (TRACI) (Bare et al. 2003). Water use is compared to a gasoline product system from the Ecoinvent (Swiss Center for Life Cycle Inventories 2009) database as the USLCI gasoline process does not contain data on water usage. Both of the gasoline life cycles begin with extraction or crude oil in the ground, include transportation and refining, and end with combustion in spark ignition (SI) engine.

Impacts for ethanol production are broken down by production segments to show the relative effects of each segment of the lifecycle and to provide guidance on where to reduce overall environmental impact.

Feedstock production and harvesting.

Feedstock production and harvesting data are obtained from operational data for willow crops that are managed by at the Woody Biomass Program at State University of New York, Syracuse (http://www.esf.edu/willow/). Willow is grown on seven three-year rotations and includes one year of site preparation prior to planting the crop as unrooted cuttings. After the first growing season the willow is coppiced and produces multiple stems on each plant the following spring. The willow is left to grow for three years, harvested with a single pass cut and chip harvester based on a New Holland FR 9080 forage harvester and a 130FB short rotation coppice head. Chipped material is placed in a truck and ready for transport with no need of preprocessing once arriving at the biorefinery. After harvest the plants resprout and grow for another three years. Nitrogen fertilizer (100 kg N ha^{-1}) is applied in the spring after each harvest in this model (Quaye et al. 2011). Seven three year rotations are included in the life of the crop. Plants are killed with herbicide following the final harvest and stools are ground down (Buchholz and Volk 2011). Detailed tables of feedstock production can be found in appendix A.

The carbon content of willow is assumed to be 494 grams per kg of wood (Keoleian and Volk 2005) resulting in biomass CO_2 sequestration of 1.82 kg CO_2 per kg of wood. Similar values were used by Garcia-Gonzalez et al. (2010) for poplar.

Transport to the refinery

Feedstock is transported from the farm to the conversion facility. The mode of transportation is assumed to be diesel truck. Distances are based on literature review. It was assumed that the willow would be transported an estimated average distance of 160km (round-trip) (Wojnar 2010) as the bioethanol plant is intended to operate at a large-scale, 1200 dry tonnes willow/ day(1320 dry U.S. short ton willow/day). The composition of the willow feedstock is presented in Table 2.1 (Sassner et al. 2008). This category also includes the transportation of all other materials delivered to the biorefinery.

Bioconversion

While primary LCI survey data are often collected to be representative of industrial operations, no commercial-scale cellulosic ethanol facilities are operating yet to supply processing impact data. Processing impacts were modeled in ASPEN Plus software to generate conversion process LCI inputs for our SimaPro LCA model. The model is a modification of the NREL model for corn-stover feedstock (Aden et al, 2002), which was altered to be suitable for willow feedstock. For the base case investigated in this work, it was assumed that 1200 dry tonne willow would be fed to the biorefinery each day (419000 dry tonne/yr), which results in production of 130 million liters ethanol per year (310 liters/tonne).

The main process parameters used in the bioconversion model are shown in Table 2.2. Preteatment conditions and xylan recovery are those given by Sassner et al. (2006) and are similar to what has been used in our laboratory for poplar. Minor hemicellulose sugars are assumed to have the same recovery as xylan. The saccarification yield (75%) is a conservative estimate based on our experience with steam exploded hardwoods and low enzyme loadings. Fermentation conditions and yields are provided by Aden et al. (2002) for *Zymomonas mobilis*.

Table 2.1 – Willow feedstock chemical composition (Sassner et al. 2008).

Chemical	**% dry weight**
Cellulose	42.5
Hemicellulose	22
Lignin	26
Ash	2
Acetate	3
Extractives	4.5

Table 2.2 – Parameters used in Aspen bioconversion model.

Processing step	**Process parameter**	**Value**
Pretreatment	SO_2 charge (%, wt/wt)	2
	Temperature (^{o}C)	205
	Xylan to xylose (%)	74
Saccharification	Temperature (^{o}C)	65
	Enzyme loading (FPU/g cellulose)	5
	Cellulose to glucose (%)	75
Cofermentation	Temperature (^{o}C)	41
	Glucose to ethanol (%)	95
	Xylose to ethanol (%)	85

The bioconversion process begins when chipped willow enters the factory and undergoes sulfur dioxide catalyzed steam explosion pretreatment. Steam explosion was selected because it will result in a somewhat higher glucose yield with reduced fermentation inhibitor production than other pretreatment methods (Ewanick and Bura 2010). Endo-beta-1,4-glucanase, Cellobiohydrolase, and Beta-glucosidase are used for enzymatic hydrolysis and *Zymomonas mobilis* is assumed to be the fermentation organism. Ethanol is distilled and dehydrated until 99.5% purity is obtained. Lignin and unreacted carbohydrates are combusted in a boiler to provide process heat and electricity. At the assumed plant production capacity of 130 million liters per year, the biorefinery produces 28 MW of electricity. The bioconversion process consumes 9 MW and 19 MW of electricity is exported to the national grid. No auxiliary fuel is required for heat or power. Gypsum is produced as a byproduct but is assumed to be a solid waste material (Foust et al. 2009). Waste water is filtered and processed in anaerobic and aerobic environments. Waste water treatment results in clean process water, sludge, and methane. The sludge and methane are sent to the burner. The building and maintenance of required capital goods and infrastructure are outside the bounds of this study. Major chemical inputs and outputs from the biorefinery are listed in Table 2.3. Detailed data of all biorefinery operations can be found in appendix A.

Table 2.3 – Major inputs and outs of the biorefinery per mega joule of ethanol

Input	**Amount (kg)**
Water	0.211
Output	
Ethanol (MJ)	1
Electricity (MJ)	0.197
Wastes to landfill	
Gypsum	0.00435
Ash	0.00346
Emissions to air	
CO_2	0.197
Sulfur dioxide	0.000199
Diammoniaphosphate	0.000259
Nitrogen oxides	0.000136
Sulfur monoxide	0.000298
Carbon monoxide	0.000136

Process chemicals and enzymes are lumped into the “ancillary chemicals” category. The chemical production and use included in this category are sulfur dioxide, lime, sulfuric acid, diammonium phosphate, phosphoric acid, and urea. Of special interest for the LCA is the production of enzymes. There are no life cycle data for cellulase production that can be applied to this study. To estimate the emissions and material (especially water) and energy demands of cellulase production we used values published by Wooley et al. (1999 a & b) and Sheehan et al. (2004). Using an enzyme charge of 5 FPU/g cellulose (an economically viable enzyme charge) and a bioreactor productivity of 75 FPU/L/hour (Sheehan et al. 2004) we could estimate the resource demands and emissions associated with enzymes used in our ethanol conversion process. These factors were then input to SimaPro, either as a process or a direct inventory input. Resources required for enzyme production include cellulose (modeled with dissolving pulp) corn oil, corn steep liquor, and potassium biphosphate. Major ancillary chemicals are listed in table 2.4. Detailed data for the ancillary chemicals and enzyme production can be found in appendix A.

Table 2.4 – Major ancillary chemicals required per mega joule of ethanol.

Chemical	**Amount (kg)**
Lime	0.00128
Sulfuric acid	0.00167
Sulfur dioxide	0.00286
Natural gas	0.000394
Diammonium phosphate	0.000276
Enzymes	0.00197

Ethanol distribution and use.

Ethanol is distributed from the conversion plant to a blending terminal. This fuel is then transported to the regional storage facility. The transportation mode is assumed to be diesel truck. Total transportation distance for ethanol distribution is assumed to be 160km (round trip)(Wojnar, 2010). Infrastructure needed for ethanol distribution is not included in the analysis.

2012 passenger vehicle operation is the end use of the biofuel. LCI data for vehicle operation is derived from the GREET 1.8d model (Wang 2010). Although hypothetical, this study considered the use of E100 in a flex-fuel spark ignition vehicle. Pure ethanol was chosen to facilitate direct comparison with pure gasoline. Direct comparison enables us to judge whether the biofuel produced here meets the GHG threshold requirement set by EPA (EPA 2009). Other life stages of the vehicle, such as vehicle manufacture, servicing, and end-of-life are not included. Vehicle operation data for ethanol fuel was generated in the GREET model primarily with default parameters. The only parameters that were specified were the feedstock type and blend ratio (100 in our case). The ethanol vehicle emissions are compared to gasoline which is comprised of GREET default market shares for 2012. The gasoline is combusted in a spark ignition vehicle.

Results and Discussion

Global warming potential

A comparison of the GWP, using the system expansion model, between ethanol fuel and gasoline fuel is shown in Figure 2.2. The graph shows the GWP calculated in carbon dioxide equivalents per mega joule fuel equivalent. The contribution of each processing stage to the GWP as well as the overall average is shown in Figure 2. "CO_2 absorption" is presented as a separate category to show the significant effect of CO_2 sequestration in willow feedstock on GWP for the ethanol life cycle. The following stages of GWP were considered.

- CO_2 absorption: includes CO2 absorbed during photosynthesis.

- Feedstock production and harvesting: includes all crop management and production activities from site preparation through seven harvest cycles (except photosynthesis).

- Transport to refinery: includes transport of feedstock, materials in ancillary chemicals, and product fuel.

- Ancillary chemicals: includes production of all the chemicals and enzymes required by the biorefinery.

- Conversion process: includes biochemical conversion of willow chips to ethanol.

- Avoided production: includes avoided production of grid electricity due to export of excess electricity from biorefinery to grid.

- Fuel distribution and use: includes the transportation and emissions associated with distributing the E100 fuel and its combustion in a flex-fuel vehicle.

- Disposal of solid wastes: includes disposal of gypsum waste and wood ash streams.

- Gasoline production and use: includes all process and emissions associated with the manufacturing of gasoline and its combustion in a single-injection vehicle.

GWP of willow-derived ethanol fuel is slightly negative and 120 percent less than the value of 2005 gasoline, the standard for measurement set in EISA. This result is greater but consistent with that of Stephenson et al. (2010), who found a 90 percent reduction in GWP for ethanol produced by bioconversion process. The larger percent reduction in global warming potential is a consequence of a lower ethanol yield and greater electricity displacement (310 liters/tonne and 1.3 kwh/liter of ethanol [74 gal/ton and 4.9 kwh/gal ethanol]) in our model than those used by Stephenson et al. 2010 (340 liters/tonne and 0.29 kwh/liter of ethanol [81 gal/ton and 1.1 kwh/gal ethanol]). The difference in electricity displaced has a large impact: the Stephenson et al. (2010) study is located in the United Kingdom, where the electrical grid is supplied by 29 percent coal (Department of Energy and Climate Change 2012), as compared with the US electrical grid, at 51 percent coal (NREL 2011). The greater use of coal in the United States provides for greater GHG benefits in the displacement energy.

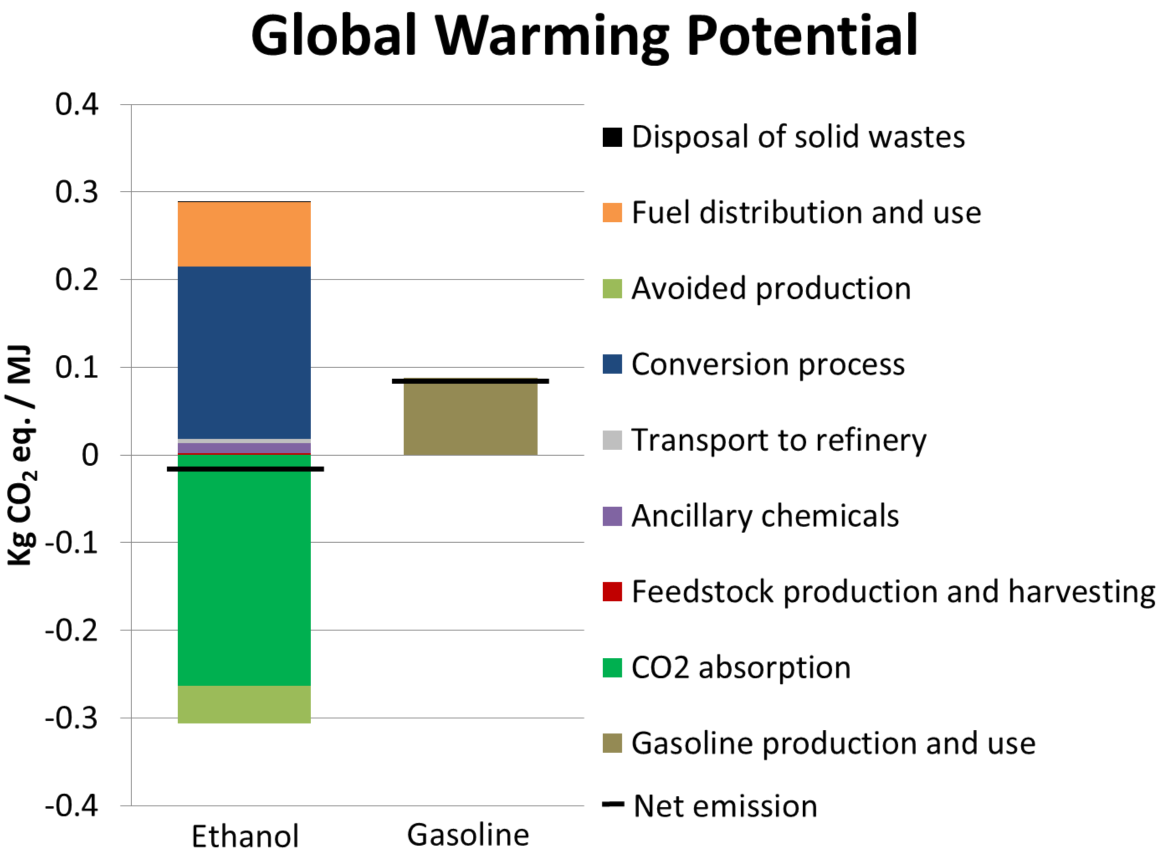

Figure 2.2—Global warming potential for ethanol and gasoline fuels using the system expansion model. The net emissions are indicated with the black bar.

Ethanol GHG emissions from feedstock processing to vehicle use amount to 0.289 kg CO_2 equivalent per mega joule (CO_2 eq./MJ). Carbon sequestration of the growing feedstock reduces emissions by 0.263 kg CO_2 eq./MJ, and displacement of fossil fuel in national grid electricity production results in an additional reduction of 0.043 kg CO_2 eq./MJ. The net result is that the life-cycle carbon emission of willow-derived ethanol product is −0.017 kg CO_2 eq./MJ fuel use. Willow-derived bioethanol is essentially carbon neutral. In contrast, there is a 0.088-kg CO_2 eq./MJ emission when gasoline is used as a transportation fuel. Substituting willow-based ethanol for gasoline reduces CO_2 equivalent emissions by 0.11 kg CO_2 eq./MJ of fuel energy used.

We investigated the impact of national grid electricity displacement on net carbon emissions by performing a comparable LCA where carbon emissions are allocated to electricity production. In our process, 0.197 MJ of excess electricity is generated and exported to the national grid for every mega joule of ethanol production. Allocating carbon emissions on energy content results in 83.5 percent of the global warming emissions being apportioned to ethanol and 16.5 percent to electricity. Applying this allocation approach yields the global warming potential results shown in Figure 2.3.

