Impacts of Feedstock Composition on Alcohol Yields and Greenhouse Gas Emissions from the NREL Thermochemical Ethanol Conversion Process

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There has been great attention focused on the effects of first and second generation biofuels on global warming. The Energy Independence and Security Act (EISA) and the Renewable Fuel Standard (RFS) have mandated production levels and performance criteria of biofuels in the United States. The thermochemical conversion of biomass to ethanol shows potential as a biofuel production pathway. The objective of this research was to examine the alcohol yields and GHG emissions from the thermochemical conversion process for six different feedstocks on a gate-to-gate basis. GHG analyses and life cycle assessments were performed for natural hardwood, loblolly pine, eucalyptus, miscanthus, corn stover, and switchgrass feedstocks using a NREL thermochemical model and SimaPro. Alcohol yield and GHG emission for the hybrid poplar baseline feedstock conversion were 105,400 L dry metric ton^{-1} and 2.8 kg CO_2 eq. per liter, respectively. Compared with the baseline, loblolly pine produced the highest alcohol yields, an 8.5% increase, and the lowest GHG emissions per liter of ethanol, a 9.1% decrease. Corn stover, due to its high ash content, had the lowest yields and the highest GHG emissions per liter of ethanol. The results were highly sensitive to the ash and water content of the biomass, indicating that biomass properties can significantly affect the environmental impact of the thermochemical ethanol conversion process.

Keywords: Biofuel; Thermochemical; Gasification; Ethanol; LCA; GHG; Cellulose

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INTRODUCTION

"The evidence of human-induced climate change goes beyond observed increases in average surface temperatures; it includes melting ice in the Arctic, melting glaciers around the world, increasing ocean temperatures, rising sea levels, acidification of the oceans due to excess carbon dioxide, changing precipitation patterns, and changing patterns of ecosystems and wildlife" (Jackson 2009). This quote from Lisa Jackson's (then EPA Administrator) announcement of Greenhouse Gases Threaten Public Health and the Environment outlines the potential impacts of global warming. These as well as unanticipated impacts are the motivating force behind greenhouse gas (GHG) monitoring/ regulations and renewable fuels initiatives. Responding to the current and potential impacts of global warming, the EPA has determined that GHG emissions are harmful to human health and will be regulated under the Clean Air Act (CAA).

The U.S. is the world's largest producer of bioethanol at 49.2 billion liters per year as of 2010 (RFA 2011). However, controversy around 1st-generation biofuels based on the conversion of corn grain (USA) and sugar cane (Brazil) (Daschle *et al.* 2007; Mitchell *et al.* 2008; Gonzalez *et al.* 2011a) have prompted research and investment in 2nd-generation biofuels produced from non-food–based lignocellulosic feedstocks. Lignocellulosic biomass has also been identified as a key player in non-liquid fuel forms of energy. Additionally, studies suggest that the use of lignocellulosic feedstocks (as agriculture residues and forest feedstocks) have clear benefits in the mitigation of GHG emissions (Schneider and McCarl 2003; Hill 2009; Zhang *et al.* 2010).

The Energy Independence and Security Act of 2007 (EISA 2007) outlined a set of goals to increase energy security and reduce GHG emissions. As biofuels are seen as a key component of energy security and GHG reduction (Sims *et al.* 2010), the Renewable Fuels Standard (RFS) requires production of approximately 136 billion liters of blended renewable transportation fuels by 2022. However, there is much controversy over the GHG reductions due to 1st-generation biofuels production and use (Davis *et al.* 2009); EISA also required the EPA to apply life cycle GHG threshold standards to ensure net reductions through the production and use of renewable fuels. By following these threshold requirements, 60% GHG reduction for cellulosic ethanol and 20% for other biofuels, the use of biofuels will decrease anthropogenic GHG emissions and create a more sustainable path forward.

Previous Biofuels GHG Analysis

For the CAA and EISA requirements to be successful, research must be carried out to develop tools and knowledge to assist industry in reducing GHG emissions while maintaining economic feasibility. Wang and Argonne National Laboratory developed the Greenhouse Gases, Regulated Emissions, and Energy use in Transportation Model (GREET) to analyze the GHG emissions from biofuels using various production pathways and blending options (Wang 2001). This tool has been the backbone for a large part of the research contributing to the knowledge base and publications related to biofuel GHG emissions.

