

# Supply Chain Sustainability Analysis of Three Biofuel Pathways

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*Biochemical Conversion of Corn Stover to Ethanol*

*Indirect Gasification of Southern Pine to Ethanol*

*Pyrolysis of Hybrid Poplar to Hydrocarbon Fuels*

**Energy Systems Division**

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## 1 INTRODUCTION

The Department of Energy's (DOE) Bioenergy Technologies Office (BETO) collaborates with industrial, agricultural, and non-profit partners to develop and deploy biofuels and other biologically-derived products. As part of this effort, BETO and its national laboratory teams conduct in-depth techno-economic assessments (TEA) of technologies to produce biofuels as part state of technology (SOT) analyses. An SOT assesses progress within and across relevant technology areas based on actual experimental results relative to technical targets and cost goals from design cases and includes technical, economic, and environmental criteria as available.<sup>1</sup> Overall assessments of biofuel pathways begin with feedstock production and the logistics of transporting the feedstock from the farm or plantation to the conversion facility or biorefinery. The conversion process itself is modeled in detail as part of the SOT analysis. The teams then develop an estimate of the biofuel minimum selling price (MSP) and assess the cost competitiveness of the biofuel with conventional fuels such as gasoline.

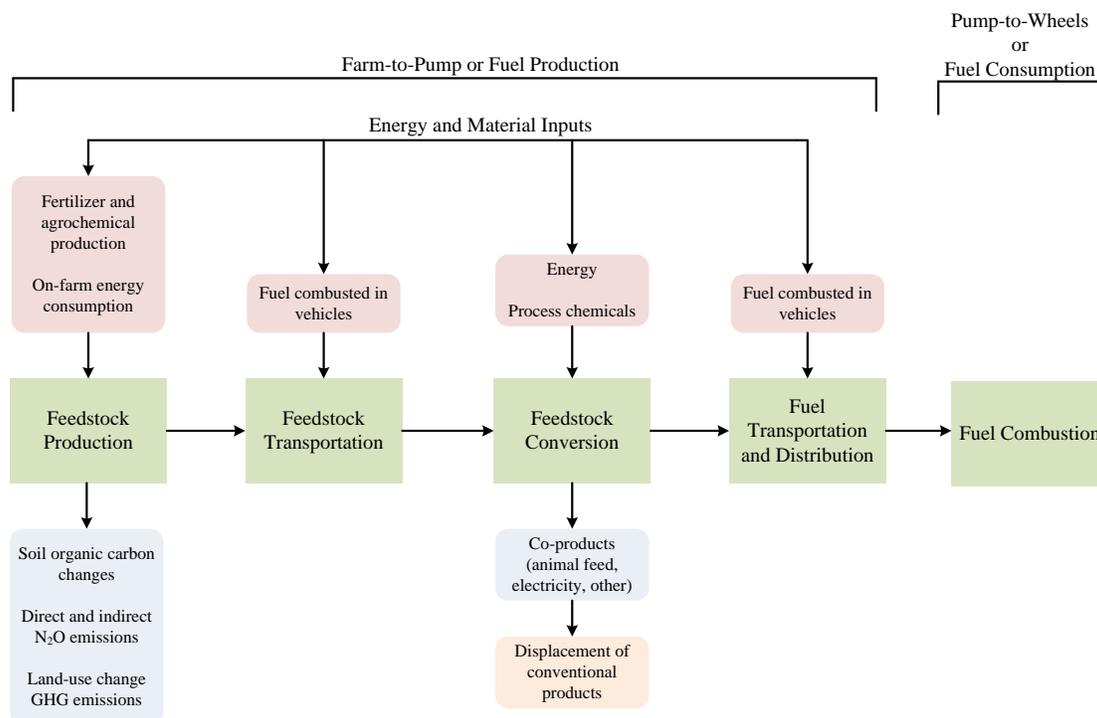
Recently, BETO has decided to conduct supply chain sustainability analysis (SCSA) of selected biofuel pathways subject to SOT analysis. The SCSA takes the life-cycle analysis approach that BETO has been supporting for over 17 years. This addition enables BETO to identify energy consumption or environmental issues that may be associated with biofuel production. Approaches to mitigate these issues can then be developed. Additionally, the supply chain sustainability analysis allows for comparison of energy and environmental impacts across biofuel pathways in BETO's research and development portfolio.