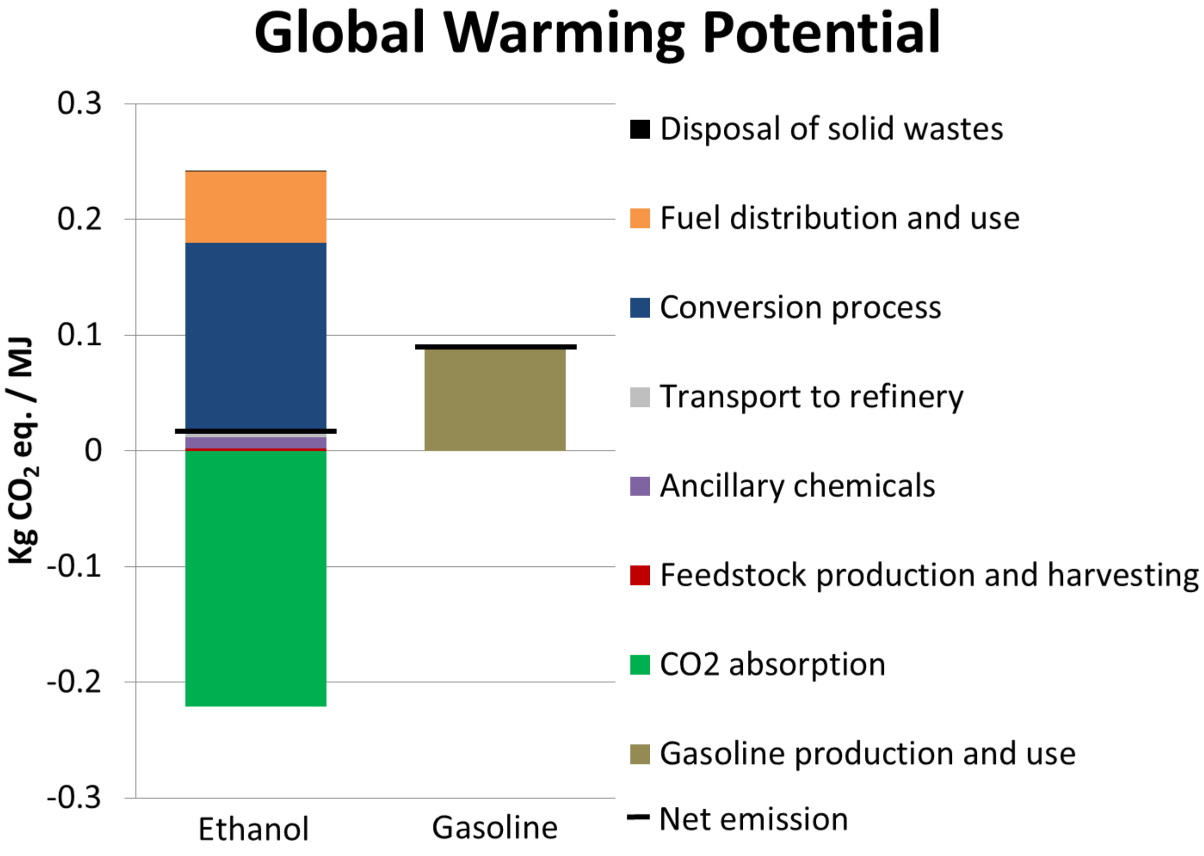

Figure 2.3—Global warming potential for ethanol with allocation. The net emissions are indicated with the black bar.

For ethanol use, the net emissions for GWP assuming co-product allocation is 0.02 kg CO_2 eq./MJ from bioethanol. This is a 77 percent reduction compared with gasoline. This reduction in GWP is similar to studies that reported values of 78 percent (willow feedstock; Stephenson et al. 2010) and 62.4 percent (poplar feedstock; González-García et al. 2010) when not including the export of excess electricity in the results. In treating excess electricity produced on site as a co-product and allocating the inputs and emissions based on energy content, there is a 0.038-kg CO_2 eq./MJ increase in GWP of ethanol use compared with the method using system expansion (Fig. 2.2). While the GWP assuming allocation does increase relative to the system expansion model, it is still a much better alternative to using gasoline.

Fossil fuel use

Life cycle fossil fuel is monitored using the LCI generated from SimaPro. The raw fossil fuel inputs were tracked by adding up all raw material fossil fuel demand. The use of fossil fuels in ethanol production is compared with gasoline production from the USLCI database. The resulting net fossil fuel usage for ethanol and gasoline are -0.50 and 1.2 MJ of fossil fuel per MJ of fuel energy respectively (Figure 4). The lower net value of ethanol (141% less than gasoline) is not unexpected as the heat and power required for the bioconversion process is fueled by the combustion of lignin and other residuals produced at the biorefinery during the conversion process. In addition, exportation of excess electricity offsets the fossil fuel demand to generate this power on the national grid. The fossil fuel use is 80% lower than gasoline without the credit for avoided electricity production. This value is line with that calculated by Stephenson (Stephenson et al. 2010) and Gonzalez-Garcia (Gonzalez-Garcia et al. 2010).

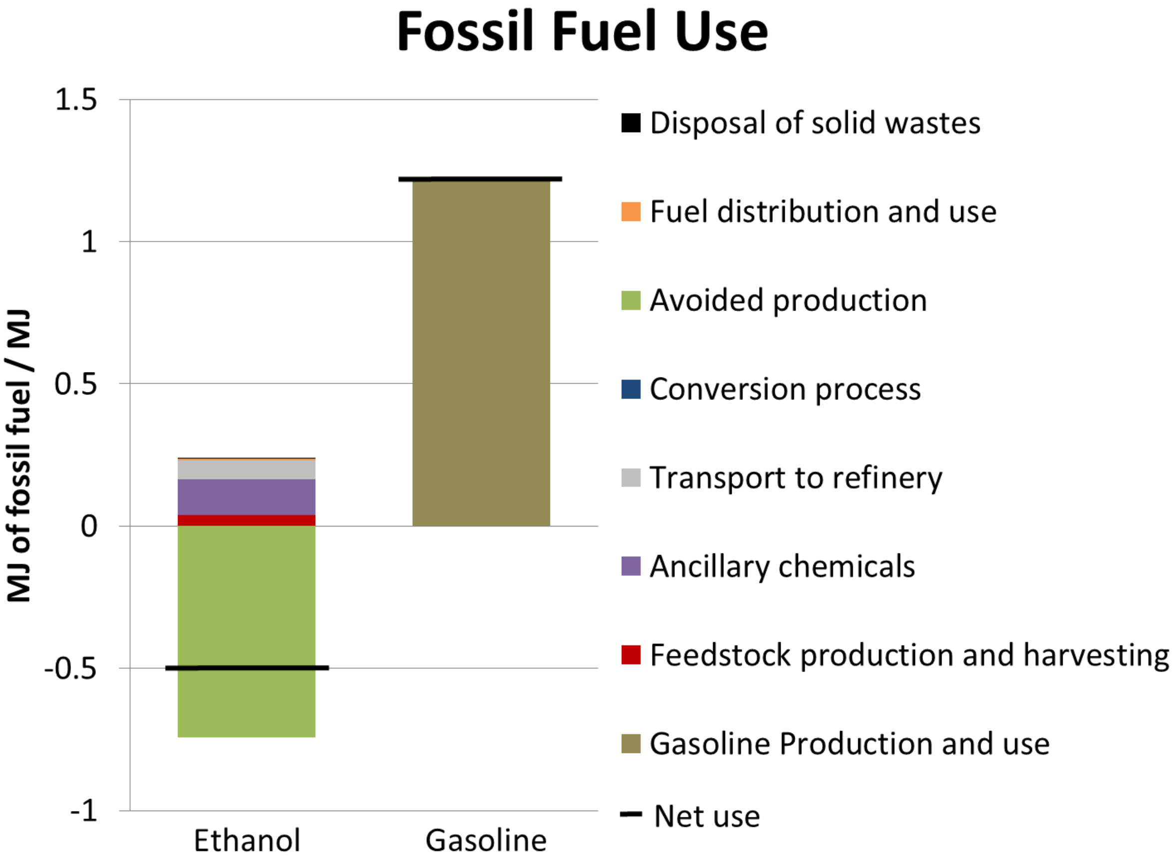

Figure 2.4.—Comparison of fossil fuel use to produce gasoline and willow- based ethanol.

Water use

Water use is tracked in SimaPro in the same manner as fossil fuel use. All fresh water inputs are summed per MJ of fuel energy. The ethanol data are compared with Ecoinvent European gasoline since there are no water data for USLCI gasoline (Figure 5). The amount of water needed to produce 1 MJ of energy from willow based ethanol is 166% greater than it is for the production of 1 MJ from gasoline. 0.53 kg of water is needed to create 1 MJ of fuel from willow based ethanol while 0.32 kg are needed to create 1 MJ of gasoline. 51% of the water demand comes from the ancillary chemicals category. The processes in the ancillary chemicals category responsible for the high water demand are sulfur dioxide, enzyme, and sulfuric acid production. The conversion process accounts for 40% of the water demand (Figure 5). As noted earlier, feedstock production creates little water demand since we assumed the willow is grown without irrigation. Expressing water usage in units of liters of water used per liter of fuel produced results in 12 liters used to produce one liter of ethanol from willow; of this 6.1 liters of water are used in the ancillary chemicals category and 4.8 liters are used in the bioconversion process itself.

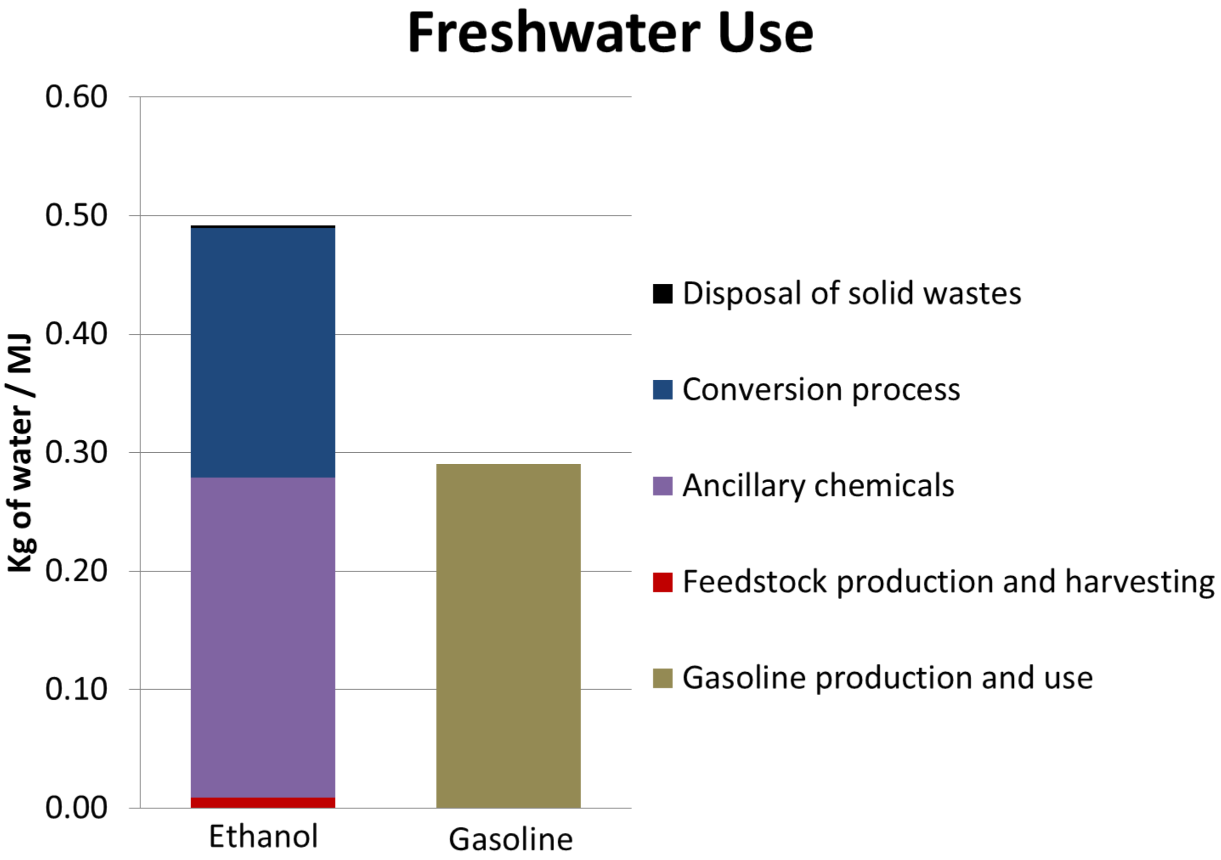

Figure 2.5—Water use (kilograms) per mega joule of energy produced.

A regionally specific LCA water impact analysis such as the one described by Pfister et al. (2009) was not included in this study since our analysis used United States aggregated averages. LCA water impact analyses are most meaningful when done at the watershed level because of large regional differences in water availability (Pfister et al. 2009). Significant water demand is an issue if the supply is limited or constrained. A water scarcity index has been one approach to address constrained water availability in a specific region (Berger and Finkbeiner 2010). We also made no attempt to differentiate water usage. To create consistency in water use analysis, UNEP/SETAC recently proposed that water use be classified as in-stream or off-stream and consumptive or degradative (Bayart et al. 2010). Incorporation of regional factors and details of water usage would improve the significance of any LCA results regarding water. This level of detail would be difficult to incorporate into this LCA analysis, however, since the majority of the water usage is associated with production of materials and chemicals used in the conversion process. These materials will come from diverse sources, making it difficult to quantify regional impacts or have good assessment of the appropriate water usage category. A future research goal of our laboratory is to develop more meaningful measures of lifecycle water impacts associated with the production of biofuels. The results in Figure 5 suggest, however, that water use to produce biofuels may be significant and should be an important environmental consideration.

Conclusions

We investigated the lifecycle impact of ethanol production using short rotation willow feedstock. A bioconversion process was applied in the analysis that produced 310 liters of ethanol per tonne of feedstock (74 gallons/ OD U.S. short ton of willow). An ASPEN simulation of the process was developed since there are no data from a working biorefinery. A significant feature of the modeled process is the export of 19.2 MW from the biorefinery. Lifecycle impacts of willow based ethanol are compared with those of gasoline on a per MJ basis. The results of the LCA show that producing and using E100 from willow in place of gasoline can reduce GHG by 120%. Significant carbon sequestration by fast growing willow feedstock and the displacement of fossil fuel electricity generated on the national grid were the largest contributor to ethanol's low carbon footprint. It was found that production and use of willow based ethanol is virtually carbon neutral. As expected, the fossil fuel inputs needed for bioethanol are 141% less than they are for production of 1 MJ of energy from gasoline. Minimal fossil fuel is required for bioethanol production and the displacement of fossil fuel to produce electricity on the national grid contributes to ethanol's low usage.

The use of bioethanol from willow does require more water than needed for gasoline production and use. Producing and consuming ethanol requires 166% more water than required for gasoline. Much of this water use is associated with the manufacture of enzymes and chemicals used in the bioconversions process. The life cycle impact of water usage is complex, however, and requires further analysis before a definitive impact conclusion can be drawn.

Results of this study show that willow based ethanol can be an excellent fuel to help our nation reach its greenhouse gas emission goals. There are some environmental categories, however, that may be exacerbated by large scale ethanol production. Attention to these categories while designing and operating plantations and biorefineries will help avoid any unintended negative consequences with this new fuel source.

Acknowledgments

This article is one of several organized by CORRIM, a consortium of 17 research institutions, to provide life-cycle information covering biofuel collection and processing options. Funding was provided by the US Forest Service through the Forest Products Laboratory with matching funds from donors and participating institutions.

References

Aden, A., M. Ruth, K. Ibsen, J. Jechura, K. Neeves, J. Sheehan, B. Wallace, L. Montague, A. Slayton, and J. Lukas. 2002. Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis and enzymatic hydrolysis for corn stover. National Renewable Energy Laboratory, Golden, Colorado.

Aspen Technology Inc. (ATI). 2005. Aspen Plus. Version 2004.1. ATI Inc., Cambridge, Massachusetts.

Bare, J. C. 2002. The tool for the reduction and assessment of chemical and other environmental impacts. *J. Ind. Ecol.* 6:49–78.