In addition, there have been many studies of the GHG balance of various ethanol conversion processes and feedstocks. The two commonly studied 2nd-generation biofuels processes are alcohol production through i) gasification (Phillips *et al.* 2007) and ii) biochemical pathways (Wooley *et al.* 1999; Aden *et al.* 2002). Both of these approaches, despite lacking commercial production facilities, are considered to emit fewer GHGs than 1st-generation biofuel pathways (Searchinger *et al.* 2008; Cherubini *et al.* 2009; Davis *et al.* 2009; Cherubini and Jungmeier 2010). Due to the potential GHG reduction through the production and use of 2nd-generation biofuels, EISA has required that approximately 79 billion liters of biofuels be produced solely from non-starch feedstocks (EISA 2007). The increase of non-commercial 2nd-generation biofuel production to 79 billion liters by 2022 may have unknown environmental impacts. GHG analysis and life cycle assessment studies can predict the potential environmental impacts of biofuel production and inform process and feedstock decisions that can minimize environmental impacts.

Davis *et al.* (2009) performed a comprehensive biofuel GHG emissions literature review examining 1st- and 2nd-generation biofuels. GHG emissions from many feedstocks, primarily using a biochemical conversion pathway, were tabulated and ranked from the greatest GHG reductions to the least GHG reductions (see Table 1). Cornstarch–

based biofuel was reported from one study to have an 86% GHG savings and from another study to have a 93% GHG burden increase as compared to gasoline.

These vastly varying results illustrate the inconsistency between studies and the mishandling of the following factors (Cherubini *et al.* 2009):

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

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

Table 1. GHG Emissions from Various Feedstocks (biochemical conversion except as noted) Relative to Gasoline

Feedstock	Relative GHG Emissions %	Source
Switchgrass	−114	Adler *et al*. 2007
Switchgrass (combustion compared with coal combustion)	−109	Ney and Schnoor 2002
Miscanthus (gasification)	−98	Lettens *et al*. 2003
Switchgrass	−93	Schmer *et al.* 2008
Corn	−86	Wang 2005
Reed canary grass	−84	Adler *et al.* 2007
Cellulosic	−80	DiPardo 2004
Switchgrass	−73	Wu *et al*. 2006
Corn–soy	−38	Adler *et al.* 2007
Corn	−25	DiPardo 2004
Corn	−24	Wu *et al.* 2006
Switchgrass	−11	Lemus and Lal 2005
Corn	−3	Niven 2005
Switchgrass	43	Delucchi 2006
Switchgrass	50	Searchinger *et al*. 2008
Corn	66	Delucchi 2006
Corn	93	Searchinger *et al.* 2008

Process Technology Overview

Bioethanol production technologies can be broken down into two major categories: biochemical and thermochemical. The biochemical conversion pathway is defined by the use of microorganisms to convert cellulosic monomeric sugars into ethanol. The thermochemical pathway uses high temperatures and catalyzed reactions to convert feedstocks into fuels.

To provide a basis of comparison for future process technologies, the National Renewable Energy Laboratory (NREL) performed technical and economic evaluations for both of these process technologies. The biochemical technology NREL proposed employs dilute acid pretreatment followed by enzymatic hydrolysis and fermentation, as reported in Aden *et al.* (2002). For the thermochemical technology, production using indirect gasification and catalyzed mixed alcohol was examined in Phillips *et al.* (2007) and was the basis for the present study. For both processes, the advantages, disadvantages, and major barriers have been identified around biomass cost and availability (Adebayo *et al.* 2009; Wu *et al.* 2010; Gonzalez *et al.* 2011a, 2011b, 2011c), pretreatment costs, capital expenditure (CAPEX), equipment scale up, and overall production costs (Aden *et al.* 2002; Mosier *et al.* 2003; Mosier *et al.* 2005; Wyman 2007; Wyman 2008; Tao and Aden 2009; Wu *et al.* 2010). As the most heavily supported production route, biochemical conversion relies mainly on hydrolysis (acid and/or enzymatic hydrolysis) to reduce polymeric carbohydrate chains into fermentable monomeric sugars.

The other and less understood approach is thermochemical conversion, with numerous versions and hybrid designs. The major concept behind thermo-chemical processes is the production of synthesis gas (syngas) from cellulosic biomass; the gasses are then reformed and passed through catalytic reactors to produce alcohol species (Mosier *et al.* 2005; Phillips *et al.* 2007; Mu *et al.* 2010).

Economic and life cycle analysis studies comparing biochemical and thermochemical pathways do not clearly identify a superior conversion technology (Foust *et al.* 2009; Mu *et al.* 2010; Sims *et al.* 2010). There is a general and logical agreement that marketplace economics, based on available biomass type and delivered costs, would be used to decide which conversion approach to use (Blaschek and Boateng 2009; Mu *et al.* 2010).

