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Life cycle assessment of the production of hydrogen and transportation fuels from corn stover via fast pyrolysis

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Abstract

This life cycle assessment evaluates and quantifies the environmental impacts of the production of hydrogen and transportation fuels from the fast pyrolysis and upgrading of corn stover. Input data for this analysis come from Aspen Plus modeling, a GREET (Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation) model database and a US Life Cycle Inventory Database. SimaPro 7.3 software is employed to estimate the environmental impacts. The results indicate that the net fossil energy input is 0.25 MJ and 0.23 MJ per km traveled for a light-duty vehicle fueled by gasoline and diesel fuel, respectively. Bio-oil production requires the largest fossil energy input. The net global warming potential (GWP) is 0.037 kg CO₂eq and 0.015 kg CO₂eq per km traveled for a vehicle fueled by gasoline and diesel fuel, respectively. Vehicle operations contribute up to 33% of the total positive GWP, which is the largest greenhouse gas footprint of all the unit processes. The net GWPs in this study are 88% and 94% lower than for petroleum-based gasoline and diesel fuel (2005 baseline), respectively. Biomass transportation has the largest impact on ozone depletion among all of the unit processes. Sensitivity analysis shows that fuel economy, transportation fuel yield, bio-oil yield, and electricity consumption are the key factors that influence greenhouse gas emissions.

Keywords: life cycle assessment, fast pyrolysis, bio-oil upgrading, greenhouse gas emission, energy demand

1. Introduction

Growing concerns over greenhouse gas (GHG) emissions from petroleum-based fuel consumption have prompted interest in the production of alternative transportation fuels from biorenewable sources. As required by the Energy Independence and Security Act of 2005, the US Environ-

mental Protection Agency (EPA) finalized the Renewable Fuel Standard (RFS) and mandated petroleum refineries and oil importers to increase the volume of renewable fuel that is blended into petroleum-based transportation fuels. Life cycle assessment (LCA), a standard evaluation method of environmental impact, is increasingly being used to evaluate biofuel production systems. In previous life cycle assessments, evaluations have emphasized the environmental impacts of ethanol-based transportation fuels (Bai *et al* 2010, González-García *et al* 2010, Hsu *et al* 2010, Kauffman *et al* 2011, Kemppainen and Shonnard 2005, Luo *et al* 2009a, Pawelzik and Zhang 2012, Singh *et al*



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2010, Spatari *et al* 2010, 2005). The majority of these studies found that bioethanol has fewer GHG emissions than petroleum-based gasoline and diesel, which can potentially improve the environmental performance of the transportation and energy sectors. In these studies, both first generation (such as corn grain) and second generation feedstocks, (for example, corn stover, forest residues, and switchgrass) were analyzed for bioethanol production using both biochemical and thermochemical pathways.

The Energy Independence and Security Act of 2007 amended RFS to RFS2, which expanded the mandate for the utilization of 36 billion gallons of biofuel annually in 2022, of which no more than 15 billion gallons can be ethanol from corn starch, and no less than 16 billion must be from cellulosic biofuels (US Congress 2007). RFS2 also mandates the inclusion of other biofuels such as biodiesel into the petroleum-based fuel supply and requires renewable fuels other than corn-based ethanol with at least a 50% reduction of GHG emissions (60% for cellulosic biofuels) compared to petroleum-based gasoline and diesel (US Congress 2007). The issue of RFS2 drives a growing interest in advanced biofuels production such as renewable gasoline and diesel fuels from second generation feedstocks.

Fast pyrolysis, which is carried out at a moderate temperature (around 500 °C) and short reaction time (about two seconds), has attracted considerable interest as a means for converting biomass fuels and residues into biofuels (Bridgwater 2012). Fast pyrolysis can generate up to 75 wt% of liquid bio-oil, which can then be used in various applications such as supplying energy for transportation, heating, and electricity generation (Czernik and Bridgwater 2004). With the growing interest in fast pyrolysis of biomass and catalytic upgrading of the resulting bio-oil into hydrocarbon fuels, a number of LCA studies have been recently conducted to explore the environmental impacts of this pathway to biofuels (Fan *et al* 2011, Heracleous 2011, Hsu 2012, Iribarren *et al* 2012, Kauffman *et al* 2011, Zhong *et al* 2010). In these studies, different types of biomass feedstocks (willow, poplar, wood logging residue, corn stover etc) were investigated and various applications of the bio-oil were examined, such as power generation from bio-oil combustion and hydrogen production from steam reforming of bio-oil.

Catalytic upgrading methods can be employed to upgrade bio-oil to a variety of gaseous and liquid fuels including diesel fuel, gasoline, kerosene, and methane (Bridgwater 2012). However, only a small number of LCAs have been conducted on the production of renewable gasoline and diesel fuel from biomass fast pyrolysis and upgrading. Hsu (2012) conducted a well-to-wheel analysis of transportation fuel from the fast pyrolysis and upgrading of forest residues, based on data from a Pacific Northwest National Laboratory (PNNL) process design report (Jones *et al* 2009). An uncertainty analysis for GHG emissions was also conducted in this study and found that all scenarios considered had lower GHG emissions than petroleum-based gasoline. Iribarren *et al* (2012) performed an LCA for fast pyrolysis and upgrading of woody biomass using a cradle-to-gate approach. Kauffman *et al* (2011) conducted

an LCA for combined ethanol and drop-in fuels production from corn grain and corn stover cornstover, respectively, on the basis of an hectare farmland and found that a 52% reduction in GHG emissions was possible.

In all of these studies, hydrotreating is employed to deoxygenate bio-oil to hydrocarbons. Hydrotreating, done either in a single stage or two stages, is a common pretreatment in the oil refinery process, but it requires a large amount of hydrogen. Currently, the majority of industrial hydrogen is obtained from steam reforming of natural gas (Milbrandt and Mann 2009). However, hydrogen can be produced from other sources. The aqueous phase of bio-oil contains carbohydrate-derived compounds that can be catalytically steam reformed to renewable hydrogen (Medrano *et al* 2011). Catalytic steam reforming of bio-oil compounds has been investigated in previous studies (Basagiannis and Verykios 2007, Chen *et al* 2011, Czernik *et al* 2007, Domine *et al* 2008, Garcia *et al* 2000, Hou *et al* 2009, Liu *et al* 2011, Medrano *et al* 2011, Ortiz-Toral *et al* 2011, Seyedeyn-Azad *et al* 2011, Thaicharoensutcharittham *et al* 2011, Vagia and Lemonidou 2008, Yan *et al* 2010, Zhang *et al* 2011). In these studies, various metal-supported catalysts, bio-oil modeling components, pyrolysis reactor designs, and biomass-feedstock selections have been tested and compared for their efficiency in biohydrogen production. Through hydrogen production via a bio-oil reforming pathway, natural gas consumption could be reduced. In this study, the environmental impacts of the production of hydrogen and transportation fuels from corn stover fast pyrolysis and upgrading are evaluated.