Bayart, J. B., C. Bulle, L. Deschenes, M. Margni, S. Pfister, F. Vince, and A. Koehler. 2010. A framework for assessing off-stream freshwater use in LCA. *Int. J. Life Cycle Assess.* 15(5):439–453.

Berger, M. and M. Finkbeiner. 2010. Water foot printing: How to address water use in life cycle assessment? *Sustainability* 2(4):919–944.

Buchholz, T. and T. A. Volk. 2011. Identifying opportunities to improve the profitability of willow biomass crops with a crop budget model. *Bioenergy Res.* 4(2):85–95.

Department of Energy and Climate Change (DECC). 2012. Fuel mix disclosure data table. UK Department of Energy and Climate Change. http://www.decc.gov.uk/en/content/cms/statistics/energy_stats/fuel_mix/fuel_mix.aspx. Accessed September 5, 2012.

Energy Independence and Security Act (EISA). 2007. Energy Independence and Security Act of 2007. Public Law 110-140. US Government, Washington, D.C. 311 pp.

Ewanick, S. and R. Bura. 2010. Hydrothermal Pretreatment of Lignocellulosic Biomass. Woodhead Publications Ltd., Cambridge, UK.

González-García, S., C. M. Gasol, X. Gabarrell, J. Rieradevall, M. T. Moreira, and G. Feijoo. 2010. Environmental profile of ethanol from poplar biomass as transport fuel in Southern Europe. *Renewable Energy* 35(5):1014–1023.

International Organization for Standardization (ISO). 2006a. Environmental management. Life cycle assessment. Principles and framework. ISO 14040:2006. ISO, Geneva.

International Organization for Standardization (ISO). 2006b. Environmental management. Life cycle assessment. Requirements and guidelines. ISO 14044:2006. ISO, Geneva.

Keoleian, G. A. and T. A. Volk. 2005. Renewable energy from willow biomass crops: Life cycle energy, environmental and economic performance. *Critical Rev. Plant Sci.* 24(5–6):385–406.

Mansfield, S. D., C. Mooney, and J. N. Saddler. 1999. Substrate and enzyme characteristics that limit cellulose hydrolysis. *Biotechnol. Prog.* 15(5):804–816.

National Academy of Sciences (NAS). 2009. Liquid transportation fuels from coal and biomass: Technological status, costs, and environmental impacts. NAS, National Academies Press, Washington, D.C.http://sites.nationalacademies.org/xpedio/groups/energysite/documents/webpage/energy_054519.pdf. Accessed September 5, 2012.

National Renewable Energy Laboratory (NREL). 2011. US life cycle inventory database. http://www.nrel.gov/lci/. Accessed September 5, 2012.

Oak Ridge National Laboratory. 2012. Bioenergy conversion factors. https://bioenergy.ornl.gov/papers/misc/energy_conv.html. Accessed September 5, 2012.

Pacaldo, R. S., T. A. Volk, L. P. Abrahamson, and R. D. Briggs. 2010. Above- and below-ground biomass and soil organic carbon inventories of willow biomass crops across a 19-year chronosequence. *In:* Proceedings of the 8th Biennial Short Rotation Woody Crops Operations Working Group—Short Rotation Woody Crops in a Renewable Energy Future: Challenges and Opportunities, October 17–19, 2010, Syracuse, New York.

Pfister, S., A. Koehler, and S. Hellweg. 2009. Assessing the environmental impacts of freshwater consumption in LCA. *Environ. Sci. Technol.* 43(11):4098–4104.

PRé Consultants. 2011. SimaPro 7 life-cycle assessment software package, version 7.3.0. Amersfoort, The Netherlands. http://www.pre-sustainability.com. Accessed September 5, 2012.

Quaye, A., T. A. Volk, S. Hafner, D. Leopold, and C. Schirmer. 2011. Impacts of paper sludge and manure on soil and biomass production of willow. *Biomass Bioenergy* 35:2796–2806.

Sassner, P., M. Galbe, and G. Zacchi. 2005. Steam pretreatment of *Salix* with and without SO_2 impregnation for production of bioethanol. *Appl. Biochem. Biotechnol.* 121–124:1101–1117.

Sassner, P., M. Galbe, and G. Zacchi. 2006. Bioethanol production based on simultaneous saccharification and fermentation of steam-pretreated *Salix* at high dry-matter content. *Enzyme Microb. Technol.* 39:756–762.

Sassner, P., M. Galbe, and G. Zacchi. 2008. Techno-economic evaluation of bioethanol production from three different lignocellulosic materials. *Biomass Bioenergy* (32):422–430.

Sheehan, J., A. Aden, K. Paustian, K. Killian, J. Brenner, M. Walsh, and R. Nelson. 2004. Energy and environmental aspects of using corn stover for fuel ethanol. *J. Ind. Ecol.* 7:117–146.

Stephenson, A. L., P. Dupree, S. A. Scott, and J. S. Dennis. 2010. The environmental and economic sustainability of potential bioethanol from willow in the UK. *Bioresour. Technol.* 101(24):9612–9623.

Swiss Centre for Life Cycle Inventories (SCLCI). 2009. EcoInvent Database 2.1. SCLCI, Duebendorf.

US Environmental Protection Agency (US EPA). 2009. EPA proposes new regulations for the national renewable fuel standard program for 2010 and beyond. Regulatory announcement EPA420-D-09-023. US EPA, Office of Transportation and Air Quality, Washington, D.C. May 2009. http://www.epa.gov/oms/renewablefuels/420f09023.pdf. Accessed September 5, 2012.

Wang, M. 2010. The greenhouse gases, regulated emissions, and energy use in transportation (GREET) Model 1.8d. Argonne National Laboratory. http://greet.es.anl.gov/. Accessed September 5, 2012.

Wojnar, Z. April 2010. Renewable fuels roadmap and sustainable biomass feedstock supply for New York. NYSERDA Report 10-05.

Woody Biomass Program (WBP). 2011. Woody biomass program. State University of New York, Syracuse. http://www.esf.edu/willow/. Accessed September 5, 2012.

Wooley, R., M. Ruth, D. Glassner, and J. Sheehan. 1999a. Process design and costing of bioethanol technology: A tool for determining the status and direction of research and development. *Biotechnol. Prog.* 15(5):794–803.

Wooley, R., M. Ruth, J. Sheehan, and K. Ibsen. 1999b. Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis and enzymatic hydrolysis current and future scenarios. National Renewable Energy Laboratory, Golden, Colorado.

3. Ethanologens vs. Acetogens: Environmental impacts of two bioethanol fermentation pathways.

Erik Budsberg, Jordan Crawford, Rick Gustafson, Renata Bura

Abstract

Life Cycle Assessments (LCA) for two lignocellulosic bioethanol production pathways that use hybrid poplar as a feedstock are developed and compared. Both processes are simulated begin with a dilute acid pretreatment followed by enzymatic hydrolysis. The processes differ in the fermentation process. In the first pathway an ethanologen is used to produce ethanol. The second pathway is fermented with an acetogen to produce acetic acid. Acetic acid undergoes hydrogenation to produce ethanol. Both bioconversion pathways are modeled in ASPEN-plus simulations. In both processes lignin is recovered and burned onsite to produce electricity. The critical difference between the two processes is that the acetic acid pathway has a higher product yield but requires hydrogen for the process. Steam methane reforming is assumed to be the source of hydrogen. Greenhouse gases, regulated emissions, and energy use in transportation (GREET) is used to model combustion of ethanol from each scenario in a flex fuel vehicle. All necessary chemicals, transportation, and processes required by each production pathway are included within the LCAs. Each pathway is assessed to determine the global warming potential (GWP), fossil fuel use, and freshwater use. Compared to gasoline the ethanologen pathway has a GWP that is 97 percent lower, uses 97 percent less fossil fuels, and 180 percent more water. The acetogen pathway has a GWP 53 percent lower than gasoline, reduces fossil fuel use by 55 percent, and increases water use by 81 percent. In regards to the GWP and fossil fuel use the ethanologen pathway achieves larger reductions. However, the acetogen pathway will produce more ethanol per unit of land and this may play a crucial role in choosing a lignocellulosic ethanol production method if land is a limited resource.

Introduction

In an effort to find a substitute for petroleum based liquid transportation fuels many countries are turning to biofuels. The newest form of these biofuels, also known as the second generation or cellulosic biofuels, have received considerable attention (Borrion et al. 2012, Wiloso et al. 2012). In the U.S. yearly requirements for production of cellulosic biofuels have been set at 1 billion gallons in 2013 and ramp up to 16 billion gallons in 2022 (EISA 2007). Currently the yearly minimum requirements have not been met as commercial cellulosic bioethanol plants are only now starting to come online. These yearly requirements can be met using a diverse range feedstocks along with optimal conversion technologies.

Short Rotation Woody Crops (SRWC), such as *Populus* (poplar) and *Salix* (willow), present an attractive option for diversifying and expanding biomass available for biofuel production. Used in the past for various products such as fuel wood, lumber, and paper, these well-established crops present good characteristics for biofuel use. In general they require little fertilizer input, can be cultivated on marginal lands, have the ability to resprout after multiple harvests, and have a high biomass production (Keoleian and Volk 2005, Stephenson et al. 2010, Gonzalez Garcia et al. 2010, Budsberg et al. 2012). The lignocellulosic material in the wood can also be separated without extensive pretreatment (Sassner et al. 2005) and hardwoods don't exhibit the recalcitrance reported in softwoods (Mansfield et al. 1999).

Appropriate conversion technologies must be used to convert the lignocellulosic material in SRWC to ethanol. A bioconversion process designed at the National Renewable Energy Laboratory (NREL) (Aden et al. 2002, Humbird et al. 2011) is one prominent process proposed in the last decade (Sheehan et al. 2004; Gonzalez Garcia et al. 2010, Stephenson et al. 2010, Budsberg et al. 2012, Gonzalez Garcia et al. 2012.). This process can be broken down into a few key steps beginning with a pretreatment step using chemical and/or physical processes that exposes cellulose and other carbohydrates. Next cellulose is hydrolyzed to glucose using either enzymes or acid. An ethanologen (yeast or bacteria) ferments the glucose and other sugars to ethanol. The lignin and unfermented carbohydrates are burned to produce process steam and electricity. In many cases, there is an excess of electricity that can be sold to the electrical grid. Using the NREL platform researchers have reported ethanol yields ranging from 310 to 429 L/Bone Dry tonne (BDt) and excess electricity generation of 0 to 0.2 MJ/MJ of ethanol (Huang et al. 2009; Gnansounou and Dauriat, 2010; Gonzalez-Garcia et al. 2010; Stephenson et al. 2010; Budsberg et al. 2012; Gonzalez-Garcia et al. 2012). The range in values is related to assumptions made regarding conversion rates (polymers to monomers, sugars to ethanol) and the amount of biomass used for electricity production (if the biorefinery is designed with a turbine).

The use of an ethanologen in the fermentation step is potentially an inefficient way to produce ethanol. For every mole of glucose consumed by an ethanologen a mole of ethanol and a mole of CO_2 are produced. The production of CO_2 limits the maximum theoretical carbon efficiency at 67% (Cherubini and Stromman, 2010). Different fermentation organisms could be used to overcome this inefficiency. An acetogen, an organism that ferments sugars to acetic acid, can potentially make the bioconversion process more efficient. These organisms will only produce acetic acid as it consumes glucose (and other sugars) and has a theoretical conversion yield of 100% (Verser and Eggeman, 2011). The acetic acid produced can then be converted to ethanol using catalytic hydrogenation. The end result is a much higher yield of ethanol per tonne of biomass (Verser and Eggeman, 2011).

An increased ethanol yield through the use of an acetogen could be very beneficial, but environmental impacts associated with this process must be investigated. In this study Life Cycle Assessment (LCA) is used to investigate the cradle to grave environmental impacts that could result from a biorefinery that uses an acetogen fermentation process to convert poplar biomass to ethanol for use in a flex fuel vehicle. An LCA of a comparable system using a traditional ethanologen fermentation pathway is simulated as well. Both fermentation pathways are compared to gasoline produced in 2005, the baseline set by EISA (2007).

Methods

Life cycle assessment was chosen to investigate the environmental impacts as it allows for a detailed study of both current and proposed systems. To begin an LCA, the goal and scope of the project is determined. The boundaries of the project will determine what technosphere flows will be need to be accounted for and represented in the Life Cycle Inventory (LCI). Each technosphere flow will have environmental flows that are a specific to the unit or system process it represents. These environmental flows can include the depletion of raw materials or emissions that result from producing, using, and disposing of a given product. In the Life Cycle Inventory Assessment (LCIA) the environmental flows are grouped into environmental impacts that they contribute too. How an emission contributes to a given impact is calculated using a characterization factor. Characterization factors assign point values to each emission or resource use based on their observed contribution to an impact. In the case of the 100 year GWP, CO_2 is given a score of one. All other GHGs are given values based on their atmospheric radiative forcing and decay rate relative to CO_2 (Solomon et al. 2007). The unit for GWP is known as CO_2 equivalence. The CO_2 eq. of CH_4 and N_2O, common GHGs, are 25 and 298 respectively. Other environmental impact characterization factors are calculated in a similar format. Using the results of the LCIA, the environmental performance of the product can be assessed. The environmental impact of each process or system within the products life cycle can be identified. These results can be used to identify areas that may be problematic and suggest ways to improve environmental performance. LCA results of the product can also be compared to the LCA results of other similar products to determine the environmental tradeoffs of using one system over another.

Goal and scope

LCA is used to investigate the environmental impacts that result from growing poplar trees and converting the lignocellulosic material into ethanol for use as fuel in a Flex Fuel Vehicle (FFV) over a 21 year time horizon. The LCA approach characterizes resource consumption and emissions into specific categories that allows for a detailed analysis of how the biofuel pathways could affect the environment. Overall impacts are determined as well as identification of processes within each model that contribute to a given impact category. The structure and proper method for conducting a LCA is set by ISO 14040 & 14044 (ISO, 2006a & 2006b) and every attempt was made to follow this design. The LCA models are developed in SimaPro v.7.3.3 (PRe´ Consultants 2012). Unit processes used within each model come from the USLCI (NREL 2011), EcoInvent (Swiss Centre for Life Cycle Inventories [SCLCI] 2009), literature, and the private sector. In all cases electricity was assumed to come from the 2012 U.S. national grid (except for 2005 gasoline, which uses the 2005 national grid)(Table 3.1) (U.S. Department of Energy, Energy Information Administration (EIA), 2013).

Table 3.1: Energy sources for the U.S. National Grid (EIA, 2012). 2012 data is used for proposed ethanol pathways. 2005 data is used for gasoline. Other renewables include energy produced from wind, wood and waste combustion, geothermal, and solar.

Electricity Source	**2012 U.S. National Grid (%)**	**2005 U.S. National Grid (%)**
Coal	37	50
Natural gas	31	19
Nuclear	19	19
Hydropower	6.7	6.5
Other renewables	5.4	2.1
Petroleum	0.56	3
Other fossil fuels	0.31	0.32

Environmental impacts assessed in the research include the 100 year global warming potential (GWP), fossil fuel use, and freshwater use. The 100 year GWP is calculated using The Tool for the Reduction and Assessment of Chemicals and other environmental Impacts (TRACI)(Bare, 2002). CO_2 produced from fossil fuel combustion and CO_2 produced from combustion of biomass (biogenic CO_2) are both included in the results. Biogenic CO_2 is not typically included when calculating the GWP as this CO_2 is part of the carbon cycle, but is included in this study so that a full carbon mass balance can be presented. Biogenic and fossil CO_2 emissions are identified and tracked separately so that the source of the emission can be identified. Fossil fuel use is determined by summing all fossil fuel inputs (coal, natural gas, crude oil) in terms of energy content (MJ). Freshwater use is calculated for the life cycle of each fuel by summing all freshwater use in the life cycle inventories (LCI).