Biochemical technologies seem to be more feasible in regions where large volumes of consistent biomass are available, while thermochemical pathways are less sensitive to feedstock variables (Schuetzle *et al.* 2007; Foust *et al.* 2009; Mu *et al.* 2010). Moreover, some studies suggest that hardwood and herbaceous feedstock are more suitable for biochemical pathways, whereas more recalcitrant raw materials such as softwood feedstock are better suited for the thermochemical processes (Foust *et al.* 2009; Gonzalez *et al.* 2011a, 2011b). Conversion pathways capable of processing multiple biomass types, such as the thermochemical process, present a strategic advantage to the economy of the biorefinery as it can use feedstocks with the lowest delivered cost throughout the year.

The objective of this research is to determine if the predicted alcohol yields and GHG emissions from the NREL thermochemical ethanol production model are affected by incoming feedstock characteristics. Unlike many other studies, this research focuses on process conversion and performs simulations for multiple feedstocks. Detailed process modeling results were used as input to an LCA software package (SimaPro 7). The environmental results of the gate-to-gate analysis were determined to be significantly impacted by feedstock characteristics.

EXPERIMENTAL

Gasification Process Modeling

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

Major Unit Process Description

The thermochemical process was divided into seven major process areas (Fig. 1). Each area comprised multiple unit operations such as reactors, separations, heat exchangers, and other matter-altering operations. The following describes the major processes areas.

Feedstock handling and drying (Area 100): The incoming feedstock was dried and screened to remove unusable biomass and contaminants. Flue gas from the char combustor and syngas boiler was the primary source of heat for drying. Biomass moisture content was reduced to approximately 5%.

Gasification (Area 200): Incoming biomass was further heated by olivine, a sand-like substance, circulated from the char combustor. Endothermic reactions released syngas, primarily CO and H_2, in the gasifier. For this model, the syngas composition was dictated by biomass composition and correlations within the Aspen process model.

Gas cleanup and conditioning (Area 300): Tars and other hydrocarbons were reformed into CO and H_2, syngas was cooled/quenched, and acid gas was removed and reduced to sulfur. These actions can be achieved through the use of fluidized bed reactors with online catalysis regenerators, heat exchangers and scrubbers, and an “amine” unit, respectfully. This step was critical in preventing catalysis fouling in the alcohol synthesis step.

Alcohol synthesis (Area 400): Purified syngas was converted to alcohols using a molybdenum-disulfide catalyst in a fixed-bed reactor. The unconverted syngas may be recycled back to the alcohol synthesis, or sent to the char combustor to avoid excess CO_2 accumulation and subsequent catalyst fouling.

Alcohol separation (Area 500): The alcohol stream was depressurized in preparation for the dehydration using a molecular sieve. Once water was removed from the alcohol stream, a distillation column was used to separate ethanol from other alcohols. The higher alcohols were sold as a co-product, while most of the methanol was recycled back to the molecular sieve to flush the adsorbed water.

Power and steam (Area 600): Process steam and electrical power were generated and supplied to other unit processes by burning dirty syngas and capturing process heat. The power boiler was controlled to maintain energy self-sufficiency, supplying the exact amount of process energy and steam to operate without buying or selling any energy or heat.

Utilities (Area 700): Low-quality steam from power production and other unit processes was condensed using cooling towers fed by well water. The condensate was recycled back to the process for further use.