The objective of this study is to perform a life cycle assessment of the environmental impacts of the production of hydrogen and transportation fuels from the fast pyrolysis and upgrading of corn stover. An Aspen Plus model of the pyrolysis and upgrading processes in combination with a GREET model database and a US Life Cycle Inventory Database provide data to support the LCA using SimaPro 7.3.

2. Description for the biofuel production pathway

The plant capacity for the fast pyrolysis and bio-oil upgrading facility is assumed to be 2000 metric tons per day of dry biomass feedstock and the bio-oil yield is assumed to be 65% of the dry biomass, based on a previous techno-economic analysis we have performed (Zhang *et al* 2013b). Corn stover is selected as the feedstock for the production of hydrogen and transportation fuels. Bio-oil production from raw feedstock includes biomass preprocessing, biomass fast pyrolysis, bio-oil recovery, solids removal, and heat generation. All of the five steps are identical to those of previous techno-economic analyses (Brown *et al* 2011, 2012, Wright *et al* 2010a, Zhang *et al* 2013a). In the biomass preprocessing step, biomass containing 25 wt% moisture is chopped to 10 mm particle diameter, dried to 7 wt% moisture content, and ground to 3 mm particle diameter. In the fast pyrolysis step, biomass is converted into non-condensable gases, bio-oil vapors, and solid char phases in a fluidized bed reactor operating at 500 °C and ambient pressure. The bio-oil

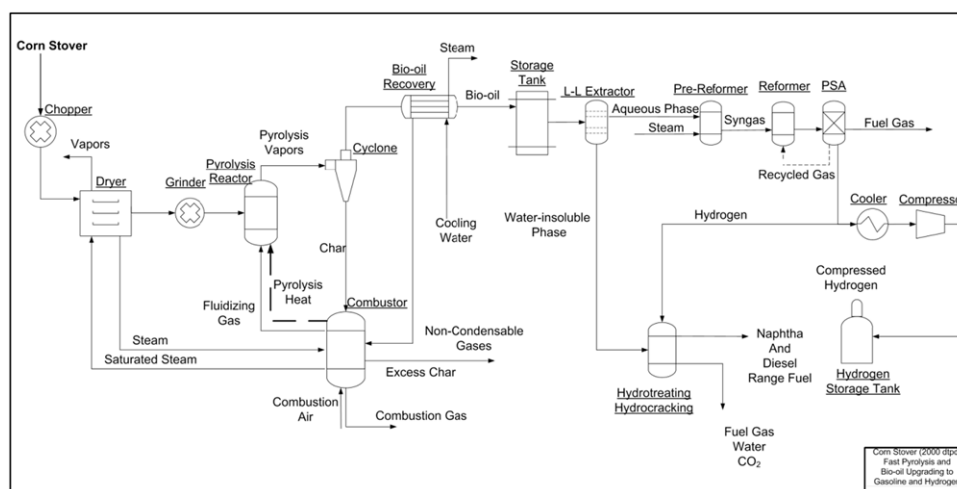


Figure 1. Process diagram for fast pyrolysis of corn stover and upgrading of the resulting bio-oil to hydrogen, gasoline and diesel fuel (adapted from Wright *et al* 2010a).

vapors are recovered using a condenser and an electrostatic precipitator. In the solids removal step, 90% of the entrained char and ash particles are removed from the pyrolysis products through cyclones. Finally, in the combustion step, the non-condensable gases and a portion of the solid char are burned to generate heat for operating the pyrolyzer. The remainder of the char is treated as coal substitute locally consumed. The complete process diagram is illustrated in figure 1.

The bio-oil is phase separated into a water-insoluble phase and an aqueous phase using a liquid–liquid (L–L) extractor. The insoluble phase is upgraded to gasoline and diesel fuel through hydrotreating and hydrocracking. Although some studies assume hydrogen for upgrading is obtained from steam reforming of natural gas, this study assumes that hydrogen is produced from steam reforming of the aqueous phase of bio-oil (Marker 2005), which has advantages in decreasing GHG emissions, but at the cost of lower carbon yields of gasoline and diesel fuel from bio-oil. The water-insoluble phase is first hydrotreated followed by hydrocracking under zeolite catalysts to produce gasoline and diesel fuel. The aqueous phase is reformed to hydrogen through a two-stage catalytic process. A pressure swing adsorption (PSA) unit is employed to separate hydrogen from the reformed gas. A portion of the hydrogen is used to hydrocrack the water-insoluble phase of the bio-oil, and the rest of the hydrogen is treated as a co-product.

3. LCA goal and scope definition

The goal of this LCA study is to identify the environmental impacts of the production of hydrogen and transportation fuels from corn stover fast pyrolysis with upgrading. This well-to-wheel analysis is divided into seven unit processes, which include biomass production, biomass transportation, biomass preprocessing, bio-oil production, bio-oil upgrading, product distribution, and vehicle operations. It includes all resource consumption from biomass production to vehicle

operations. Figure 2 illustrates the system boundary for the LCA. The bio-oil production unit is a combination of the steps of biomass fast pyrolysis, bio-oil recovery, solids removal, and heat generation. The bio-oil production unit is shown as a sub-block within the system boundary. Initially, corn stover is produced on farms and transported to an integrated biomass fast pyrolysis and upgrading facility. In the integrated facility, the biomass is preprocessed and converted to intermediate bio-oil that is upgraded to transportation fuels. The transportation fuels are then transported and distributed to the customer zones, where the fuel is used for vehicle operations. Electricity needed for processing is assumed to be generated from the same fuel mix in the Midwest region of the US (EIA 2012). Indirect effects such as indirect land use change (ILUC) are not included in this study. The effects of ILUC are potentially large (Fargione *et al* 2008, Plevin *et al* 2010, Searchinger *et al* 2008) but also highly controversial. ILUC is thought to be too diffuse and subject to too many arbitrary assumptions to be useful for rule making (Mathews and Tan 2009). In addition, severe qualifications are required for measurement of GHG emissions associated with ILUC (Mathews and Tan 2009). So the indirect land use change effects are not considered in this LCA study.