Functional unit

The functional unit is used to relate the environmental impacts to the processes being studied. The choice of functional unit type will depend on the goal of the study. In this study the functional unit used is 1 mega joule (MJ). Using a unit of energy is common practice in biofuel LCAs as it allows for the comparison of different types of fuels regardless of their respective energy densities (Borrion et al. 2012; Wiloso et al. 2012). The energy densities for ethanol and gasoline were assumed to be 29.6 MJ/Kg and 47.9 MJ/Kg respectively (Oak Ridge National Laboratory, 2012).

The GWP is also assessed on a per hectare of land basis. Few biofuel LCAs have used this functional unit (Borrion et al. 2001, Wiloso et al. 2012), but it provides valuable insight to the best use of limited lands to reduce greenhouse gas emissions (Cherubini et al. 2009). The benefit of an increased ethanol yield may not fully be captured when emissions are referenced to a MJ of fuel and used to make relative comparisons to gasoline. A higher efficiency conversion process may mean greater absolute reductions for a given land basis compared to the baseline fuel replaced. Therefore relating the GWP to the land allows another way of analyzing the potential life cycle emissions and has been used to compare carbon impacts across all types of biomass use (Cherubini et al. 2009, Lippke et al. 2012). Furthermore, if land resources are limited using the pathway that is most efficient per unit of land will have substantial benefits. The GWP is calculated by determining the amount of poplar chips produce during the 21 year timeframe of the LCAs. Chip yield is divided by 21 to average out chip production during the time the land is in use as a poplar cropland. The respective ethanol yields are used to calculate the amount of ethanol produced per hectare per year. Ethanol (MJ) produced per ha per year is multiplied by the GWP/ MJ to get the GWP/ha/yr. The amount of ethanol (in MJ) produced /ha/yr is also multiplied by the GWP/MJ for gasoline to calculate how much gasoline would be displaced. The difference between the GWP/ha/yr of ethanol and GWP of displaced gasoline per year is equal to the GWP savings per hectare per year if the ethanol were to be used instead of gasoline.

System boundaries

In this study four sections are included within the system boundaries: feedstock production and harvesting, the biorefinery, chemical inputs and fuel use. The feedstock production and harvesting and fuel use sections are the same for both fermentation pathways. The biorefinery section and chemical inputs will vary depending on the fermentation pathway. The biorefinery section is further broken down into subsections. The first subsection involves pretreatment and hydrolysis and is the same for both fermentation pathways. The models diverge in the second subsection as these processes are dependent on the fermentation pathway considered. System boundaries along with a flow diagram of the two processes are shown in Figure 3.1. A detailed description of each section is included below. Manufacturing and maintenance of all capital goods is excluded from the system boundaries.

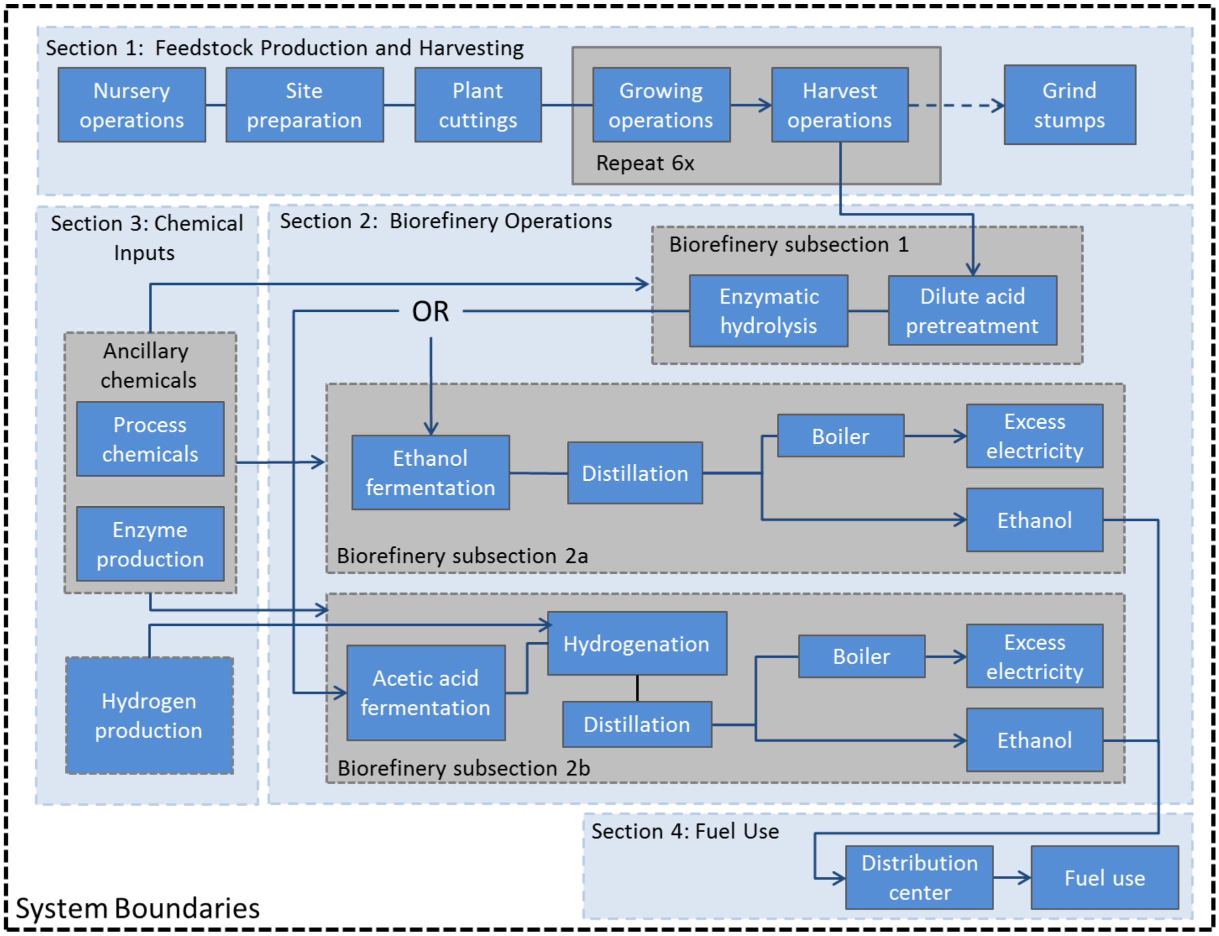

Figure 3.1: Cradle to grave system boundaries of the ethanologen and acetogen pathways. In Section 1 direct land use change is included in site prep and below ground carbon storage is included in growing operations. Biorefinery subsection 1 includes the pretreatment and hydrolysis which are the same for both fermentation pathways. Biorefinery subsection 2a includes all operations for the Ethanologen Pathway (EP). Biorefinery subsection 2b includes all operations for the Acetogen Pathway (AP). Not pictured in each biorefinery is onsite waste water treatment.

Section 1: Feedstock production and harvesting

The feedstock production and harvesting model is supported by operational data from industry (GreenWood Resources, personal communication, 2011-2013) and literature (Quaye et al. 2011; Buchholz and Volk, 2011; Caputo et al. 2013). The first year of feedstock production includes growing poplar trees at a nursery and preparing the plantation location for poplar to be transplanted the following year. Nursery operations include herbicide, fertilizer, and pest control application as well as irrigation. Once large enough, the poplar trees are turned into cuttings and transported to cold storage. Preparing the plantation location for the cuttings will depend on the site specific characteristics, but in general the land will undergo heavy and finish disking, smoothing, row marking, and herbicide application. The cuttings are planted the following year and are grown for two years before the first coppicing which will promote the growth of multiple branches per stump. Following this the trees are harvested every 3 years for 6 cycles. The poplar trees are harvested with a forage harvester and forage wagons are towed alongside the harvest to collect the chips. The chips are loaded into a chip van using a silage blower and transported to the biorefinery. A transportation distance of 40 kilometers from farm to biorefinery is assumed. This distance is based on the assumption that poplar plantations will need to be placed near biorefineries to reduce feedstock delivery costs at the biorefinery gate. Nitrogen fertilizer is applied in the spring following a harvest, herbicide is used in non-harvest years, and a pesticide is used every year. After 6 harvests (21 years counting site prep and nursery operations) the stumps are ground down on site and herbicide is applied to the soil. Irrigation is only assumed to be needed for nursery operations. Data for the nursery operations, site preparation, and growth and harvesting of the poplar trees can be found in appendix B.

Below ground carbon stores, comprised of above ground stump (the part that remains after a harvest), below ground stump, and coarse roots, are included within this LCA. The amount of carbon stored within the below ground carbon stores is assumed to be the same as willow SRWC (Pacaldo et al. 2012). No change in soil carbon down to a depth of 45 cm is expected to occur during tree growth as demonstrated by Pacaldo et al. (2010). The system boundary ends immediately after the below ground biomass is chipped and herbicide is applied.

Direct land use change associated with establishing the plantation is calculated using the Forest Industry Carbon Assessment Tool (FICAT)((NCASI, 2011) assuming a scenario of converting fallow land to a poplar tree farm. Data for the amount of carbon on these lands that would be released as CO_2 as a result of land use change is calculated in the 2007 IPCC report (Solomon et al. 2007). The values used are from tier 1 data which has a high degree of uncertainty (Solomon et al. 2007). More accurate data are not available as the focus of the research is site agnostic and therefore details on the type of land converted are not available. The IPCC numbers are used to get a rough idea of what changes may be observed. Indirect land use (ILUC) change is not included in this LCA as there is a great deal of uncertainty related to current ILUC models (Sanchez et al. 2012). In addition, the amount of indirect land use change is expected to be modest since the study targets use of fallowed land. ILUC is important to consider, but more reliable land use models are needed to enable their use in life cycle assessments (Sanchez et al. 2012).

Section 2: The biorefinery

Currently there are no commercial scale ethanol plants in operation from which to gather processing data. To obtain biorefinery chemical and energy demands as well as emissions data, simulations for each fermentation path are created using ASPEN-Plus (Aspen Technology Inc. 2005). The NREL corn stover model (Humbird et al. 2011), modified to use a poplar feedstock, is used to assess the ethanologen fermentation pathway (EP). The acetogen fermentation pathway (AP) ASPEN simulation is based on a combination of the NREL model (Humbird et al. 2011), ZeaChem's proposed fermentation process (Verser and Eggeman, 2011), and laboratory work at the Biofuels and Bioproducts Laboratory at the University of Washington. The two biorefineries are each designed to operate on 3200 bonne dry tonnes (BDt) per day (1.1 million BDt/yr). The EP is predicted to produce 312 L/BDt (352 million L/yr). The AP is predicted to have a much higher yield of 536 L/BDt (606 million L/year). All necessary steam, heat, and electricity are provided by the combustion of lignin and unreacted carbohydrates. Each biorefinery also produces excess electricity. The process of producing electricity from combustible waste streams is common practice in pulp mills (Gustafson and Raffaeli, 2009) and has been observed in other SRWC to ethanol studies (Stephenson et al. 2010, Budsberg et al. 2012, Gonzalez-Garcia et al. 2012). The electricity by-product is treated using system expansion per ISO standards (ISO, 2006b). The electricity by-product meets the requirements for using system expansion as it is currently produced from other sources and life cycle data for the production of electricity from these other sources can be obtained (Ekvall and Finnveden, 2001). It is assumed that the electricity will be sold to the grid and displace electricity produced from natural gas, a likely candidate for the marginal electricity source (Thomas, 2012). An avoided production credit is generated for displacing this fossil fuel source of electricity with electricity produced from a renewable source. The use of system expansion is also the most common method used in other biofuel LCAs to deal with by-products (Gnansounou et al. 2009)

The biorefineries begin with the same pretreatment and hydrolysis steps, and then diverge to their respective fermentation pathways and conversion processes to produce ethanol. Process parameters for pretreatment and enzymatic hydrolysis are listed in Table 3.2. The conversion process begins with dilute acid pretreatment of poplar chips. This process is outlined by NREL (Humbird et al. 2011) and has been modified for a poplar feedstock. Following pretreatment, cellulose in the poplar biomass is broken down to glucose using enzymatic hydrolysis.

Table 3.2: Biorefinery subsection 1 – Process parameters for pretreatment and enzymatic hydrolysis. This is the same for both the ethanologen and acetogen biorefineries.

Processing step	Process parameter	Value
Pretreatment	H_2SO_4 charge (%wt/wt)	1.1
	Temperature (^oC)	200
	Xylan to xylose conversion (%)	75
Saccharification	Temperature (^oC)	50
	Enzyme loading (mg protein / g cellulose)	20
	Cellulose to glucose conversion (%)	89

In the Ethanologen Pathway (EP) (Figure 3.1: Subsection 2a) glucose and xylose are fermented using *Zymomonas mobilis*. Fermentation conditions and yields come from NREL (Humbird et al. 2011).

Ethanol produced during fermentation is distilled to 99.5% purity. Lignin and unreacted carbohydrates are combusted in a boiler to provide process steam. 275,000 kg/hr of 86 atm steam is generated which is sent to a turbine to produce 67 MW of power. The biorefinery consumes 46 MW of this electricity sending 21 MW of electricity on to the grid to displace marginal electricity production. EP biorefinery process parameters are listed in Table 3.3. Major chemical demands and emissions are listed in Table 3.4. For a complete list of chemical demands see appendix B.

Table 3.3: Biorefinery subsection 2a – Process parameters unique to the ethanologen pathway (EP).

Process parameter	**Value**
Temperature (^{o}C)	32
Glucose to ethanol conversion (%)	49
Xylose to ethanol conversion (%)	43

Table 3.4: Major Biorefinery subsection 2a inputs/outputs – Process inputs and outputs for the ethanologen pathway (EP) referenced to 1 MJ of ethanol

Input	**Value (g)**
Feedstock (bone dry)	139
Water	0.270
Enzymes	0.569
Sulfuric Acid	4.96
Lime	3.74
Calcium carbonate	0.0196
Ammonia	.666
Corn Steep Liquor	3.74
Sodium hydroxide	2.13
Output	
Ethanol	1 (MJ)
Excess electricity	0.0214 (kwh)
CO_2 (biogenic)	189
Gypsum	8.74
Ash	2.66

In the Acetogen Pathway (AP)(Figure 3.1: Subsection 2b) glucose and xylose are fermented to acetic acid using *Moorella thermoacetica*. The acetic acid undergoes hydrogenation to be converted into ethanol. During the conversion of acetic acid to ethanol multiple distillation steps are required to produce 99.5% purity ethanol. Yields and conversion rates are provided by data from ZeaChem's patent (Verser and Eggeman, 2011). As in the ethanologen pathway, lignin and unreacted carbohydrates are combusted to produce process steam and electricity. Total electricity produced is 33 MW of power. The biorefinery consumes 15 MW, leaving 18 MW to displace marginal electricity production. AP biorefinery process parameters are listed in Table 3.5. Major chemical demands and emissions are listed in Table 3.6. For a complete list of chemical demands see appendix B.

Table 3.5: Biorefinery subsection 2b – Process parameters unique to the acetogen pathway (AP).

Process parameter	**Value**
Temperature (°C)	58
Glucose to ethanol conversion (%)	94
Xylose to ethanol conversion (%)	92
Hydrogen requirement (kg/kg ethanol)	0.089

Table 3.6: Major Biorefinery subsection 2b inputs/outputs – Process inputs and outputs for the acetogen pathway (AP) referenced to 1 MJ of ethanol.