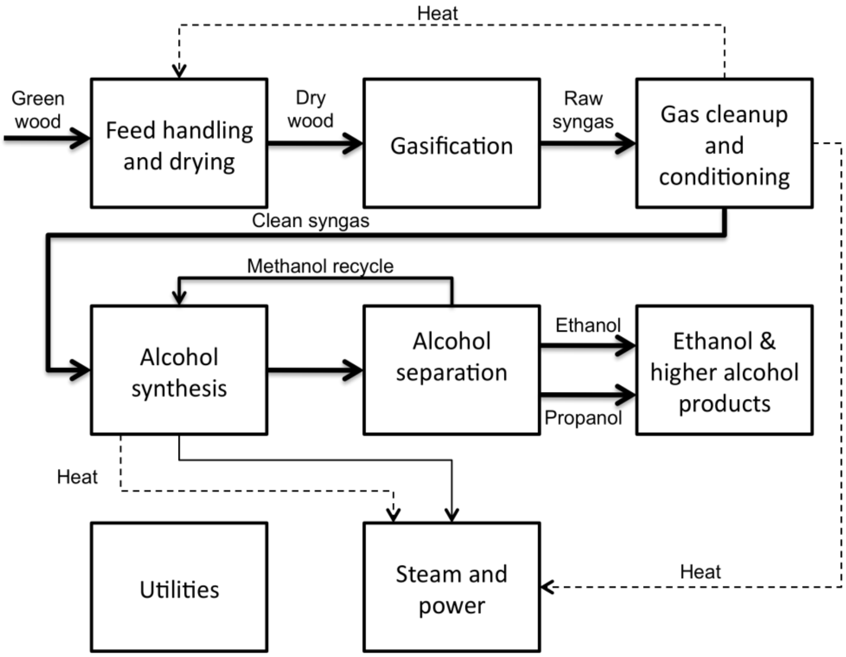

Fig. 1. Major unit processes for the NREL thermochemical alcohol conversion process (Phillips *et al.* 2007)

This process description presents the basic unit processes of the thermochemical conversion pathway. A detailed process description was included in the Phillips *et al.* (2007) technical feasibility study, and detailed assumptions and process variable values are available in Daystar (2011).

Model version and supporting files

The Aspen Plus simulation model was downloaded from the NREL Biorefinery Analysis Process Models website. To run the simulation, five files were downloaded from NREL: Aspen file sp0612M.bkp, two Fortran files contained in "fortran Mixed Alcohols.zip," Aspen tool kit files in "AspenToolKit.zip", and a simulation analysis file SP0612.xls. The Aspen, Fortran, and toolkit files are required to run the simulation whereas the Excel analysis file was used to assist in the analysis of the results. To use the simulation and analysis spreadsheet, several additional pieces of software were required and downloaded from other sources. As the Aspen model used correlations calculated in Fortran, a compiler was needed to operate the model. Newer Fortran compilers were run with the model but were unsuccessful. As a result of this, the original version FORTRAN 2004.1 was used. Obtaining this Fortran compiler was difficult as it is no longer produced or supported by the company. However, it can be bought from some select software vendors. Without every component of the software, the model would not run or compute results. Therefore, anyone attempting to use this program must pay particular attention to attaining the correct software and program versions.

Simulation modification

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

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

Operation parameters

To demonstrate model characteristics, multiple input parameters were manipulated. The original feed rate of 700,000 metric tonnes per year of dry biomass was maintained during investigations of the biomass type and moisture content (Table 2). In total, six feedstocks types were examined in addition to the original hybrid poplar feedstock. These feedstocks were selected based on an extensive literature review to identify potential feedstock for energy conversion in the Southern U.S. (Lettens *et al.* 2003; Gonzalez *et al.* 2008, 2011a,b). However, the moisture content of the originally modeled feedstock baseline, hybrid poplar, was changed to 45% to match the other forest-based feedstocks. The moisture content of the energy crops and agricultural residue were set at 16%. Both the ultimate and proximate analyses for each biomass type are included in Table 2. A sensitivity analysis around moisture and ash content was performed and described in further detail in the "Sensitivity Analysis" section.

Table 2: Biomass Composition of Studied Lignocellulosic Materials*

	Ultimate Analysis						Proximate Analysis			
Feedstock Type	**% C**	**% H**	**% N**	**% O**	**% S**	**% Ash**	**% Fixed Carbon**	**% Volatile Matter**	**% Ash**	**% Moisture Content**
Hybrid poplar (NREL) (5)	50.88	6.04	0.17	41.9	0.09	0.92	15.29	83.84	0.87	45*
Eucalyptus (1)	49.74	5.95	0.20	42.59	0.02	0.98	18.19	81.06	0.98	45
Mixed hardwoods (2)	50.43	6.54	0	42.48	0	0.60	18.94	80.39	0.67	45
Loblolly (3)	51.85	6.45	0	41.3	0	0.40	14.21	85.34	0.4	45
Corn stover (1)	46.6	5.70	0.70	39.4	0.1	11.9	21.1	72.5	11.9	16
Switchgrass (1)	47.26	5.60	0.58	40.63	0.08	5.84	20.57	74.25	5.84	16
Miscanthus (4)	48.00	6.00	0.10	45.9	0	1.40	15.7	74.9	1.4	16

Sources: 1 (U.S. DOE 2005), 2 (U.S. DOE 2005; Adebayo *et al.* 2009), 3 (Yan *et al.* 2009), 4 (Heo *et al.* 2010), 5 (Phillips *et al.* 2007).
* The moisture content of the hybrid poplar in Phillips *et al.* (2007) of 50% was changed to 45% to match the other forest-based biomaterials.