The Aspen Plus process model for the production of hydrogen and transportation fuels from fast pyrolysis of corn stover is adapted from a previous model developed as part of a joint study by Iowa State University, the National Renewable Energy Laboratory, and ConocoPhillips Company (Wright *et al* 2010b). This Aspen Plus model has been adapted for subsequent techno-economic analysis of the production of hydrogen and transportation fuels from corn stover (Zhang *et al* 2013b). In the present study, the model assumes an *n*th plant facility with mature technology processing 2000 metric tons per day of dry biomass. The functional unit for interpreting the LCA results is 1 km traveled by a light-duty passenger vehicle operated on fuels generated via fast pyrolysis. The required materials and energy inputs associated with the unit processes of the LCA are derived from an Aspen

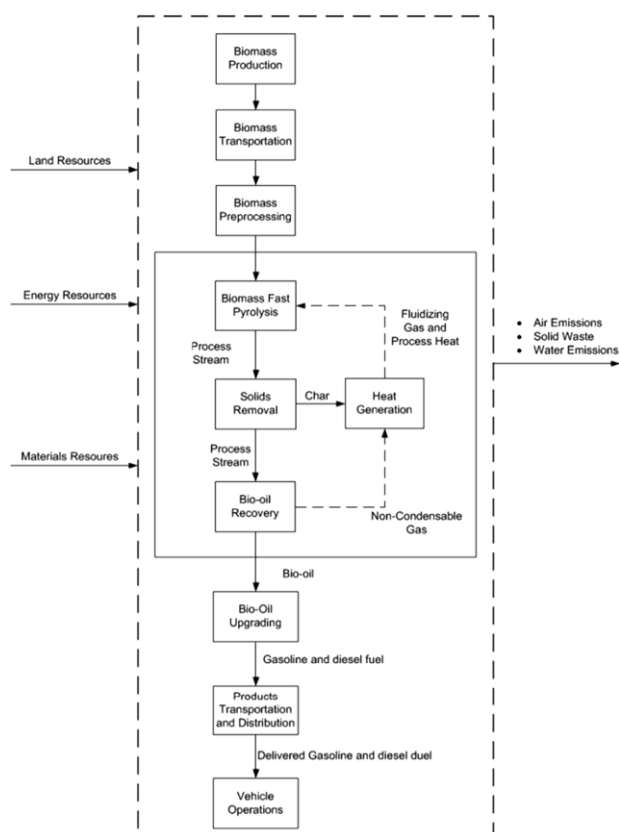


Figure 2. Life cycle system boundary for the production of hydrogen and transportation fuels from corn stover via fast pyrolysis and upgrading.

Plus model (Zhang *et al* 2013b) along with GREET model (Argonne National Laboratory 2011) and US Life Cycle Inventory Database (National Renewable Energy Laboratory 2012). SimaPro 7.3 software with an Eco-invent 2.2 database is employed to estimate environmental aspects such as climate change, fossil energy input, land use, and ozone layer impacts for the primary unit processes. IPCC 2007 GWP 100a, Cumulative Energy Demand (CED), and TRACI 2 methods developed by the US Environmental Protection Agency (EPA) are used to calculate life cycle impacts. The IPCC 2007 GWP 100a method is employed to evaluate life cycle GHG emissions for the production of hydrogen and transportation fuels from corn stover (IPCC 2007). The Cumulative Energy Demand (CED) method (Goedkoop *et al* 2008) is used to estimate the energy demand for the production of hydrogen and transportation fuels. The TRACI 2 method (Bare *et al* 2002) is employed to evaluate other potential environmental impacts (acidification, eutrophication, ecotoxicity, etc).

4. Inventory analysis

4.1. Biomass production

Biomass production is based on the cultivation and collection of corn stover residue. The input energy and GHG emissions associated with corn stover cultivation and collection are included in the overall inventory analysis. Inventory data for

Table 1. Inventory data for biomass production.

Item	Amount	Unit
<i>Outputs</i>		
Collected corn stover	1	kg
<i>Resources</i>		
Biomass energy	15.4	MJ
<i>Materials and fuels</i>		
N fertilizer	8.5	g
P ₂ O ₅	2.2	g
K ₂ O	13.2	g
Diesel fuel for corn stover loader	0.12	g
Diesel fuel for corn stover collection	5.15	g
<i>Emission to air</i>		
N ₂ O	0.085	g
NO	0.12	g

corn stover collection is compiled from a US Life Cycle Inventory Database (National Renewable Energy Laboratory 2012) and a GREET model (Argonne National Laboratory 2011). The low heating value (LHV) for corn stover is assumed to be 15.4 MJ kg⁻¹ (National Renewable Energy Laboratory 2012). The yield of corn stover is assumed to be 2.1 dry tons acre⁻¹ (Han *et al* 2011). The mass ratio and energy content ratio of stover to corn produced in agriculture are roughly 1:1 (Kim and Dale 2004, Pordesimo *et al* 2005). We assume a corn stover removal rate of 62% from a previous LCA (Spatari *et al* 2005). The ratio of energy and emissions allocation between corn and stover for partitioning is assumed to be 1:0.62 (Spatari *et al* 2005). Diesel fuel input data for the corn stover production is adopted from the GREET model (Argonne National Laboratory 2011).

Traditionally, the bulk of corn stover has been left in the field to replenish the soil with nitrogen (N), phosphorus (P), and potassium (K) (Han *et al* 2011). If the corn stover is used for biofuels production, it will require farmers to replenish lost nutrients through supplementary fertilization (Han *et al* 2011). Based on the GREET model analysis, the replacement rates for N, P, and K fertilizer sources are 7700 g N, 2000 g P₂O₅ (873 g P) and 12 000 g K₂O (9957 g K) for 1 ton of removed corn stover (Argonne National Laboratory 2011). Direct N₂O and NO emissions from agricultural soil due to N fertilizer application are assumed to be 1.325% and 0.65% (Argonne National Laboratory 2011). Diesel fuel is consumed during biomass production. All of the input data for biomass production are detailed in table 1.

4.2. Biomass transportation

For biomass transportation, it is assumed that the wet feedstock, which contains 25 wt% moisture, is transported by 40 ton trucks (one way). The transportation distance of feedstock is 60 miles one way for corn stover, based on analysis of the GREET model (Argonne National Laboratory 2011). The delivered wet biomass is 2670 metric tons with 25 wt% moisture. Detailed input data for the biomass transportation are summarized in table 2.

Table 2. Inventory data for biomass transportation.

Item	Amount	Unit
<i>Outputs</i>		
Delivered corn stover	2 670	Metric ton
<i>Input from material</i>		
Truck 40 ton	284 000	ton km
Collected corn stover	2 670	Metric ton

Table 3. Inventory data for biomass preprocessing.