Input	**Value (g)**
Feedstock (bone dry)	78.5
Water	0.155
Enzymes	0.320
Sulfuric Acid	2.79
Lime	2.11
Carbon dioxide	0.166
Calcium carbonate	0.377
Ammonia	0.649
Corn Steep Liquor	2.10
Hydrogen	3.02
Sodium hydroxide	1.20
Output	
Ethanol	1 (MJ)
Excess electricity	0.0106 (kwh)
CO_2 (biogenic)	80.7
Gypsum	4.93
Ash	1.50

Incorporated into both models is a wastewater treatment system. Wastewater streams are treated in aerobic and aerobic environments to produce clean process water, sludge, and methane. The sludge and methane are sent to the boiler. Solid waste produced from the biorefineries includes ash from the boiler and gypsum produced during acid neutralization after pretreatment. The gypsum could potentially be considered a byproduct, but in this LCA it is treated as waste (Foust et al. 2009).

Section 3: Chemical inputs

Each biorefinery requires chemical inputs that are produced outside of the factory. All chemical inputs are grouped into ancillary chemicals except for hydrogen production. Chemicals used in each biorefinery are list in Tables 3.4 & 3.6. Life cycle data for the ancillary chemicals are provided by EcoInvent, the USLCI, and the literature. Data for enzyme production is supplied from Novozymes for their Cellic Ctec3 cellulases (Novozymes, personal communication, 2012). Transportation distances for each chemical are determined using the 2007 U.S. commodity flow survey (US DOT, 2010). Transportation data is reported in appendix B.

Hydrogen gas is required in the acetogen pathway to hydrogenate acetic acid to ethanol. It is modeled to be produced from a standalone steam methane reforming (SMR) plant(Table 3.7). Natural gas is used as the methane source and is used to produce the necessary process steam and heat. Excess high pressure steam is converted to electricity at 30% efficiency (Energy and Environmental Analysis, 2008). It is assumed that this electricity would be cycled back into plant operations, thereby decreasing the amount of electricity imported from the U.S. national grid. Operations and emissions data from this process are provided by an Idaho National Laboratory report (Wood, 2010). Production of hydrogen gas is kept separate from other chemicals to identify its contribution to the life cycle impact assessment.

Table 3.7: Steam Methane Reforming: Inputs and outputs to produce 1 kg hydrogen (Wood, 2010).

Input	**Value**
Water	16.3 L
Electricity (imported)	0.136 kwh
Natural gas	3.04 kg
Output	
Hydrogen	1 kg
CO_2 (fossil)	9.21 kg
CH_4 (fugitive loss)	0.0560 kg

Section 4: Fuel distribution and use.

The bioethanol produced from either fermentation pathway will be transported to a distribution center. The transportation distance is assumed to be 160km roundtrip (US DOT, 2010). The end use of the ethanol is combustion in a flex fuel vehicle that is capable of using 100% ethanol (E100). Emissions produced from combustion in a vehicle are modeled in The Greenhouse Gases, Regulated Emissions, and Energy use in Transportation model (GREET, 2012) 2015 using a flex fuel vehicle. In GREET all default parameters were used accept for the ethanol blend ratio (100% ethanol). E100 fuel is used as the final end product (without any blending or additives) so that direct LCA comparisons can be made with gasoline.

To identify areas within the system boundaries that contribute to environmental impact categories, the life cycle assessment is broken up into the following categories:

- Carbon in biomass: CO_2 absorbed by photosynthesis in harvested chips, above ground and below ground stumps, and coarse roots, modeled over 21 years. The amount of CO_2 stored in the poplar wood is calculated using the stoichiometric relationship of 44.01g CO_2 / 12.01g carbon and an elemental carbon composition of 50% dry wood weight.
- Poplar growth & harvesting: All technosphere processes associated with growing and harvesting poplar. Includes direct land use change emissions.
- Ancillary chemicals: All chemical listed in section 3 except hydrogen production.
- Hydrogen production: Steam methane reforming.
- Transportation: Includes transportation of poplar from farm to biorefinery gate, transportation associated with all chemical inputs including hydrogen to the biorefinery, and ethanol from biorefinery to a distribution center.
- Biorefinery: All operations performed, raw materials used, and emissions at each biorefinery.
- Avoided production: Avoided production of electricity resulting from the production of excess electricity. It is assumed that marginal electricity, created by natural gas combustion, will be displaced.
- Ethanol use: Combustion of ethanol in FFV vehicle.
- Gasoline production and use: All processes, raw material use, and emissions associated with production and use of gasoline.

Results

Global Warming Potential (per MJ)

The GWP net values, as well as contributions from each area within the biorefinery life cycles, are displayed in Figure 3.2. The Ethanologen Pathway (EP) has a net GWP of 0.0030 kg CO_2 eq./ MJ. In the EP the biorefinery and ethanol fuel use are the largest sources of GHGs. Within the biorefinery CO_2 is emitted during ethanologen fermentation, combustion of lignin and unreacted carbohydrates to produce steam, and decomposition of organic matter in the waste water treatment. Combustion of ethanol in a FFV produces CO_2 and other GHGs. Both biorefinery and fuel use CO_2 emissions originate from the poplar trees (biogenic source). CO_2 stored as carbon in the harvested wood and non-harvested biomass (carbon in biomass in Figure 3.2) offset the CO_2 emissions produced during the life cycle within the GWP. With the addition of the avoided production of marginal electricity the life cycle of EP is almost carbon neutral. Compared to gasoline a net reduction of 97% in GWP per MJ of fuel is observed.

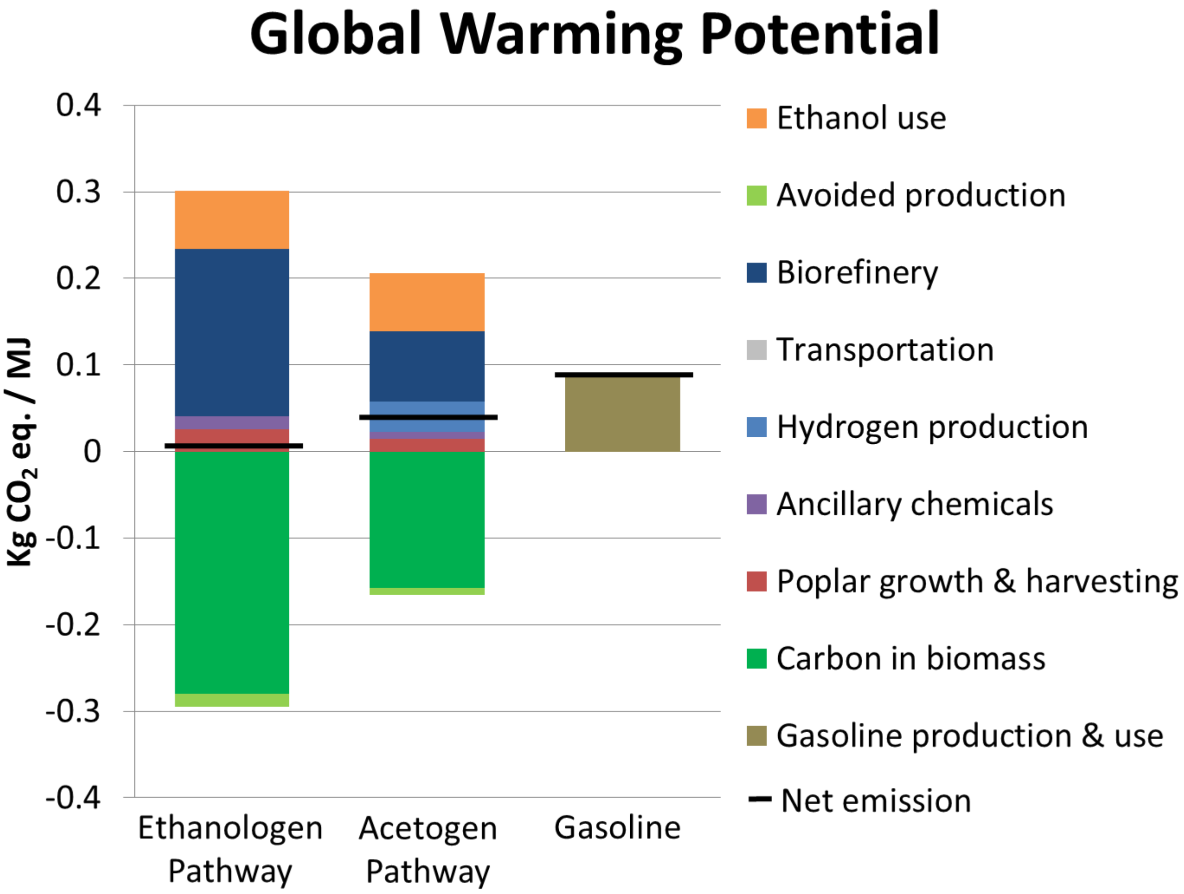

Figure 3.2: Global warming potential of the two bioethanol pathways and gasoline on a per MJ basis – Biogenic CO_2 is removed from the atmosphere in the carbon in biomass stage and emitted back to the atmosphere during the biorefinery and ethanol use stages. An avoided production credit is achieved by offsetting electricity produced from natural gas. Hydrogen production is largely responsible for the higher net emission in the acetogen pathway relative to ethanologen pathway.

The Acetogen Pathway (AP) GWP net value is 0.041 kg CO_2 eq./ MJ. The main sources of GHG emissions within the AP are hydrogen production, the biorefinery, and fuel use (Figure 3.2). GHGs emitted during hydrogen production are a result of using natural gas in the steam methane reforming process. The biorefinery emits only CO_2 from the combustion of lignin and unreacted carbohydrates and decomposition of organic matter in the waste water treatment. Combustion of ethanol in a FFV produces CO_2 and other GHGs. Of these three areas (biorefinery, hydrogen production, and fuel use) carbon emissions from hydrogen production are the only ones not considered biogenic. The addition of non-biogenic carbon (fossil carbon) to the atmosphere results in a larger GWP for the AP compared to the EP. The credit from avoided production is not enough to offset all GHG emissions during the AP life cycle. Compared to gasoline a net reduction of 53% is observed. In both the EP and AP poplar growth and harvesting, ancillary chemicals production, and transportation have only a minor contribution to the GWP.

Global Warming Potential (per ha)

Over the lifespan of the proposed poplar plantation (21 years) 324 BDt of chips would be harvested per hectare. Using the EP this will produce 101,000 liters of ethanol/ha. Averaged out over 21 years a hectare of land would produce 4,810 liters or 112 gigajoules (GJ) of ethanol. The GWP for 112 GJ of ethanol is 0.34 tonnes CO_2 eq. and the GWP for 112 GJ of gasoline is 9.9 tonnes CO_2 eq. Using a hectare of land to grow poplar would result in a GWP savings of 9.6 tonnes CO2 eq./ha/yr when ethanol is produced with the ethanologen process (Table 3.8).

By comparison, assuming the same poplar chip yield of 324 BDt/ha over 21 years, the AP would produce 174,000 liters of ethanol/ha. Averaged over 21 years a hectare of land would produce 8,290 liters or 194 GJ of ethanol. The GWP of 194 GJ of ethanol produced by the AP process is 7.9 tonnes CO_2 eq. and the GWP of 190 GJ of gasoline is 17 tonnes CO_2 eq. If the ethanol from the AP process replaced this gasoline for fuel use it would have a GWP savings of 9.1 tonnes CO_2 eq./ha/yr. The GWP savings of the acetogen pathway on a per hectare basis is almost identical to the ethanologen pathway (Table 3.8).

Table 3.8: Global Warming Potential per hectare calculation numbers

	Ethanologen	Acetogen	Unit
Poplar chip yield (21 year total)	324	324	Bone Dry tonnes / hectare
Ethanol yield / BDt of poplar	312	536	Liters / BDt
Ethanol yield (21 year total)	101,00	174,000	L / ha
Ethanol yield (liters per year)	4,810	8,290	L / ha / yr
Ethanol yield (MJ per year)	112,000	194,000	Mega Joules / ha / yr
GWP of ethanol (per MJ)	0.0030	0.041	Kg CO_2 eq. / MJ
GWP of gasoline (per MJ)	0.088	0.088	Kg CO_2 eq. / MJ
GWP of displaced gasoline	9,900	17,000	Kg CO_2 eq. / yr
GWP of ethanol produced	340	9,100	Kg CO_2 eq. / ha / yr
GWP savings	9,600	9,100	Kg CO_2 eq. / ha / yr

Fossil Fuel Use

The EP has a net fossil fuel use of 0.029 MJ of fossil fuel / MJ of ethanol (Figure 3.3). The process uses 0.26 MJ of fossil fuel / MJ of ethanol. Most of the fossil fuel use occurred in the ancillary chemicals production, especially enzymes and ammonia. The excess electricity produced in the biorefinery does not originate from a fossil fuel source, however it can be used to displace electricity from a fossil fuel source (in this case natural gas) and is therefore included in this impact calculation. Displaced electricity by electricity exported from the biorefinery generates a credit of 0.23 MJ of fossil fuel / MJ of ethanol. The EP reduces fossil fuel use by 97% compared to gasoline.

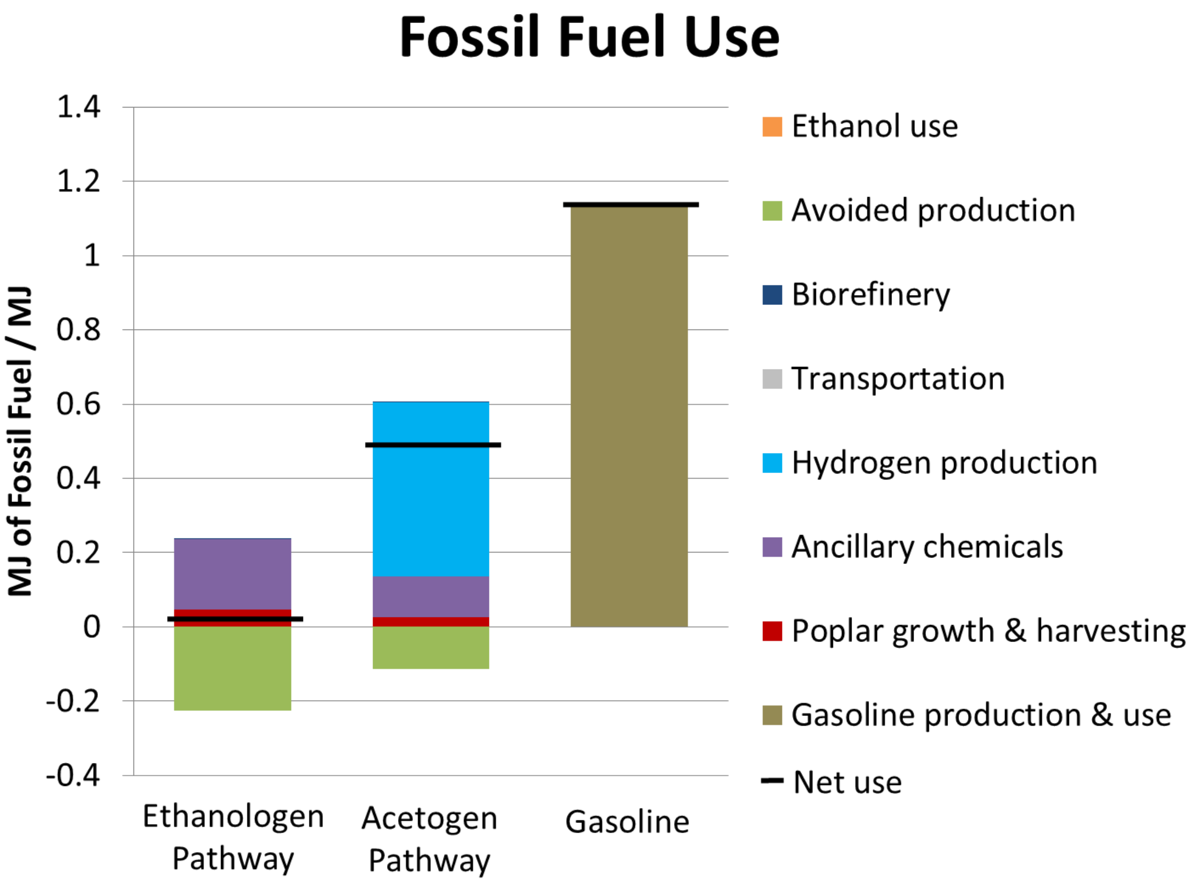

Figure 3.3: Fossil fuel use of the two bioethanol pathways and gasoline on a per MJ basis – An avoided production credit is achieved by offsetting electricity produced from natural gas. Natural gas use in hydrogen production is largely responsible for the higher net use in the acetogen pathway relative to ethanologen pathway.