LCA Methodology

Goal and scope

The goal of this study was to determine the impact of various feedstocks and feedstock composition on the alcohol yield and gate-to-gate (Fig. 2) GHG emissions from the thermochemical ethanol pathway. The defined functional unit was one liter of ethanol produced and was used to compare the environmental impacts for each scenario in a fair and consistent manner.

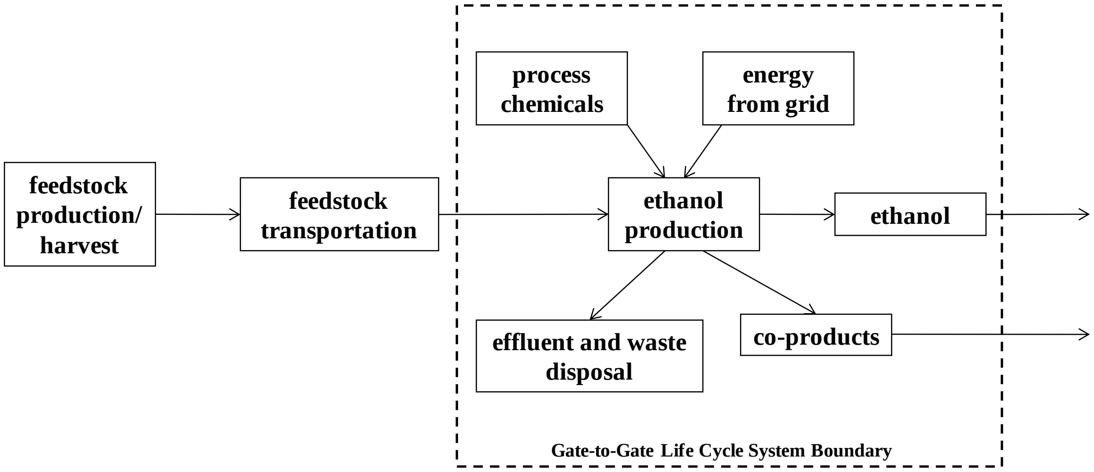

Fig. 2. Gate-to-gate life cycle assessment system boundary

Data sources

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

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

To calculate the emissions from the magnesium oxide (MgO), as required to prevent glass buildup within the gasifier, a literature review was required. A report from the European Commission (IPPC 2009) described the MgO production process providing production emissions and energy usages. Data from the IPCC 2006 report (IPCC 2006) and the USLCI database (NREL 2010) were used to convert fuel requirements to GHG emissions for petroleum coke, fuel oil, and natural gas. In addition to these fuels, the process required electricity, which was converted to GHG emissions using USLCI database (NREL 2010) emission factors for North America.

Parameters examined

Due to the mandated GHG reduction thresholds for cellulosic ethanol, GHGs were the primary focus of this study. These gases include carbon dioxide, methane, and nitrous oxide. However, as nitrous oxide and methane are stronger GHGs, 100-year global warming potentials (GWP) from the IPCC were used to calculate CO_2 equivalents. These GWP have been updated several times since 1996 (Table 3). Data from the most recent report in 2006 were used for this analysis.

Table 3. 100-year Global Warming Potential of Methane and Nitrous Oxide (Yan *et al.* 2009)

CO_2 equivalents (revision year)	CH_4	N_2O
1996	21	310
2001	23	296
2006	25	298

RESULTS AND DISCUSSION

Life Cycle Inventory

As the primary focus of this study was to examine the variation in GHGs from the alcohol conversion process, the life cycle inventory was done on a gate-to-gate basis. However, upstream emissions from process chemicals were included while emissions from feedstock procurement and production were not. Emissions from the process chemicals were calculated using data from several sources and reported in kg of CO_2 equivalents per kg of chemical usage (Table 4). As the process chemicals contributed minimally to the overall emissions (Table 5), some simplifying assumptions were taken when calculating the emissions factors. These process chemicals contributed less than 0.2% of total GHG emissions and represent the only anthropogenic source of GHG emissions on a gate-to-gate basis. Additionally, emissions due to clear water chemical use were not included, as they influenced the overall GHG emissions less than 0.1% and varied minimally between feedstocks.