Item	Amount	Unit
<i>Outputs</i>		
Pretreated corn stover	2 150	Metric ton
<i>Materials and fuels</i>		
Delivered corn stover	2 670	Metric ton
Steam	184	Metric ton
Electricity for chopping	44 600	kWh
Electricity for grinding	109 000	kWh
Electricity for compressor	124 000	kWh
<i>Emission to air</i>		
Water	519	Metric ton

4.3. Biomass preprocessing

In the drying step, steam is employed to remove water from the biomass. For the inventory analysis of biomass preprocessing, the electricity and steam usages are considered as material inputs and the ejected water vapor from the drying step is considered an emission to the air (see table 3). The electricity requirement for reducing biomass particle size is calculated from the correlation developed by Mani *et al* (2004).

4.4. Bio-oil production

The inventory analysis of bio-oil production includes the inventory for biomass fast pyrolysis, bio-oil recovery, solids removal, and heat generation (see table 4). In the biomass fast pyrolysis and recovery processes, a portion of the generated char is sent to a combustor to supply heat for pyrolysis. The heating value of the char is assumed to be 27.5 MJ kg⁻¹ (Wright *et al* 2010b). The non-condensable gases and part of the char generated during pyrolysis provide sufficient heat to operate the pyrolyzer. The excess char is treated as a product that displaces coal with an assumed heating value that is half that of the coal it displaces. Local consumption of excess char is assumed, so char transport is not considered for local consumption.

The electricity, air, and process water are considered to be the inputs while the bio-oil is considered to be the output. The electricity inputs include electricity for biomass pyrolysis, bio-oil recovery, and char combustion, which are collected from the Aspen Plus model (Zhang *et al* 2013b). The process water is mainly used in bio-oil recovery, and air provides oxygen for combustion of non-condensable gases and char. The emissions from the bio-oil production unit are gases and solids, including carbon oxides, hydrocarbons, nitrogen oxides, sulfide, PM10, and ash. Combustion accounts

Table 4. Inventory data for bio-oil production.

Item	Amount	Unit
<i>Outputs</i>		
Corn stover bio-oil	1300	Metric ton
Char	216	Metric ton
<i>Avoided products</i>		
Coal	216	Metric ton
<i>Resources</i>		
Air	4300	Metric ton
Process water	8010	Metric ton
<i>Materials and fuels</i>		
Pretreated corn stover	2150	Metric ton
Electricity for pyrolysis	543 000	kWh
<i>Emission to air</i>		
N ₂	1330	Metric ton
O ₂	20.0	Metric ton
H ₂	1.5	Metric ton
CO	113	Metric ton
CO ₂	754	Metric ton
Water	114	Metric ton
NH ₃	0.000 024	Metric ton
NO	2.4	Metric ton
NO ₂	0.000 17	Metric ton
Sulfur	0.059	Metric ton
SO ₂	0.16	Metric ton
COS	0.000 38	Metric ton
H ₂ S	0.000 84	Metric ton
N ₂ O	0.000 14	Metric ton
HCN	0.000 048	Metric ton
PM10	2.7	Metric ton
<i>Waste or emissions to treatment</i>		
Ash	84.9	Metric ton

for virtually all of the PM10 particulate emissions from processing-related activities. Studies of the emission behavior and characteristics of PM10 from combustion of biochar or coal show that there is a correlation between the inherent ash content and the amount of PM10 emitted (Gao and Wu 2011, Zhang and Ninomiya 2006). For PM10 emission calculations, linear regression was used to identify the correlation between ash content and the wt% of coal ash transferred into PM10, as reported in the literature (Gao and Wu 2011). The ash separated in cyclones is disposed to sanitary landfills for waste treatment.

4.5. Bio-oil upgrading

The final products are gasoline, diesel fuel and hydrogen from bio-oil upgrading. The total gasoline and diesel fuel yield is 164.6 metric ton day⁻¹ (50% share of gasoline and 50% share of diesel), and the hydrogen yield is 63 metric ton day⁻¹. Hydrogen is assumed to be a co-product with product displacement based on the displaced usage of natural gas. Based on a previous study, 3.53 kg of natural gas is required for 1 kg of hydrogen production (Koroneos *et al* 2004). The environmental impacts allocation is based on the mass allocation between gasoline and diesel, which is 50% of the total environmental burden. The inventory inputs include air, catalysts, process water, electricity, and bio-oil. The process water includes water used for gas cooling and separation.

Table 5. Inventory data for bio-oil upgrading.

Item	Amount	Unit
<i>Outputs</i>		
Gasoline	82.3	Metric ton
Diesel fuel	82.3	
Hydrogen	63.2	Metric ton
<i>Avoided products</i>		
Natural gas (in ground)	223	Metric ton
<i>Resources</i>		
Air	1500	Metric ton
Process water	12 300	Metric ton
<i>Materials and fuels</i>		
Corn stover bio-oil	1250	Metric ton
Electricity for upgrading	291 000	kWh
Zeolite powder	0.45	Metric ton
Ni-based catalyst	0.73	Metric ton
<i>Emission to air</i>		
N ₂	1160	Metric ton
O ₂	234	Metric ton
CO	0.0015	Metric ton
CO ₂	1070	Metric ton
Water	906	Metric ton
CH ₄	0.007	Metric ton
C ₃ H ₆	0.000 12	Metric ton
CH ₂ O ₂	0.000 14	Metric ton
NO ₂	0.000 14	Metric ton
<i>Waste or emissions to treatment</i>		
Waste water	582	Metric ton

The waste water from bio-oil upgrading step is assumed to be sent to a waste water treatment plant. The catalysts employed in bio-oil upgrading are zeolite powders (0.45 metric ton) for hydrocracking and Ni-based catalysts (0.73 metric ton) for hydrotreating, with consumption based on gas hourly space velocities (GHSV). Details of the inventory data are shown in table 5.

4.6. Product transportation and distribution

For gasoline transportation, we assume transportation by barge, pipeline, and rail apportioned as 8%, 63%, and 29%, respectively. The distances for the three modes are 520 km, 400 km and 800 km, respectively. For diesel fuel transportation, we assume transportation by barge, rail and truck apportioned as 8%, 29% and 63%, respectively. The distances for the three modes are 520 km, 800 km and 50 km, respectively. Gasoline and diesel fuel are locally distributed by truck with an average travel distance of 30 km. All the assumptions and data are based on the GREET model's fast pyrolysis pathway (Argonne National Laboratory 2011). Details of the inventory analysis for gasoline and diesel fuel transportation and distribution are shown in tables 6 and 7.

4.7. Vehicle operations

Gasoline emissions are assumed for a vehicle operated using 50% conventional and 50% reformulated gasoline. Gasoline emissions are based on combustion in a spark-ignition engine while diesel fuel emissions are based on combustion in a direct-injection compression ignition engine using low-sulfur

Table 6. Inventory data for gasoline transportation and distribution.