The AP has a higher fossil fuel use with a net value of 0.52 MJ / MJ (Figure 3.3). The higher fossil fuel use is a result of hydrogen production and the use of natural gas during SMR (0.48 MJ / MJ). The ancillary chemicals group also consumes fossil fuels (enzymes and ammonia production), but it is not as high as in the EP due to the higher ethanol yield in the AP. In total, the process uses 0.63 MJ / MJ. The avoided production of marginal electricity generates a credit (0.11 MJ / MJ) that reduces the overall fossil fuel use. Compared to gasoline the AP reduces fossil fuel use by 55%.

Freshwater use

The EP uses 0.81 liters of water per MJ of ethanol (19 L/L of ethanol) (Figure 3.4). The production of ancillary chemicals requires the most water use at 0.53 L/MJ (12 L/L). Within the ancillary chemicals group the production of sodium hydroxide and sulfuric acid are responsible for 80% of water use. The biorefinery requires 0.27 L/MJ (6.4 L/L). Compared to gasoline, the EP increases life cycle water use by 180%.

The AP uses 0.53 liters of water per MJ of ethanol (12 L/L of ethanol) (Figure 3.4). The ancillary chemical group is the largest water user at 0.30 L/MJ (7.0 L/L). As in the EP process much of the water use is driven by the production of sodium hydroxide and sulfuric acid. The AP biorefinery uses 0.16 L/MJ (3.7 L/L). The steam methane reforming process requires 0.059 L/MJ (1.3 L/L of ethanol). The AP uses 83% more water than the production of gasoline. In both the EP and AP water use is low as the poplar feedstock is assumed to be grown without irrigation. With irrigation, it is anticipated the EP water use would increase considerably more than the AP water use since the EP uses 78% more poplar feedstock to produce a MJ of ethanol fuel.

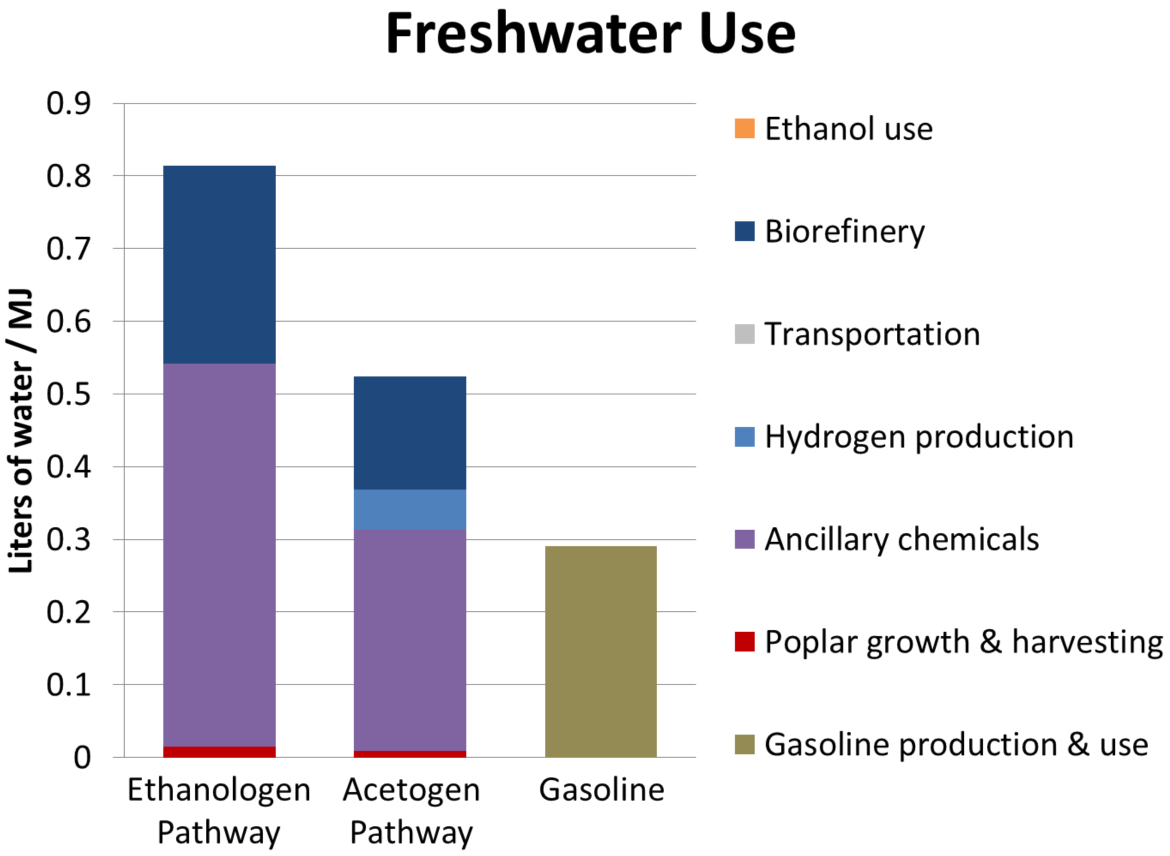

Figure 3.4: Freshwater use of the two bioethanol pathways and gasoline on a per MJ basis – Both the acetogen and ethanologen pathways use more water than conventional gasoline. The higher ethanol yield in the acetogen pathway reduces the amount of water used per MJ compared to the ethanologen pathway.

Discussion

The 96% GWP reduction (per MJ) of the ethanologen pathway (EP) compared to 2005 gasoline (Figure 3.2) is similar to values reported in other SRWC cradle to grave studies. These reductions range from 78 to 120% of gasoline and are dependent on the ethanol yield, excess electricity produced (Aden et al. 2002, Humbird et al. 2011), the type of electricity that is assumed to be displaced, direct land use change, and below ground carbon sequestration (Gonzalez-Garcia et al. 2010; Stephenson et al. 2010; Budsberg et al. 2012, Wiloso et al. 2012). The AP GWP is 53% lower than 2005 gasoline (Figure 3.2). This is a significant reduction in GHGs, but does not reduce the GWP as much as the EP. If hydrogen production is excluded, the increased yield of ethanol in the AP lowers the GWP of processes per MJ compared to the EP. However hydrogen is needed to convert acetic acid to ethanol and the production of it increases the GWP relative to biorefineries that use an ethanologen for the fermentation step. The avoided production in the AP is also lower than in the EP, resulting in a lower GWP credit in the net value. Targeting a reduction in natural gas use, hydrogen use, or producing hydrogen in a more environmentally efficient process could help lower the GWP of the AP.

When the EP and AP GWPs are assessed using a functional unit of one hectare, the GWP savings compared to gasoline are nearly identical. The benefit of a higher ethanol yield in the AP makes up for the GWP cost of hydrogen production by producing more fuel per hectare. These savings of 9.6 and 9.1 tonnes CO_2 eq./ha/yr for the EP and AP, respectively, are in the high end of the range of savings reported by other studies of 2 to 11 tonnes CO_2 ha/yr (Cherubini et al. 2009, Lippke et al. 2012) for lignocellulosic ethanol via bioconversion. This measurement of GWP savings per hectare is useful when land is a limited resource. Estimates place the amount of marginal/abandoned land available for biofuels at 320 - 1107 million ha worldwide (Cai, et al. 2011). Using second generation biofuel production methods (like the ethanologen pathway describe in this research) this amount of land would be able to meet 26 - 55% of the current world liquid fuel demand (Cai, et al. 2011). If the AP was to be used instead (and assuming the ethanol yield rates in this research) 70% more ethanol could be produced while achieving a GWP savings almost equal to the ethanologen fermentation route. The AP may not have a GWP as low as the EP, but if the desired goal is to reduce CO_2 by an absolute number rather than a relative number, and other factors favor a higher yielding ethanol process, the acetogen pathway could be a viable option.

The 97% fossil fuel reduction of the EP compared to gasoline (Figure 3.3) is similar to values reported in the literature for lignocellulosic ethanol (Borrion et al. 2012). It is lower than the 140% reduction reported by Budsberg et al. (2012). The difference is accounted for by a higher biorefinery electricity demand in this current work (Humbird et al. 2011) compared to the electricity demand in the earlier work (2012)(Aden et al. 2002). The results in this study are similar to Gonzalez-Garcia (et al. 2010) and Stephenson et al. (2010) when the avoided production credit is removed (76% reduction compared to gasoline). These large reductions in fossil fuel use are expected in lignocellulosic ethanol bioconversion process as the combustion of lignin and unreacted carbohydrates produces steam, heat and electricity (Budsberg et al. 2012).

The AP achieves a reduction of 55% in fossil fuel use compared to gasoline. If hydrogen production is excluded, the increased ethanol yield in the AP lowers the fossil fuel use of processes within the life cycle when compared to the EP (Figure 3.3). The use of natural gas in hydrogen production is large and increases fossil fuel use by 0.48 MJ/MJ, negating the benefits of the higher yield. A lower avoided electricity production credit in the AP also adds to higher fossil fuel use. Reducing natural gas consumption in the methane reformer, reducing hydrogen use in the biorefinery, or producing hydrogen in a process less dependent on natural gas would help reduce fossil fuel use.

Only a few studies have taken into account water use for lignocellulosic ethanol and fewer still have been for SRWC feedstocks. Mixed results have been observed in these studies and the use of irrigation drastically changes the amount of water required per unit of bioethanol. Use of irrigation shifts the majority use of water from the biorefinery to feedstock production (Borrion et al. 2012). In our research the EP biorefinery water use of 6.4 L of water /L of ethanol is similar to the biorefinery water use reported by other SRWC to ethanol LCAs (Gonzalez-Garcia et al. 2010, Gonzalez-Garcia et al. 2012, Budsberg et al. 2012)(Figure 3.4). It may be possible to reduce the water demand the EP and AP biorefineries place on a region, by recovering the water included in the poplar chips and use it during the conversion process (Humbird et al. 2011). Depending on the moisture content of the poplar chips, the amount of water that could be supplied to the biorefinery via the feedstock could be significant. A more detailed analysis in the future will help in understanding how these proposed lignocellulosic ethanol systems will use water.

Freshwater use in the AP is found to be lower than in the EP. The higher ethanol yield reduces the amount of freshwater used in the biorefinery per MJ. Referencing the ancillary chemical use to a higher ethanol yield also reduces the freshwater use per MJ in the AP. Steam methane reforming (SMR) requires water to produce the hydrogen and is an additional water demand not needed in the EP. Even with the SMR high water consumption, the AP freshwater use is lower than the EP demonstrating the benefit of a much higher yield.

Freshwater use in both of the biofuel pathways is larger than gasoline. This is concerning as lignocellulosic biofuels are moving to commercial scale production. Freshwater is a valuable resource and identifying ways to reduce its use in biofuel production is a priority. A first step towards understanding water use should be a more detailed analysis. However, detailing water use in LCA is currently a complicated task (Bayart et al. 2010, Berger and Finkbeiner, 2010, Kounina et al. 2013). Freshwater can be supplied from different sources, such as rainwater (greenwater), and above and below ground reservoirs (bluewater). Processes that use water will either consume it or use it for a period of time before returning it. The state of the water returned is also necessary if greywater is to be included. Furthermore water use is a local issue and watershed impacts will vary by region. Methods on measuring water use in LCA have been proposed and ongoing research is being done to identify how best to approach it (Kounina et al. 2013).

Conclusion

The Acetogen Pathway (AP) to produce ethanol does not achieve the large reductions in global warming potential (GWP) and fossil fuel use observed in the Ethanologen Pathway (EP) when assessed using an energy (MJ) functional unit. The production of hydrogen required to hydrogenate acetic acid to ethanol is largely responsible for the increased AP global warming potential and fossil fuel use. However, a higher ethanol yield equates to more efficient use of the land. When assessed on a land acreage basis the GWP savings of the AP route is comparable to the EP. If available land is limited than the AP may be considered as the more viable option that could produce more ethanol while still achieving GWP savings similar to the EP.

Acknowledgements

This project is supported in part by Agriculture and Food Research Initiative Competitive Grant no. 2011-68005-30407 from the USDA National Institute of Food and Agriculture. Material is also based upon work supported by the National Institute of Food and Agriculture, U.S. Department of Agriculture, under Project Number WNZ-04282011.

References

Aden, A., M. Ruth, K. Ibsen, J. Jechura, K. Neeves, J. Sheehan, B. Wallace, L. Montague, A. Slayton, and J. Lukas. 2002. Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis and enzymatic hydrolysis for corn stover. National Renewable Energy Laboratory.

Argonne National Laboratory. 2013. GREET Life-cycle model, version 1.0.0.8377. Argonne, IL. Downloaded from http://greet.es.anl.gov/index.php?content=download1x on 2/18/2013.

Aspen Technology Inc. (ATI). 2005. Aspen Plus, version 2004.1. ATI, Cambridge, Massachusetts.

Bare, J. C. 2002. The tool for the reduction and assessment of chemical and other environmental impacts. J. Ind. Ecol. 6:49–78.

Bayart, J.B., Bulle, C., Deschences, L., Margni, M., Pfister, S., Vince, F., and A. Koehler. 2010. A framework for assessing off-stream freshwater use in LCA. International Journal of Life Cycle Assessment 15: 439-453.

Berger, M. and M. Finkbeiner. 2010. Water Footprinting: How to Address Water Use in Life Cycle Assessment?. Sustainability 2: 919 – 944.

Borrion, A. L., McManus, M.C., and G.P. Hammond. 2012. Environmental life cycle assessment of lignocellulosic conversion to ethanol: A review. Renewable and Sustainable Energy Reviews. 16: 4638-4650.

Buchholz, T. and T.A. Volk. 2011. Identifying opportunities to improve the profitability of willow biomass crops with a crop budget model. Bioenergy Resources 4(2):85-95.

Budsberg, E., Rastogi, M., Puettmann, M. E., Caputo, J., Balogh, S., Volk, T.A., Gustafson, R., and L. Johnson. 2012. Life-Cycle Assessment for the Production of Bioethanol from Willow Biomass Crops via Biochemical Conversion. Forest Products Journal 62(4): 305 – 313.

Cai, X., Zhang, X., and D. Wang. 2011. Land availability for biofuel production. Environmental Science and Technology 45: 334-339.

Caputo, J., Balogh, S.B., Volk, T.A., Johnson, L., Puettmann, M., Lippke, B., and E. Oneil. 2013. Incorporating Uncertainty into a Life Cycle Assessment (LCA) Model of Short-Rotation Willow Biomass (Salix spp.) Crops. Bioenergy Resource. DOI 10.1007/s12155-013-9347-y

Cherubini, F., Bird, N.D, Cowie, A., Jungmeier, G., Schlamadinger, B., and S. Woess-Gallasch. 2009. Energy and greenhouse gas-based LCA of biofuel and bioenergy systems: Key issues, ranges, and recommendations. Resources, Conservation, and Recycling 53: 434 – 447.