Table 4. GHG Emission Factors for Process Chemicals and Non-Wood Inputs

Material/Process	Units (kg CO_2 eq.)	Emissions Factor	Source
Magnesium oxide	per kg material	9.21E-04	1
Olivine	per kg material	9.58E-06	2
Molybdenum	per kg material	2.64E-03	2
Waste treatment	per kg material	1.56E-10	2
Landfill transportation	per tonne * km	6.96E-05	2
Landfill	per kg material	5.99E-07	2

Sources: 1 (WRI/WBCSD 2004; IPPC 2009), 2 (NREL 2010)

Table 5. Contribution to GHG Emissions from Process Chemicals and Wastes

Feedstock	Hybrid Poplar	Mixed Hardwood	Loblolly Pine	Eucalyptus	Corn Stover	Switchgrass	Miscanthus
kg CO_2 eq. per hour	27.0	22.7	20.9	27.8	167.6	89.1	32.9
% of total process GHGs	0.03%	0.02%	0.02%	0.03%	0.17%	0.09%	0.03%

Gasification process

Material balance: The Aspen process simulation generated results for each feedstock scenario. However, to ensure proper operation, a material balance was manually performed and compared with results from Phillips *et al.* (2007). Major inputs, outputs, and system closure are reported in Table 6 for the base case scenario of hybrid poplar. These data are organized by actual streams that exit the system and are organized from least to greatest. The overall system closure, calculated by [(material out – material in)/(material in)] × 100, was 98.5%. This level of closure is generally acceptable, especially with process models of this size and detail. Additionally, these results are comparable with the results reported in Philips *et al.* (2007).

Table 6. Hybrid Poplar Feedstock Material Balance and Major Input and Output Stream Flows

Input Stream	kg/hr	Output Stream	kg/hr
Clear water chemicals	3.70E-01	Catalyst purge	4.84E-01
Make up catalyst	4.84E-01	Vent to atmosphere	8.63E-01
Magnesium oxide	3.16E+00	Solid waste	3.60E+01
Char combustor water	1.10E+02	Sulfur storage	5.11E+01
Lo-cat oxidizer air	1.24E+02	Air to atmosphere	1.27E+02
Make up olivine	2.44E+02	Water to treatment plant	5.49E+02
Steam make up water	1.48E+04	Sand fly ash	1.10E+03
Cooling make up water	3.90E+04	Windage to atmosphere	3.70E+03
Combustion air	1.19E+05	Higher alcohols	4.15E+03
Feedstock	1.52E+05	Blow turbine blow down	7.71E+03
Combustion air	1.95E+05	Ethanol product	2.30E+04
Condenser water	1.85E+06	CO_2 vent	2.48E+04
		Flue gas stack	4.24E+05
		Evaporated to atmosphere	1.92E+06
Total in	2.37E+06	Total out	2.41E+06
% System closure	98.5%		

After determining the closure of the model, six additional feedstock compositions were used as input for additional simulations. The results from the various feedstocks were compared with the results from the hybrid poplar “base case.” These results are reported in percent change calculated by:

$$\%\,\Delta\, GHG\ emissions = \frac{(scenario\ A\ process\ emissions - baseline\ process\ emissions)}{baseline\ process\ emissions} * 100\%$$

Alcohol yield: When comparing ethanol yields from various feedstocks, three numbers are of particular importance: liters of ethanol, liters of propanol, and total liters of ethanol equivalents. The propanol was converted to ethanol equivalents by energy content ratio. This ratio, energy content of ethanol divided by energy content of propanol, was approximately 0.68 (AIChE 2010). When compared with hybrid poplar, loblolly pine produced the highest yields while corn stover produced the lowest (Table 7). Overall, the forest-based feedstocks produced higher yields than the other energy crops or residues.

The corn stover yield was the lowest, with a 10.6% decrease relative to hybrid poplar, followed by switchgrass and miscanthus.

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

Table 7. Alcohol Yield for Cellulosic Feedstocks Expressed in Percent Change from Hybrid Poplar

Feedstock	Hybrid Poplar	Mixed Hardwood	Loblolly Pine	Eucalyptus	Corn Stover	Switchgrass	Miscanthus
Units	(L/OD tonne)	Δ %	Δ %	Δ %	Δ %	Δ %	Δ %
Ethanol	350	1.8	5.6	−3.5	−13.0	−5.3	−5.5
Propanol	62	1.8	5.6	−3.5	−12.8	−5.1	−5.3
Total ethanol equivalents	441	1.8	5.6	−3.5	−13.0	−5.3	−5.4

Greenhouse gas emissions: Emissions from the ethanol conversion pathway include many air pollutants, liquid pollutants, and solid waste. However, the purpose of this paper was to focus primarily on GHG emissions' variation due to feedstock compositions.