Item	Amount	Unit
<i>Outputs</i>		
Delivered gasoline	82.3	Metric ton
<i>Input from material/telescope</i>		
Gasoline	82.3	Metric ton
Barge	6070	ton km
Pipeline	36 800	ton km
Rail	33 900	ton km
Truck 40 ton (distribution)	4380	ton km

Table 7. Inventory data for diesel fuel transportation and distribution.

Item	Amount	Unit
<i>Outputs</i>		
Delivered diesel fuel	82.3	Metric ton
<i>Input from material/telescope</i>		
Gasoline	82.3	Metric ton
Barge	6070	ton km
Rail	33 900	ton km
Truck 40 ton (transportation)	4600	ton km
Truck 40 ton (distribution)	4380	ton km

Table 8. Inventory data for vehicle operations fueled by pyrolysis-derived gasoline.

Name	Amount	Unit
<i>Outputs</i>		
Car operation, by gasoline	1	mile
<i>Materials and fuels</i>		
Delivered gasoline	0.121	kg
<i>Emission to air</i>		
VOC	0.18	g
CO	3.75	g
NO _x	0.141	g
PM10	0.029	g
PM2.5	0.015	g
Sulfur oxides	0.006 12	g
CH ₄	0.0146	g
N ₂ O	0.012	g
CO ₂	371	g

diesel. The mass density and heating value of low-sulfur diesel fuel is assumed. The fuel economy for gasoline and diesel fuel are 23.4 and 28.1 MPG (miles per gallon), respectively. All of the stated assumptions and required data for assumed vehicle operations are based on default values of the GREET model (Argonne National Laboratory 2011). The inventory data of vehicle operations on gasoline and diesel fuel bases are described in tables 8 and 9.

5. Results and discussions

5.1. Fossil energy input

Figure 3 shows the breakdown of fossil energy input for various unit processes on the bases of gasoline and diesel fuel. The fossil energy input is separated into two parts: required fossil energy for various unit processes and co-products

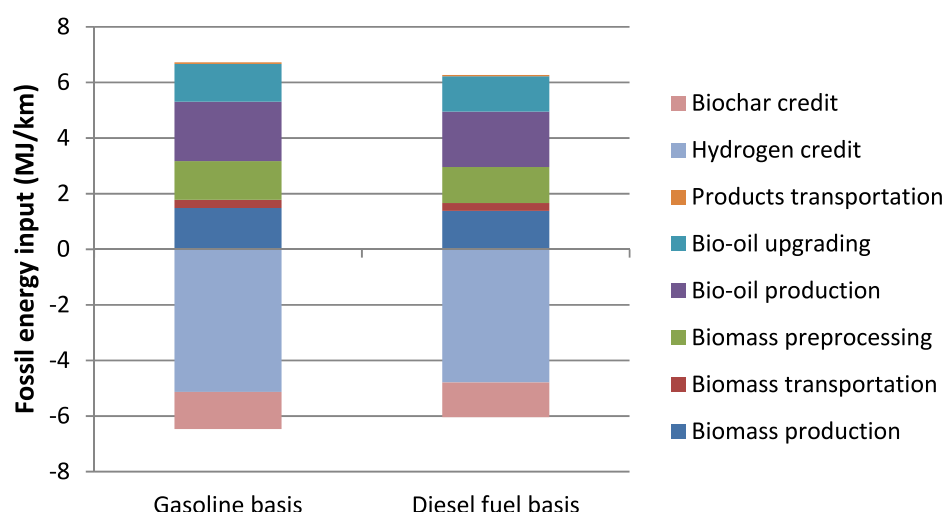


Figure 3. Fossil fuel energy inputs for various unit processes per km traveled. Note: biochar and hydrogen credits are treated as negative fossil energy inputs.

Table 9. Inventory data for vehicle operations fueled by pyrolysis-derived diesel fuel.

Name	Amount	Unit
<i>Outputs</i>		
Car operation, by diesel fuel	1	mile
<i>Materials and fuels</i>		
Delivered diesel fuel	0.113	kg
<i>Emission to air</i>		
VOC	0.088	g
CO	0.539	g
NO _x	0.141	g
PM10	0.030	g
PM2.5	0.016	g
Sulfur oxides	0.002	g
CH ₄	0.003	g
N ₂ O	0.012	g
CO ₂	322	g

credits (shown as negative fossil energy input). As indicated in the figure, bio-oil production has the largest fossil energy input. It consumes 32% of the total required fossil energy among all the unit processes. In the bio-oil production unit, char is treated as a coal substitute, which contributes to 1.34 MJ km⁻¹ and 1.25 MJ km⁻¹ reductions to the total fossil energy input. Biomass production has the second largest fossil fuel demand of approximately 22% of the total required fossil energy for both gasoline and diesel fuel bases. Biomass preprocessing also plays a significant role, which demands approximately 21% of the total required fossil energy. Electricity consumption during biomass chopping, grinding, and drying is responsible for the largest fossil energy input for biomass preprocessing. Bio-oil upgrading consumes approximately 20% of the fossil energy input. Hydrogen as a co-product is produced from bio-oil steam reforming, which results in avoided use of natural gas in the bio-oil upgrading unit. Consequently, 5.1 MJ km⁻¹ and 4.8 MJ km⁻¹ are subtracted from the total fossil energy input as hydrogen credits. Due to the hydrogen and char credits, the net fossil

energy input is 0.25 MJ km⁻¹ and 0.23 MJ km⁻¹ for gasoline and diesel fuel bases, respectively.

5.2. GHG emission

Figure 4 details the breakdown of the various contributions of unit process to GWP for both gasoline and diesel fuel bases. In the biomass production step, GWP contributions are separated into two parts: CO₂ absorption during biomass cultivation and CO₂ emissions during biomass harvesting. For 1 kg corn production, the atmosphere can uptake 1.49 kg CO₂ during cultivation based on the US Life Cycle Inventory Database (National Renewable Energy Laboratory 2012). The amount of CO₂ absorption allocated to corn stover is assumed on a basis of mass fraction. We assume corn stover occupies 38% mass fraction of total participating corn and stover; thus, the CO₂ absorption contributed by corn stover is 38% of the whole CO₂ absorption of 1 kg corn production. As a result, 1 kg corn stover could uptake 0.57 kg CO₂.