Cherubini, F. and A. H. Stromman. 2010. Production of biofuels and biochemical from lignocellulosic biomass: Estimation of maximum theoretical yields and efficiencies using matrix algebra. American Chemical Society. 24: 2657-2666.

EISA. 2007. Energy Independence and Security Act of 2007, United States Government. Public Law 110-140. 2007. P. 311.

Ekvall, T. and G. Finnveden. 2001. Allocation in ISO 14041 – A critical review. *Journal of Cleaner Production* 9: 197-208.

Energy and Environmental Analysis (EEA). 2008. *Technology characterization: Steam Turbines*. Prepared for Environmental Protection Agency combined heat and power partnership program Washington, DC. Retrieved from http://www.epa.gov/chp/documents/catalog_chptech_steam_turbines.pdf.

U.S. Department of Energy, Energy Information Administration (EIA). 2013. Electric Power Monthly. Retrieved from http://www.eia.gov/electricity/monthly/pdf/epm.pdf

Foust, T. D., A. Aden, A. Dutta, S. Phillips., 2009. An economic and environmental comparison of a biochemical and a thermochemical lignocellulosic ethanol conversion processes. Cellulose 16: 547 – 565.

Gonzlaez-Garcia, S., C. M. Gasol, X. Gabarrell, J. Rieradevall, M. T. Moreira, and G. Feijoo. 2010. Environmental profile of ethanol from poplar biomass as transport fuel in Southern Europe. Renewable Energy 35(5):1014–1023.

Gonzlaez-Garcia, S., Mola-Yudego, B., and R.J. Murphy. 2012. Life cycle assessment of potential energy uses for short rotation willow biomass in Sweden. International Journal of Life Cycle Assessment 18: 783-795.

Gnansounou, E., Dauriat, A., Villegas, J., and L. Panichelli. 2009. Life cycle assessment of biofuels: Energy and greenhouse gas balances. *Bioresource Technology* 100: 4919-4930.

Gnansounou, E. and A. Dauriat. 2010. Techno-economic analysis of lignocellulosic ethanol: A review. Bioresource Technology 101; 4980-4991.

Gustafson, R., and N. Raffaeli. 2009. Washington State Pulp and Paper Mill Boilers: Current and Potential Renewable Energy Production. Washington State Department of Ecology. Publication No. 09-07-048:1-45.

Huang, H., Ramaswamy, S., Al-Dajani, W., Tschirner, U., Cairncross, R. 2009. Effect of biomass species and plant size on cellulosic ethanol: A comparative process and economic analysis. Biomass and Bioenergy 33; 234-246.

Humbird, D., Davis, R., Tao, L., Kinchin, C., Hsu, D., Aden, A., Schoen, P., Lukas, J., Olthof, B., Worley, M., Sexton, D., and D. Dudgeon. 2011. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol; Dilute-acid Pretreatment and Enzymatic Hydroylsis of Corn Stover. National Renewable Energy Laboratory, Golden, Colorado.

IPCC AR4 WG1 (2007), Solomon, S.; Qin, D.; Manning, M.; Chen, Z.; Marquis, M.; Averyt, K.B.; Tignor, M.; and Miller, H.L., ed., Climate Change 2007: The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, ISBN 978-0-521-88009-1

International Organization for Standardization (ISO). 2006a. Environmental management. Life cycle assessment. Principles and framework. ISO 14040:2006. ISO, Geneva.

International Organization for Standardization (ISO). 2006b. Environmental management. Life cycle assessment. Requirements and guidelines. ISO 14044:2006. ISO, Geneva.

Keoleian, G. A. and T. A. Volk. 2005. Renewable energy from willow biomass crops: Life cycle energy, environmental and economic performance. Crit. Rev. Plant Sci. 24(5–6):385–406.

Kounina, A., Margni, M., Bayart, J.B., Boulary, A.M., Berger, M., Bulle, C., Frischknecht, R., Koehler, A., Mila i Canals, L., Motoshita, M., Nunez, M., Peters, G., Pfister, S., Ridoutt, B., van Zelm, R., Verones, F., and S. Humbert. 2013. Review of methods addressing freshwater use in life cycle inventory and impact assessment. International Journal of Life Cycle Assessment 18(3): 707 – 721.

Lippke, B., Gustafson, R., Venditti, R., Steele, P., Volk, T.A., Oneil, E., Johnson, L., Puettmann, M.E., and K. Skog. 2012. Comparing Life-Cycle Carbon and Energy Impacts for Biofuel, Wood Product, and Forest Management Alternatives. Forest Products Journal. 62(4):247-257.

National Council for Air and Stream Improvement, Inc. 2011. Forest Industry Carbon Assessment Tool (FICAT). Version 1.3.1.1. Available from www.ficatmodel.org.

National Renewable Energy Laboratory (NREL). 2011. US life cycle inventory database. http://www.nrel.gov/lci/. Accessed September 5, 2012.

Mansfield, S. D., C. Mooney, and J. N. Saddler. 1999. Substrate and enzyme characteristics that limit cellulose hydrolysis. Biotechnol. Prog. 15(5):804–816.

Oak Ridge National Laboratory. 2012. Bioenergy conversion factors. https://bioenergy.ornl.gov/papers/misc/energy_conv.html. Accessed September 5, 2012.

Pacaldo, R. S., T. A. Volk, L. P. Abrahamson, and R. D. Briggs. 2010. Above- and below-ground biomass and soil organic carbon inventories of willow biomass crops across a 19-year chronosequence. In: Proceedings of the 8th Biennial Short Rotation Woody Crops Operations Working Group—Short Rotation Woody Crops in a Renewable Energy Future: Challenges and Opportunities, October 17–19, 2010, Syracuse, New York.

Pacaldo, R. S., Volk, T. A., and R.D. Briggs. 2012. Greenhouse gas potentials of shrub willow biomass crops based on below- and aboveground biomass inventory along a 19-year chronosequence. Bioenergy Resources DOI 10.1007/s12155-012-9250-y.

Pre Consultants. 2012. Simapro 7 Life-Cycle Assessment Software package. Version 7.3.3. Plotter 12, 3821 BB Amersfoort, The Netherlands. Http://www.pre.nl/.

Quaye, A., T. A. Volk, S. Hafner, D. Leopold, and C. Schirmer. 2011.Impacts of paper sludge and manure on soil and biomass production of willow. Biomass Bioenergy 35:2796–2806.

Sanchez, T.S., Woods, J., Akhurst, M., Brander, M., O'Hare, M., Dawson, T.P., Edwards, R., Liska, A.J., and R. Malpas. 2012. Accounting for indirect land-use change in the life cycle assessment of biofuel supply chains. Journal of the Royal Society Interface. 9: 1105-1119.

Sassner, P., M. Galbe, and G. Zacchi. 2005. Steam pretreatment of Salix with and without SO2 impregnation for production of bioethanol. Appl. Biochem. Biotechnol. 121–124:1101–1117.

Sheehan, J., A. Aden, K. Paustian, K. Killian, J. Brenner, M. Walsh, R. Nelson. 2004. Energy and Environmental Aspects of Using Corn Stover for Fuel Ethanol. Journal of Industrial Ecology 7: 117 - 146.

Solomon, S.; Qin, D.; Manning, M.; Chen, Z.; Marquis, M.; Averyt, K.B.; Tignor, M.; and Miller, H.L., ed., Climate Change 2007: The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, ISBN 978-0-521-88009-1

Stephenson, A. L., P. Dupree, S. A. Scott, and J. S. Dennis. 2010. The environmental and economic sustainability of potential bioethanol from willow in the UK. Bioresour. Technol. 101(24):9612–9623.Simapro

Swiss Centre for Life Cycle Inventories (SCLCI). 2009. EcoInvent database 2.1. SCLCI, Duebendorf, Switzerland.

Thomas, C.E. 2012. US marginal electricity grid mixes and EV greenhouse gas emissions. *International Journal of Hydrogen Energy* 37: 19231-19240.

U.S. Department of Transportation (US DOT) and U.S. Department of Commerce (US DOC). 2010. 2007 Commodity Flow Survey. http://www.census.gov/prod/2010pubs/ec07tcf-us.pdf accessed on July 11, 2013.

Verser, D., and T.J. Eggeman. 2011. United States Patent No. 7,964,379 B2. NEED LOCATION

Wiloso, E.I., Heijungs, R., and G. R. de Snoo. 2012. LCA of second generation bioethanol: A review and some issues to be resolved for good LCA practice. Renewable and Sustainable Energy Reviews. 16: 5295-5308.

Wood, R.A. 2010. HTGR-Integrated Hydrogen Production via Steam Methane Reforming (SMR) Process Analysis. Idaho National Laboratory, Idaho Falls, Idaho.

4. Thesis Conclusion

The LCA studies indicate GWP and fossil fuel use reductions and increases in freshwater use when bioethanol is used in place of gasoline. The results of the LCA work are summarized in Table 4.1. Variation in the GWP and fossil fuel results between the two ethanologen pathways is primarily related to avoided production. The willow to ethanol process is based off Aden et al. (2002) and the poplar to ethanol process is designed around Humbird et al. (2011). Aden et al. (2002) requires less electricity to run biorefinery operations than Humbird et al. (2011) and therefore is capable of exporting more electricity. Differences between the ethanologen pathways (willow and poplar) and the acetogen pathway are tied to steam methane reforming to produce hydrogen and higher ethanol yield in the AP. The different water use in the willow to ethanol and poplar ethanologen pathway is attributed to different LCI data. The willow to ethanol LCA includes more unit processes from the USLCI and water use is not reported for some of the ancillary chemicals. The poplar ethanologen pathway is mostly comprised of unit processes from the EcoInvent database which provides water inputs for each ancillary chemical used.

Table 4.1 – Summary of LCA impacts in the two LCA projects included in this thesis.

LCA	Impact	Amount
Willow	GWP (kg CO_2 eq. / MJ)	-0.017
Poplar – ethanologen pathway	GWP (kg CO_2 eq. / MJ)	0.0030
Poplar – acetogen pathway	GWP (kg CO_2 eq. / MJ)	0.041
Willow	Fossil fuel use (MJ / MJ)	-0.50
Poplar – ethanologen pathway	Fossil fuel use (MJ / MJ)	0.029
Poplar – acetogen pathway	Fossil fuel use (MJ / MJ)	0.52
Willow	Freshwater use (L / MJ)	0.49
Poplar – ethanologen pathway	Freshwater use (L / MJ)	0.81
Poplar – acetogen pathway	Freshwater use (L / MJ)	0.53

The willow to ethanol and poplar ethanologen pathway biorefineries have larger GWP reductions than the acetogen pathway compared to gasoline on a per MJ basis. Using an energy content functional unit to assess the GWP is useful. It gives an indication of the relative GWP savings that are earned when replacing gasoline with these biofuels and is required by government legislation to qualify for renewable fuel standards (EISA, 2007). However this unit of measure does not capture all characteristics of the different biofuels. Measuring the amount of ethanol produced per hectare of land and determining the absolute GWP savings earned when replacing gasoline demonstrates the benefit of a biorefinery that achieves a higher ethanol yield. If land is a limited resource, the higher ethanol yield in the acetogen pathway can achieve the same absolute GWP savings as the ethanologen pathways while producing more fuel on a hectare of land.

In all three LCAs the combustion of lignin and unreacted carbohydrates provides the necessary process steam, heat, electricity to operate the biorefineries, and an electricity co-product. Using this biomass to produce all of the process energy is necessary for achieving the low GWPs and fossil fuel use observed in the LCAs. If the lignin was not used for providing process energy, the GWP and fossil fuel use from operating the biorefineries could increase significantly. Fossil fuel use would increase as fuels like coal and natural gas would be required to supply the necessary energy. These fossil fuels would add CO_2 and other greenhouse gases to the atmosphere and would increase the GWP. If lignin is to be used as a co-product instead of an energy source (Arato et al. 2005, Zhang, 2008) the environmental benefits observed for producing biofuels may be drastically compromised. Life cycle assessment should be used to assess possible environmental impacts of diverting lignin to the production of co-products.

Freshwater use was found to be higher in all three biofuel LCAs. These LCAs did not assume use of irrigation to grow the short rotation woody crops. If irrigation is required water use per liter of fuel can range from 500 to 3500 liters of water per liter of fuel (Borrion et al. 2012). This is a concerning result as freshwater is a valuable resource and understanding how it is used is a priority. A first step towards understanding water use should be a more detailed analysis. However, detailing water use in LCA is currently a complicated task (Bayart et al. 2010, Berger and Finkbeiner, 2010, Kounina et al. 2013). Freshwater can be supplied from different sources, such as rainwater (greenwater), and above and below ground reservoirs (bluewater). Processes that use water will either consume it or use it for a period of time before returning it. The state of the water returned is also necessary if greywater is to be included. Furthermore, water use is a local issue and watershed impacts will vary by region. Methods on measuring water use in LCA have been proposed and ongoing research is being done to identify how best to approach it (Kounina et al. 2013). Future work focusing on how to address water use modeling for biofuel LCAs is highly recommended.

The use of short rotation woody crops like poplar and willow look promising as a feedstock for biofuels. The low chemical and mechanical inputs used in growing and harvesting the biomass limit greenhouse gas emissions and fossil fuel use. The use of the wood also reduces emissions from the biorefinery by providing the energy needed to create the fuel product in a sustainable manner. Overall use of bioethanol produced from poplar or willow wood instead of conventional gasoline will greatly reduce the GWP and fossil fuel use. The high water use bioethanol production is of concern, and future work is needed to develop a more detailed model of water use.

Introduction and Conclusion References

Aden, A., M. Ruth, K. Ibsen, J. Jechura, K. Neeves, J. Sheehan, B. Wallace, L. Montague, A. Slayton, and J. Lukas. 2002. Lignocellulosic biomass to ethanol process design and economics utilizing co-current dilute acid prehydrolysis and enzymatic hydrolysis for corn stover. National Renewable Energy Laboratory.

Arato, C., Pye, E.K., and G. Gjennestad. 2005. The lignol approach to biorefining of woody biomass to produce ethanol and chemicals. *Applied Biochemistry and Biotechnology* 121-124: 871 – 882.

Bare, J. C. 2002. The tool for the reduction and assessment of chemical and other environmental impacts. J. Ind. Ecol. 6:49–78.

Bayart, J.B., Bulle, C., Deschences, L., Margni, M., Pfister, S., Vince, F., and A. Koehler. 2010. A framework for assessing off-stream freshwater use in LCA. International Journal of Life Cycle Assessment 15: 439-453.

Berger, M. and M. Finkbeiner. 2010. Water Footprinting: How to Address Water Use in Life Cycle Assessment?. Sustainability 2: 919 – 944.

Borrion, A. L., McManus, M.C., and G.P. Hammond. 2012. Environmental life cycle assessment of lignocellulosic conversion to ethanol: A review. Renewable and Sustainable Energy Reviews. 16: 4638-4650.

Bothast, R.J. and M.A. Schlicher. 2005. Biotechnological processes for conversion of corn into ethanol. *Appl. Microbiol. Biotechnol.* 67:19-25.

Budsberg, E., Rastogi, M., Puettmann, M. E., Caputo, J., Balogh, S., Volk, T.A., Gustafson, R., and L. Johnson. 2012. Life-Cycle Assessment for the Production of Bioethanol from Willow Biomass Crops via Biochemical Conversion. Forest Products Journal 62(4): 305 – 313.

Cherubini, F. and G. Jungmeier. 2010. LCA of a biorefinery concept producing bioethanol, bioenergy, and chemicals from switchgrass. *International Journal of Life Cycle Assessment* 15: 53-66.

Cherubini, F. and A. H. Stromman. 2010. Production of biofuels and biochemical from lignocellulosic biomass: Estimation of maximum theoretical yields and efficiencies using matrix algebra. American Chemical Society. 24: 2657-2666.