There are 14 streams exiting the conversion process; however, only two significantly contribute to GHG emissions. The flue gas stream released approximately 77% of the GHGs, and the CO_2 vent released 23%. The total GHG emissions from the process using hybrid poplar were approximately 1.03×10^5 kg CO_2 per hour, or 2.8 kg CO_2-equivalents per liter of ethanol equivalent produced (Table 8). Compared with hybrid poplar, the loblolly pine produced the lowest GHG emission, with a −5.4% change.

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

Table 8. GHG Emissions for Various Feedstocks Expressed in Percent Change from Hybrid Poplar Feedstock

GHG Emissions	Hybrid Poplar	Mixed Hardwood	Loblolly Pine	Eucalyptus	Corn Stover	Switchgrass	Miscanthus
kg CO_2 eq.		Δ %	Δ %	Δ %	Δ %	Δ %	Δ %
Per OD tonne feedstock	1235	–2.3	–0.1	–0.8	–12.5	–7.9	–7.8
Per L ethanol	2.8	–4.1	–5.4	2.8	–0.3	–2.8	–2.5

Since the gasification process is powered entirely by biomass, there are no direct fossil fuel emissions from the process. However, raw materials used in the process have fossil fuel–based emissions associated with them and are a source of fossil fuel–based emissions within this study. It should be noted that feedstock production would be the major source of fossil fuel emissions if it were within the scope of the study. Despite this, the fossil fuel–based emissions were magnitudes smaller than the biogenic CO_2 GHG emissions (emissions created through the burning of plant material).

Table 9. Biogenic and Fossil Fuel–Based GHG Emissions

Feedstock	Hybrid Poplar	Mixed Hardwood	Loblolly Pine	Eucalyptus	Corn Stover	Switchgrass	Miscanthus
Fossil kg CO_2 eq. per L	7.3E-04	6.1E-04	5.4E-04	7.3E-04	6.0E-03	2.9E-03	7.3E-04
Biogenic kg CO_2 eq. per L	2.80	2.68	2.65	2.88	2.81	2.72	2.73
Percent fossil-based CO_2	0.03%	0.02%	0.02%	0.03%	0.21%	0.11%	0.03%

Sensitivity Analysis

As moisture and ash content are the major influencers of process efficiencies and GHG emissions (Van Der Drift *et al.* 2001; Phillips *et al.* 2007), further analysis was performed to describe the impact of these two variables on the total alcohol yield and GHG emissions. Loblolly pine, the most promising feedstock based on alcohol yield and GHG emissions, was chosen for the sensitivity analysis.

The moisture content manipulation required only an input change within the Aspen simulation. Moisture contents (mass of water in biomass divided by the dry mass of biomass) examined included 35%, 45%, and 55%. This range covers most moisture contents possible for loblolly pine. To examine the effects of moisture content, alcohol yield and kilograms CO_2 per liter were plotted against moisture content (Fig. 3). The alcohol yield was negatively correlated with moisture content, varying by approximately 15%. A positive correlation was observed between the moisture content and the GHG emissions.

Biomass ash content significantly influenced both the yield and GHG emissions for all six biomass types. Due to the importance of this parameter, a sensitivity analysis was performed for loblolly pine varying the ash content from 0.45% to 15%. The ash content was increased and oxygen, carbon, and hydrogen were decreased proportionally to maintain a balance of 100%. Keeping the oxygen, carbon, and hydrogen ratios constant was critical to isolate and understand the effects of higher ash content.