For a light-duty vehicle fueled by gasoline, the total corn stover CO₂ absorption is 0.69 kg CO₂ eq km⁻¹, and the total positive GWP (excluding feedstock absorption) is 0.73 kg CO₂ eq km⁻¹. Vehicle operations exhibit the largest GHG footprint, contributing 33% of total positive GWP for a gasoline basis. Bio-oil production has the second largest GHG emissions, contributing 25% of total positive GWP. This is because bio-oil production involves char and non-condensable gas combustion, which release direct GHG emissions to the environment. Biomass preprocessing has a 16% contribution to total GWP.

The large quantity of GHG emissions associated with electricity usage in biomass preprocessing is the main reason for this large GWP contribution. Bio-oil upgrading contributes 9% of the total positive GWP because the reduced GWP from avoided natural gas is subtracted from the total GWP as a hydrogen credit. This means that hydrogen production from bio-oil steam reforming as co-product makes considerable contribution to GWP reduction in this step.

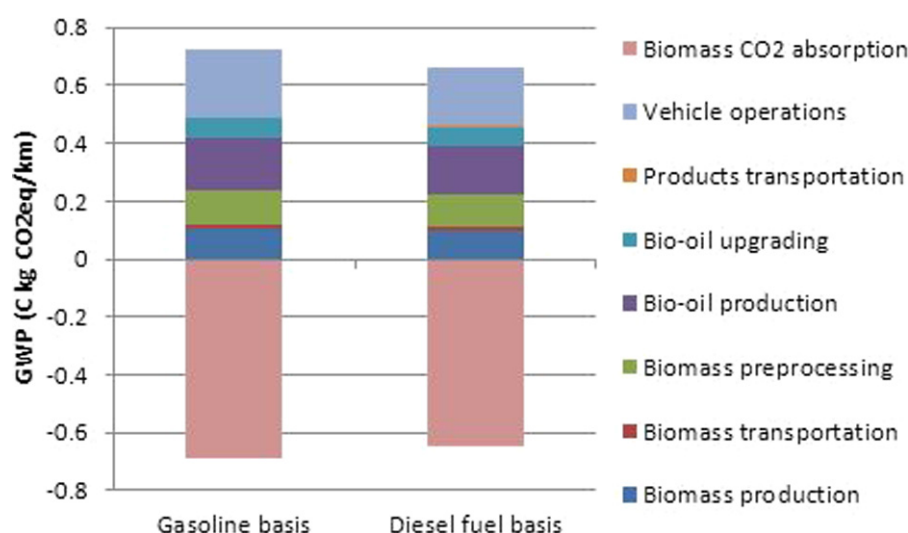


Figure 4. Contributions of unit process to global warming reported on a per km traveled basis. Note: biomass CO₂ absorption is treated as a negative contribution to total GWP.

Table 10. Environmental profile of gasoline and diesel products (based on 1 km traveled by light-duty vehicle).

Impact category	Unit	Gasoline	Diesel
Ozone depletion	kg CFC-11 eq	6.93×10^{-8}	6.07×10^{-8}
Smog	kg O ₃ eq	0.076	0.071
Acidification	mol H ⁺ eq	0.28	0.27
Eutrophication	kg N eq	0.17	0.16
Carcinogenics	CTUh	2.07×10^{-8}	1.92×10^{-8}
Non-carcinogenics	CTUh	7.29×10^{-8}	6.82×10^{-8}
Respiratory effects	kg PM ₁₀ eq	0.000 65	0.000 61
Ecotoxicity	CTUe	0.45	0.42

Biomass transportation and product distribution have the smallest contributions among all of the steps, representing 3% and 0.5% of the total positive GWP for both gasoline and diesel fuel bases.

For a light-duty vehicle using diesel fuel, the total corn stover CO₂ absorption is 0.66 kg CO₂ eq km⁻¹, and the total positive GWP (excluding feedstock absorption) is 0.66 kg CO₂ eq km⁻¹. It has a similar breakdown of contributions among the various unit processes but smaller GWP compared to travel in a light-duty vehicle using gasoline. This is because diesel fuel has better fuel economy than gasoline, even after considering the differences in energy content for gasoline and diesel. The net GWP traveled using gasoline and diesel fuel are 0.037 and 0.015 kg CO₂ eq km⁻¹, respectively.

5.3. Other impact categories

Other potential environmental impacts such as acidification, eutrophication, and ecotoxicity are evaluated by TRACI 2 method. Table 10 presents the potential environmental impacts of the gasoline and diesel fuel products.

Figure 5 shows the relative contributions of different unit process to the potential environmental impacts on a gasoline basis. Biomass transportation has the largest contribution (55%) for ozone depletion among the unit processes. For smog, acidification, and eutrophication, bio-oil production has

the largest contribution, which is up to 53% contribution to the total impact. Bio-oil upgrading has significant impacts on eutrophication, carcinogenics, non-carcinogenics, respiratory effects and ecotoxicity, with contributions ranging from 28% to 46%. Vehicle operations have comparatively small contributions to smog, acidification, and respiratory effects, representing less than 5%.

5.4. Comparison to previous studies

Table 11 compares GHG emissions and fossil energy inputs determined in the present study to results from several previous LCAs of biomass-derived transportation fuels. The first case is an analysis performed by the National Renewable Energy Laboratory (NREL) (Hsu 2011) based on fast pyrolysis of forest residue with bio-oil hydroprocessing to gasoline and diesel fuel (Case A in table 11) as proposed by Pacific Northwest National Laboratory (PNNL) (Jones *et al* 2009). Compared to this case, the net GHG emissions on gasoline and diesel fuel bases for the present study are lower by 68% and 65%, respectively. This is mainly because the present study assumes hydrogen for hydrotreating comes from steam reforming of bio-oil whereas the NREL study assumes hydrogen comes from steam reforming of natural gas.

The next three cases are variations of an LCA for an integrated biorefinery based on the GREET model (Cases

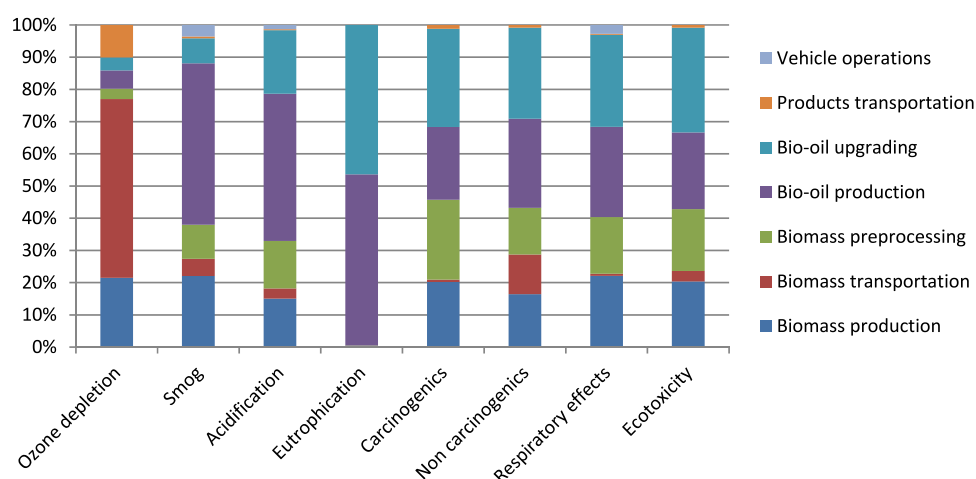


Figure 5. Contribution of unit processes to potential environmental impacts (gasoline basis).