Energy Independence and Security Act (EISA). 2007. Energy Independence and Security Act of 2007. Public Law 110-140. US Government, Washington, D.C. 311 pp.

Environmental Protection Agency (EPA) (2007). "Recent Climate Change: Atmosphere Changes". Climate Change Science Program. United States Environmental Protection Agency. Retrieved 21 April 2009.

Fargione, J., Hill, J., Tilman, D., Polasky, S., Hawthorne, P. 2008. Land clearing and the biofuel carbon debt. Science 319: 1235-1237.

Gnansounou, E., Dauriat, A. 2010. Techno-economic analysis of lignocellulosic ethanol: A review. Bioresource Technology 101; 4980-4991.

Gonzlaez-Garcia, S., C. M. Gasol, X. Gabarrell, J. Rieradevall, M. T. Moreira, and G. Feijoo. 2010. Environmental profile of ethanol from poplar biomass as transport fuel in Southern Europe. Renewable Energy 35(5):1014–1023.

Huang, H., Ramaswamy, S., Al-Dajani, W., Tschirner, U., Cairncross, R. 2009. Effect of biomass species and plant size on cellulosic ethanol: A comparative process and economic analysis. Biomass and Bioenergy 33; 234-246.

Humbird, D., Davis, R., Tao, L., Kinchin, C., Hsu, D., Aden, A., Schoen, P., Lukas, J., Olthof, B., Worley, M., Sexton, D., and D. Dudgeon. 2011. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol; Dilute-acid Pretreatment and Enzymatic Hydroylsis of Corn Stover. National Renewable Energy Laboratory, Golden, Colorado.

International Organization for Standardization (ISO). 2006a. Environmental management. Life cycle assessment. Principles and framework. ISO 14040:2006. ISO, Geneva.

International Organization for Standardization (ISO). 2006b. Environmental management. Life cycle assessment. Requirements and guidelines. ISO 14044:2006. ISO, Geneva.

Keoleian, G. A. and T. A. Volk. 2005. Renewable energy from willow biomass crops: Life cycle energy, environmental and economic performance. Crit. Rev. Plant Sci. 24(5–6):385–406.

Kounina, A., Margni, M., Bayart, J.B., Boulary, A.M., Berger, M., Bulle, C., Frischknecht, R., Koehler, A., Mila i Canals, L., Motoshita, M., Nunez, M., Peters, G., Pfister, S., Ridoutt, B., van Zelm, R., Verones, F., and S. Humbert. 2013. Review of methods addressing freshwater use in life cycle inventory and impact assessment. International Journal of Life Cycle Assessment 18(3): 707 – 721.

National Council for Air and Stream Improvement, Inc. (NCASI) 2011. Forest Industry Carbon Assessment Tool (FICAT). Version 1.3.1.1. Available from www.ficatmodel.org.

National Renewable Energy Laboratory (NREL). 2011. US life cycle inventory database. http://www.nrel.gov/lci/. Accessed September 5, 2012.

Oak Ridge National Laboratory. 2012. Bioenergy conversion factors. https://bioenergy.ornl.gov/papers/misc/energy_conv.html. Accessed September 5, 2012.

The Royal Society. (2008). *Sustainable biofuels: prospects and challenges.* The Royal Society. ISBN 978 0 85403 662 2. Retrieved from http://royalsociety.org/uploadedFiles/Royal_Society_Content/policy/publications/2008/7980.pdf

Sanchez, T.S., Woods, J., Akhurst, M., Brander, M., O'Hare, M., Dawson, T.P., Edwards, R., Liska, A.J., and R. Malpas. 2012. Accounting for indirect land-use change in the life cycle assessment of biofuel supply chains. Journal of the Royal Society Interface. 9: 1105-1119.

Sassner, P., M. Galbe, and G. Zacchi. 2005. Steam pretreatment of Salix with and without SO2 impregnation for production of bioethanol. Appl. Biochem. Biotechnol. 121–124:1101–1117.

Schmitt, E., Bura, R., Gustafson, R., Cooper, J., Vajzovic, A. 2011. Converting Lignocellulosic Solid Waste into Ethanol for the State of Washington: An investigation of treatment technologies and environmental impacts. *Bioresource Technology*. 10.10106/j.biortech.2011.10.094.

Scientific Applications International Corporation (SAIC). 2006. Life cycle assessment: Principles and Practice. National Risk Management Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency. Cincinnati, Ohio.

Searchinger, T., Heimlich, R., Houghton, R.A., Dong, F., Alobeid, A., Fabiosa, J., Tokgoz, S., Hayes, D., and T.H. Yu. 2008. Use of U.S. Croplands for Biofuels Increases Greenhouse Gases Through Emissions from Land-Use Change. *Science* 319: 1238 – 1240.

Solomon, S.; Qin, D.; Manning, M.; Chen, Z.; Marquis, M.; Averyt, K.B.; Tignor, M.; and Miller, H.L., ed., Climate Change 2007: The Physical Science Basis, Contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge University Press, ISBN 978-0-521-88009-1

Stephenson, A. L., P. Dupree, S. A. Scott, and J. S. Dennis. 2010. The environmental and economic sustainability of potential bioethanol from willow in the UK. Bioresour. Technol. 101(24):9612–9623.

Swiss Centre for Life Cycle Inventories (SCLCI). 2009. EcoInvent database 2.1. SCLCI, Duebendorf, Switzerland.

Verser, D., and T.J. Eggeman. 2011. United States Patent No. 7,964,379 B2. NEED LOCATION

Wiloso, E.I., Heijungs, R., and G. R. de Snoo. 2012. LCA of second generation bioethanol: A review and some issues to be resolved for good LCA practice. Renewable and Sustainable Energy Reviews. 16: 5295-5308.

Wang, M. Q., Han, J., Haq, Z., Tyner, W.E., Wu, M., and A. Elgowainy. 2011. Energy and Greenhouse Gas Emissions Effects of Corn and Cellulosic Ethanol With Technology Improvements and Land Use Changes. *Biomass and Bioenergy* 35(5): 1885-1896.

Zhang, Y. H. P. 2008. Reviving the carbohydrate economy via multi-product lignocellulose biorefineries. *Journal of Industrial Microbiology and Biotechnology* 35: 367-375.

Appendix A

Life-Cycle Assessment for the Production of Bioethanol from Willow Biomass Crops via Biochemical Conversion. Life cycle assessment data.

Table A.1 – Willow growth and harvest data: Nursery Operations per 1000 cuttings.

Input	**Amount**	**Unit**
Potassium fertilizer	1.809	kg
Water	116	kg
Gasoline	1.6585	l
Nitrogen fertilizer	1.809	kg
Phosphorous fertilizer	1.809	kg
Diesel	0.4973	l
Residual fuel oil	4.973	l
Urea	0.5455	kg
Ammonium sulphate	0.5455	kg
Glyphosate	0.008	kg
Insecticide	0.0143	kg
Electricity	19.7179	kwh

Table A.2 – Willow growth and harvest data: Site preparation, plant cuttings, and growth and harvesting stages. All input data is per hectare.

		Input (kg)	Diesel (l)	Lubricant (kg)	Year operation is performed
Site prep	Mow existing vegetation		9.9	0.038	0
	Apply glyphosate herbicide (amount of active ingredient)	2.5	4.1	0.019	0
	Plow field		22.78	0.084	0
	Disk field		16.8	0.065	0
	Cultipack		8.52	0.033	0
	Seed cover crop (rye seed)	27.31	0.41	0.002	0
Plant field	Disk field		16.8	0.065	1
	Culitpack		8.52	0.033	1
	Plant cuttings	15300 cuttings	43.5	0.146	1
Growth and harvesting	Apply glyphosate herbicide	2.5	4.1	0.019	1
	Mechanical weed control		8.269	0.034	1
	Chemical weed control (Atrizine)	0.112	0.189	0.001	1
	Coppice first year growth		18	0.069	1
	Fertilize between harvest (ammonium sulfate)	100	3.507	0.0138	2,5,8,11,14,17,20
	Harvest		52.2	0.2031	4,7,10,13,16,19,22
	Eliminate stools		22.78	0.084	22

Table A.3 – Willow to ethanol ancillary chemical inputs per mega joule of ethanol.

Chemical	**Amount (kg)**
Lime	0.00128
Sulfuric acid	0.00167
Sulfur dioxide	0.00286
Natural gas	0.000394
Diammonium phosphate	0.000276
Phosphoric acid	0.00000520
Urea	0.00000173
Sodium hydroxide	0.0000639
Enzymes (see Table A.1.4)	0.00197

Table A.4 – Enzyme unit process. Based on Wooley et al. 1999a&b and Sheehan et al. 2004.

Input	**Amount (kg)**
Water	2.24
Ammonium sulfate	0.0269
Magnesium sulfate	0.00577
Calcium chloride	0.0077
Sodium phosphate	0.0385
Ammonia	0.141
Sulfite pulp	0.279
Palm oil*	0.032
Corn steep liquor	0.065
Electricity (kwh)	1.12
Output	
Enzymes	1
Emissions to air	
Furfural	0.0144
Acetic acid	0.00493
CO_2	1.55

***** Substituted for corn oil.

Table A.5 – Biorefinery Inputs and Outputs per mega joule of ethanol.

Input	**Amount (kg)**
Water	0.211
Output	
Ethanol (MJ)	1
Electricity (MJ)	0.197
Wastes to landfill	
Gypsum	0.00435
Ash	0.00346
Emissions to air	
Ethanol	1.24E-05
Furfural	1.7E-07
CO_2	0.197
Acetic acid	2.8E-05
Sulfur dioxide	0.000199
Water	0.141
Methane	3.98E-06
Hydroxy compounds	3.16E-06
Lactic acid	2.81E-05
Diammoniaphosphate	0.000259
Nitrogen oxides	0.000136
Sulfur monoxide	0.000298
Carbon monoxide	0.000136

Appendix B

Ethanologens vs. Acetogens: Environmental impacts of two bioethanol fermentation pathways. Life Cycle Assessment data.

Table B.1 – Poplar nursery operation data per 43,200 cuttings. Management scheme, amount of chemicals used, and yields based on GreenWood Resources' operation data. Diesel and Lubricant use based on Caputo et al. (2013)

Year of Nursery operation	Operation	Input (kg)	Diesel (L)	Lubricant (kg)	Energy (kwh)
1	Glyphosate Herbicide by tractor	1.23*	6.7	5.9	
	Glyphosate Herbicide by backpack	1.23*			
	Nitrogen fertilizer	56⁺	2.81	2.5	
	Pest control (imidacloprid)	.238 (L)	6.7	5.9	
	Cold storage (5°C)				204
2	Glyphosate Herbicide by tractor	1.23*	6.7	5.9	
	Glyphosate Herbicide by backpack	1.23*			
	Pest control (imidacloprid)	.238 (L)	6.7	5.9	
	Cold storage (5°C)				204

* Applied as roundup (41% glyphosate). Weight is in terms of glyphosate.

⁺ Applied as urea ammonium nitrate. Weight is in terms of nitrogen.

Table B.2 - Poplar growth and harvest data: Site preparation, plant cuttings, and growth and harvesting stages. All input data is per hectare. Management scheme, amount of chemicals used, and yields based on GreenWood Resources' operation data. Diesel and Lubricant use based on Caputo et al. (2013).

Stage of Process and Year	Operation	Input (kg)	Diesel (L)	Lubricant (kg)
Site Preparation				
Year 0	Heavy Disking		22.78	20
	Fininsh Disking and Smoothing		18.76	17
	Row Marking		9.51	8.4
	Glyphosate herbicide	1.23*	6.7	5.9
Plant Cuttings				
Year 0	Tractor to carry cuttings		6.7	5.9
	Plant cuttings (See Table B.1)	3580 cuttings		
Growth and Harvest Operations				
Year 1	Glyphosate Herbicide by tractor	1.23*	6.7	5.9
	Glyphosate Herbicide by backpack	1.23*		
	Nitrogen fertilizer	56^{+}	2.81	2.5
	Pest control (imidacloprid)	.238 (L)	6.7	5.9
	Cultivation		9.51	8.4
Year 2	Glyphosate Herbicide by tractor	1.23*	6.7	5.9
	Glyphosate Herbicide by backpack	1.23*		
	Pest control (imidacloprid)	.238 (L)	6.7	5.9
	Cultivation		9.51	8.4
	Forage harvester		121.6	107
	Tractor with forage wagon (x2)		13	11
	Tractor with silage blower		6.5	5.7
Harvest operations (repeat for 6 cycles)				
First year	Glyphosate Herbicide by tractor	1.23*	6.7	5.9
	Glyphosate Herbicide by backpack	1.23*		
	Nitrogen fertilizer	56^{+}	2.81	2.5
	Pest control (imidacloprid)	.238 (L)	6.7	5.9
	Cultivation		9.51	8.4
Second year	Glyphosate Herbicide by tractor	1.23*	6.7	5.9

	Glyphosate Herbicide by backpack	1.23*		
	Pest control (imidacloprid)	.238 (L)	6.7	5.9
	Cultivation		9.51	8.4
Third year	Pest control (imidacloprid)	.238 (L)	6.7	5.9
	Forage harvester		121.6	107
	Tractor with forage wagon (x2)		13	11
	Tractor with silage blower		6.5	5.7
Remove stumps				
Year 21	Heavy glyphosate application	1.9*	6.7	5.9
	Mulch		29.48	26

***** Applied as roundup (41% glyphosate). Weight is in terms of glyphosate.

⁺ Applied as urea ammonium nitrate. Weight is in terms of nitrogen.

Table B.3 – Ethanologen pathway ancillary chemicals input data per mega joule of ethanol.

Input	**Amount (kg)**
Cellic Ctec System (Enzymes)*	0.000568
Sulfuric acid	0.004964
Lime	0.00374
Limestone	0.000666
Ammonia	0.001153
Clarifier polymer	8.02E-05
Corn steep liquor	0.00374
Sodium hydroxide	0.002132

*LCI data provided from Novozymes.

Table B.4 – Ethanologen pathway biorefinery input and output data per mega joule of ethanol.

Input	**Amount (kg)**
Water	0.270
Output	
Ethanol (MJ)	1
Electricity (kwh)	0.0214
Waste to landfill	
Gypsum	0.00874
Ash	0.00266
Emissions to air	
CO_2	0.193
CO	2.14E-05
Nitrogen oxides	2.14E-05
SO_2	6.43E-05

Table B.5 – Ethanologen pathway transportation data per mega joule of ethanol.

Transportation type	**Tonnes*kilometer**
Train	0.00510
Ship	0.00213
Truck	0.0219

Table B.6 – Acetogen pathway ancillary chemicals input data per mega joule of ethanol.

Ancillary Chemicals	**kg**
Cellic Ctec System (Enzymes)*	0.00032
Sulfuric acid	0.00279
Lime	0.00211
Limestone	0.000377
Ammonia	0.000649
Clarifier polymer	4.52E-05
Corn steep liquor	0.00210
Sodium hydroxide	0.00120
CO_2	0.000166
Tributylamine	5.81E-06
Nickel (catalyst)	6.8E-07

*LCI data provided from Novozymes.

Table B.7 – Acetogen pathway biorefinery input and output data per mega joule of ethanol.

Input	**Amount (kg)**
Water	0.15368
Output	
Ethanol (MJ)	1
Electricity (kwh)	0.010608
Waste to landfill	
Gypsum	0.00493
Ash	0.001499
Emissions to air	
CO_2	0.080699
CO	5.95E-06
Nitrogen oxides	5.95E-06
SO_2	1.99E-05

Table B.8 – Acetogen pathway transportation data per mega joule of ethanol.

Transportation type	**Tonnes*kilometer**
Train	0.00296
Ship	0.00121
Truck	0.0137