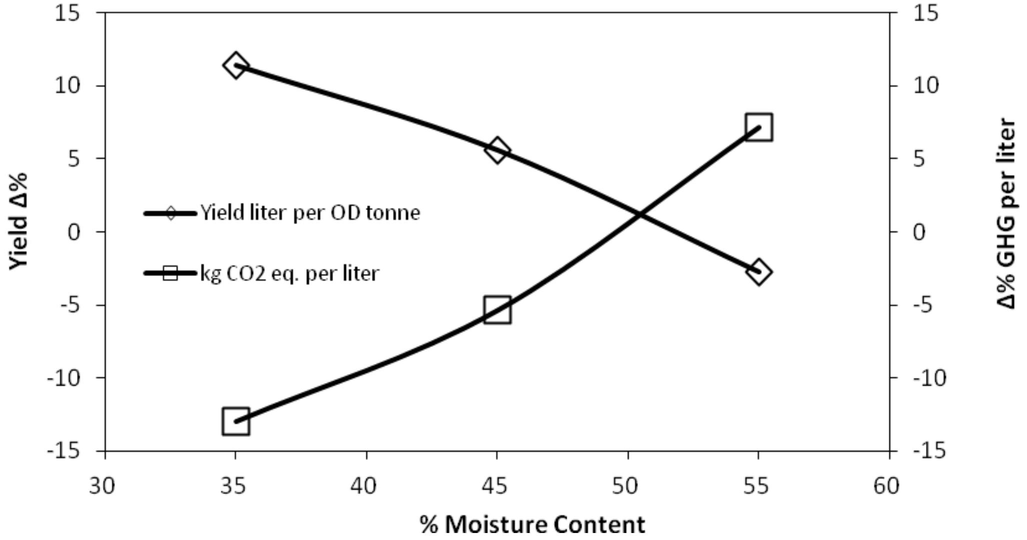

Fig. 3. Effects of pine feedstock moisture content on GHG emissions and alcohol yield relative to the hybrid poplar base case (lines for visual appearance only)

The volatile and fixed carbon were also adjusted proportionally to compensate for the increased ash and to maintain the 100% balance. However, pine ash content is not expected to vary drastically from species to species and the range of ash contents examined is not expected in real pine species. Despite this, the results in Table 10 showed the significance of ash independent of other variables. All compositions used for this sensitivity analysis are listed in Table 10. Additionally, the moisture content was held constant at 45%.

Table 10. Biomass Composition Used for Ash Sensitivity Analysis

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

Alcohol yield and GHG emissions for feedstocks listed in Table 10 were plotted as a function of ash content (Fig. 4). As the ash content increased, the yield decreased from approximately 5% to negative 16% as compared with the hybrid polar baseline results. The GHG emissions per liter experienced an increase from approximately negative 6% to 14% as compared with the hybrid polar baseline results.

The primary driver of these trends was lower usable carbon content to convert to syngas. With less syngas produced, the alcohol production decreased. This sensitivity analysis further supports the previous conclusion of the negative correlation between ash content and alcohol yields and the positive correlation between ash content and GHG emissions.

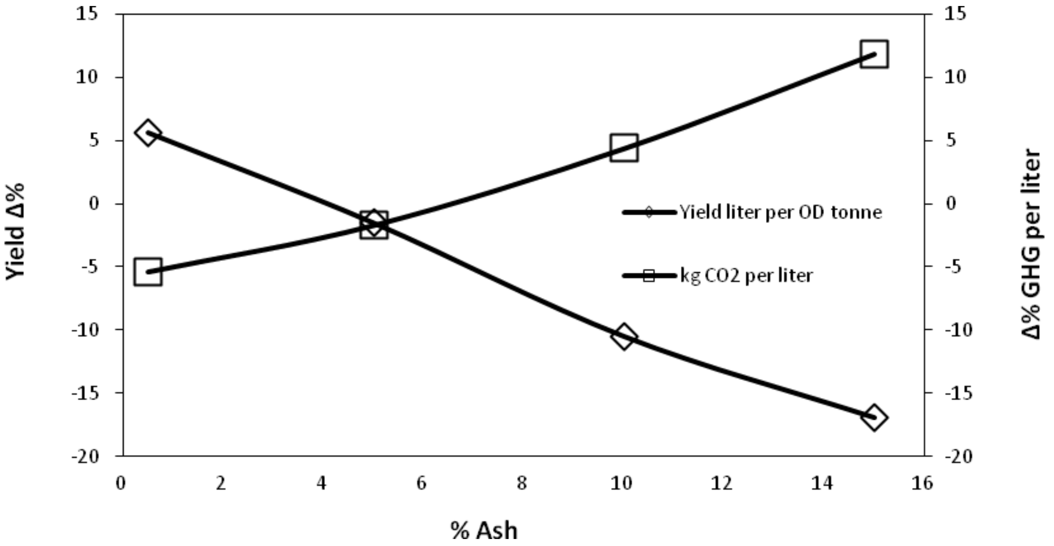

Fig. 4. Effects of pine ash content on alcohol yields and GHG emissions relative to the hybrid poplar base case (lines for visual appearance only)

CONCLUSIONS

1. Biomass with low ash and moisture content resulted in higher alcohol yields and lower GHG emissions from the thermochemical conversion process.
2. Moisture content of loblolly pine (35% to 55%) can influence the alcohol yield by approximately 15% and GHG emissions per liter by about 20%.
3. Alcohol yields for non-wood biomass types were significantly lower than for woody biomass types, possibly reducing the financial feasibility of these feedstocks.
4. Increased drying times in the field or in storage could lower biomass moisture content and improve system performance.
5. To gain a full understanding of the overall life cycle emissions of these feedstocks, a detailed feedstock model is necessary.

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