Table 11. Comparison results of environmental impacts for 1 km driven by car operated on gasoline or diesel fuel.

Gasoline basis	GHG emissions (kg CO ₂ eq km ⁻¹)	Fossil energy input (MJ km ⁻¹)
Pyrolysis gasoline for the current study	0.037	0.25
Case A: pyrolysis gasoline from forest residue ^a	0.117	1.7
Case B1: pyrolysis gasoline from corn stover (hydrogen from bio-oil reforming) ^b	0.0422	0.4
Case B2: pyrolysis gasoline from corn stover (hydrogen from natural gas steam reforming) ^b	0.0975	1.22
Case B3: pyrolysis gasoline from forest residue (hydrogen from natural gas steam reforming) ^b	0.115	1.5
Case C: ethanol via gasification ^c	0.15	1.2
Case D: 2005 petroleum-based gasoline ^d	0.3	4.5
Diesel fuel basis	GHG emissions (kg CO ₂ eq km ⁻¹)	Fossil energy input (MJ km ⁻¹)
Pyrolysis diesel fuel for the current study	0.015	0.23
Case A: pyrolysis diesel fuel from forest residue ^a	0.098	1.42
Case B1: pyrolysis diesel fuel from corn stover (hydrogen from bio-oil reforming) ^b	0.0354	0.325
Case B2: pyrolysis diesel fuel from corn stover (hydrogen from natural gas steam reforming) ^b	0.0814	1.02
Case B3: pyrolysis diesel fuel from forest residue (hydrogen from natural gas steam reforming) ^b	0.0963	1.22
Case D: 2005 petroleum-based diesel fuel ^d	0.258	3.1

^a Data is from NREL report (Hsu 2011). ^b Data is from GREET model (Han *et al* 2011). ^c Data is from Hsu *et al* (2010).

^d Data is from GREET model (Han *et al* 2011).

B1, B2 and B3 in table 11). These cases are: transportation fuels from fast pyrolysis of forest residue with hydrogen from natural gas reforming (Case B1), transportation fuels from fast pyrolysis of corn stover with hydrogen from natural gas reforming (Case B2) and transportation fuels from fast pyrolysis of corn stover with hydrogen from bio-oil reforming (Case B3). Production of both hydrogen and transportation fuels from corn stover has less GHG emissions than the other cases. For Case B1, the amount of internal hydrogen production from bio-oil reforming is only used for

hydrotreating so there is no excess hydrogen as co-product. The amount of GHG emissions for the present study on a gasoline basis is 12% lower than for Case B1. The present study showed 62% and 68% reductions in GHG emissions on a gasoline basis compared to Case B2 and Case B3, respectively.

The present study is also compared to ethanol production via indirect gasification of forest residue and mixed alcohol synthesis process (Case C in table 11) (Hsu *et al* 2010), which has the largest GHG emissions and fossil energy

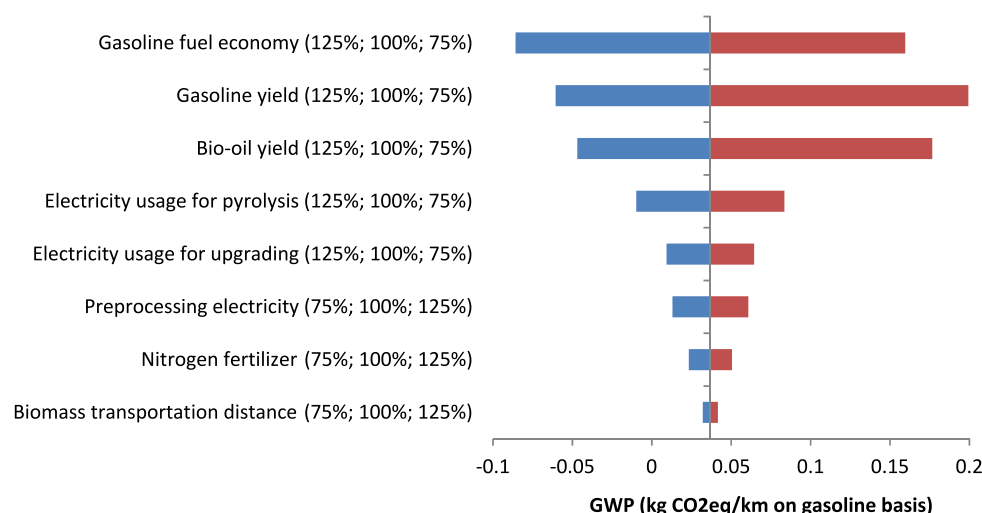


Figure 6. Sensitivity of GHG emissions to operating conditions on a gasoline basis (changes in operating parameters are expressed as a percentage of the baseline case).

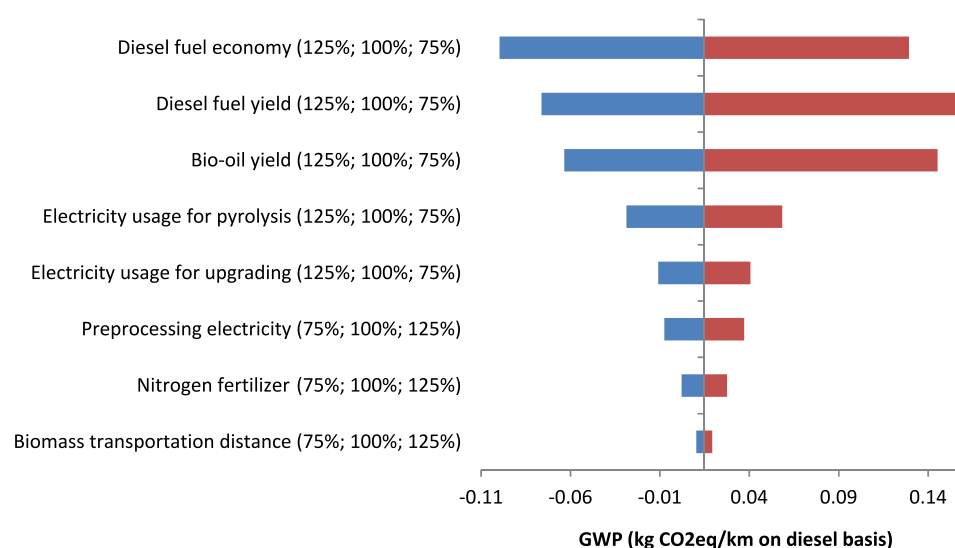


Figure 7. Sensitivity of GHG emissions to operating conditions on a diesel fuel basis (changes in operating parameters are expressed as a percentage of the baseline case).

input for biofuels among the previous studies examined ($0.15 \text{ CO}_2 \text{ eq km}^{-1}$ and $0.258 \text{ CO}_2 \text{ eq km}^{-1}$ on a gasoline basis and diesel fuel basis, respectively). Greenhouse gas emissions from petroleum-based gasoline and diesel fuel in 2005 (Case D in table 11) are assumed to be 0.3 and $0.258 \text{ kg CO}_2 \text{ eq km}^{-1}$ which are based on an well-to-wheel analysis using the GREET model (Han *et al* 2011). Net GWP for the present study are 88% and 94% lower than petroleum-based gasoline and diesel fuel GHG emissions in 2005, respectively, which meet the criteria of 50% GHG emissions reduction mandated by RFS2.

The co-production of hydrogen and transportation fuels in the present study has the smallest GHG emissions and fossil energy input compared to the selected previous studies when transportation fuels are the only product. This indicates that the co-production of hydrogen, gasoline and diesel fuel via fast pyrolysis and upgrading of corn stover, although

producing lower yields of gasoline and diesel, has lower GHG emissions and fewer fossil energy inputs than these other studies because of their use of natural gas as a source of hydrogen for upgrading.

5.5. Sensitivity analysis

The sensitivity analysis of GHG emissions to various operational parameters in the production of hydrogen and transportation fuels from corn stover is illustrated in figures 6 and 7. The parameters investigated include fuel economy, bio-oil yield, products yield, electricity consumption, biomass transportation distances and nitrogen fertilizer consumption. Sensitivity analysis is conducted by changing each operating parameter by a prescribed amount around the baseline operating conditions (expressed as a percentage of the baseline case).

As indicated in figure 6, overall net GWP ranges from -0.086 to $0.2 \text{ kg CO}_2 \text{ eq km}^{-1}$ on gasoline basis. Gasoline fuel economy has the greatest impact on GHG emissions. A $\pm 25\%$ variation of fuel economy on the baseline results in a -0.086 to $0.16 \text{ kg CO}_2 \text{ eq km}^{-1}$ range of GWP. Yields of bio-oil and gasoline have significant impacts on GHG emissions. Low yield of gasoline (75% of the baseline) generates the highest GWP of $0.2 \text{ kg CO}_2 \text{ eq km}^{-1}$. Electricity consumption also has an important impact. If the electricity consumption for biomass fast pyrolysis varies $\pm 25\%$ from the baseline, GHG emissions vary from -0.01 to $0.084 \text{ kg CO}_2 \text{ eq km}^{-1}$. A variation of $\pm 25\%$ in bio-oil upgrading, electricity consumption, or electricity consumption for biomass preprocessing would also change GWP in a range of 0.01 – $0.064 \text{ kg CO}_2 \text{ eq km}^{-1}$ on gasoline basis. Nitrogen fertilizer has comparatively smaller impact than the previous parameters. When nitrogen fertilizer is reduced to 75% of the baseline, a GWP of $0.023 \text{ kg CO}_2 \text{ eq km}^{-1}$ on a gasoline basis can be achieved with 92% GHG emissions reduction compared to the 2005 petroleum-based gasoline baseline.

The sensitivity analysis on a diesel fuel basis is illustrated in figure 7. Diesel fuel economy, diesel fuel yield and bio-oil yield are the most important parameters for GWP. The overall range of GWP based on this sensitivity analysis ranges from -0.1 to $0.17 \text{ kg CO}_2 \text{ eq km}^{-1}$ traveled by light-duty vehicle fueled by diesel fuel. If diesel fuel yield is only 75% of the baseline, GWP reaches its highest value of $0.17 \text{ kg CO}_2 \text{ eq km}^{-1}$. GWP reaches its lowest value of $-0.1 \text{ kg CO}_2 \text{ eq km}^{-1}$ if diesel fuel economy increases to 125% of the baseline. Generally, the trend of the sensitivity analysis for the diesel fuel basis is similar to the gasoline basis. But because diesel fuel has a higher fuel economy than gasoline, the GWP for biobased diesel fuel is smaller than for biobased gasoline under the same operating conditions.

6. Conclusions

A life cycle assessment of the production of hydrogen and transportation fuels from fast pyrolysis and upgrading of corn stover is examined in this study. The co-production of hydrogen and transportation fuels have lower GHG emissions and fossil energy input than scenarios where transportation fuels are the only products from pyrolysis of biomass. The results indicate that bio-oil production, biomass preprocessing, and bio-oil upgrading are the key drivers in determining overall environmental impacts of this biofuels pathway. Among the unit processes, bio-oil production has the largest energy demand and contributes the largest GHG emissions. The co-products hydrogen and char greatly reduce fossil fuel consumption in the production of transportation fuels by this pathway. Fossil energy input is 0.25 MJ and 0.23 MJ km^{-1} traveled by a light-duty vehicle fueled by pyrolysis-derived gasoline and diesel fuel, respectively. The fossil energy input for this pathway is 0.25 MJ km^{-1} and 0.23 MJ km^{-1} for the gasoline and diesel fuel bases, respectively. Hydrogen for hydrotreating is produced from reforming of bio-oil instead of reforming

of natural gas, so significant quantities of fossil energy are saved compared to generating hydrogen from natural gas. The net GWP is $0.037 \text{ kg CO}_2 \text{ eq}$ and $0.015 \text{ kg CO}_2 \text{ eq km}^{-1}$ traveled by light-duty vehicle fueled by gasoline and diesel fuel, respectively. Compared to petroleum-based gasoline and diesel fuel, GHG emissions are reduced 88% and 94%, respectively, which exceeds the RFS2 requirements. Biomass transportation has the largest impact on ozone depletion among the unit processes. Bio-oil production makes the largest contribution to smog, acidification, and eutrophication. Sensitivity analysis indicates that fuel economy is the most sensitive parameter in determining GWP. Transportation fuel yield, bio-oil yield, and electricity consumption also play significant roles in determining the GHG footprint, so there is potential to reduce GHG emissions with improvements to electricity generation.

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