Figure 1 displays the stages in the supply chain that are considered in the sustainability analysis regardless of the specific pathway. In this analysis, we consider the upstream impacts of producing each input to the supply chain. The supply chain begins with feedstock production. At the feedstock production site, fertilizers, agrochemicals, and energy are consumed. Nitrogen fertilizer contributes N to the soil, a portion of which is converted to N<sub>2</sub>O, a potent greenhouse gas (GHG), through microbial and chemical processes. N<sub>2</sub>O emissions from these processes are called direct emissions. Indirect N<sub>2</sub>O emissions stem from transport of N from farming areas to ground and surface waters, and subsequent volatilization. The production of the feedstock may change soil organic carbon (SOC) content at the site. In the case of corn production with or without stover collection, feedstock production likely decreases soil carbon (Dunn et al. 2013a). In the case of switchgrass and miscanthus, however, SOC can rise as a result of feedstock production. SOC changes are less well-understood for woody feedstocks. Changes in soil carbon result in CO<sub>2</sub> emissions or sequestration. Some amount of feedstock processing, such as baling and chipping, may occur at the feedstock production site. During these processes, dry matter loss may occur, reducing the effective feedstock yield. As a result, to deliver a given amount of

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<sup>1</sup> A design case is different than an SOT case. A design case is a TEA that outlines a target case for a particular biofuel pathway. It enables preliminary identification of data gaps and research and development needs and provides goals and targets against which technology progress is assessed.

feedstock at the production facility gate the energy consumed rises. The amount of fertilizers and agrochemicals consumed may increase if dry matter loss occurs off the field (e.g., in storage).



**FIGURE 1** General Stages Considered in the Supply Chain Sustainability Analysis. Red boxes contain inputs to the supply chain. The energy and materials consumed to produce these inputs are rolled in to the analysis. Blue boxes contain supply chain impacts and co-products. The displacement of conventional co-products (orange box) is incorporated when the displacement allocation methodology is used.

The next stage of the supply chain is feedstock transportation. In some advanced supply system designs a depot is included to stabilize and densify the biomass prior to shipment to the biorefinery. If the supply chain includes a depot (Hess et al. 2009) then the impact of that step must be included in the analysis. No such intermediate process is considered here. The main impact of this stage is the production and use of the fuel consumed as the feedstock is moved from the feedstock production site to the conversion facility. The method of transportation and its impacts depend on the feedstock format and density at the time of transportation. For example, corn stover could be transported as square or round bales. At present, the most common means of feedstock transport is heavy-duty trucks, with a payload dependent on feedstock density. The distance that the feedstock must travel is a function of the conversion facility capacity, the yield of the feedstock in the field, and the amount of land surrounding the conversion facility that is available for feedstock production.

Once at the conversion facility, the feedstock may undergo further processing before conversion via biochemical or thermochemical processes. Examples of biochemical process inputs are enzymes, sulfuric acid, diammonium phosphate, and others. Thermochemical

processes often use catalysts. It should be noted that some conversion facilities are modeled as energy independent because they generate electricity and heat from the combustion of residual lignin from the feedstock or the feedstock itself. (Note that CO<sub>2</sub> emitted during the combustion of biomass is biogenic and is subtracted from total biorefinery CO<sub>2</sub> emissions.) In some cases, excess electricity is a co-product and could be sent to the grid, displacing conventional electricity. This analysis takes such displacement into account. Other examples of co-products are animal feeds, bio-char, other fuels, and steam. In each of the pathways this report describes, co-products from biofuel production are analyzed for their impacts on supply chain sustainability.

Once produced, the biofuel must be transported to a pumping station via train, barge, and trucks. As the fuel is combusted in a vehicle in the final stage of the supply chain, it releases biogenic CO<sub>2</sub> that the feedstock incorporated during its growth. This analysis subtracts biogenic GHG emissions from total use phase GHG emissions, in effect rendering net zero emissions for this phase in the case of biofuels.

In this supply chain report, we consider three biofuel pathways and use parameters the National Renewable Energy Laboratory (NREL), Idaho National Laboratory (INL), and the Pacific Northwest National Laboratory (PNNL) developed in SOT analyses of three biofuel pathways. All parameters were incorporated into Argonne National Laboratory's Greenhouse gases, Regulated Emissions, and Energy use in Transportation (GREET<sup>TM</sup>) model to determine the full supply chain impacts (Argonne National Laboratory, 2013). For example, GREET calculates the total energy consumption associated with natural gas consumed at a biorefinery as the energy inherent in the natural gas in addition to the energy consumed during natural gas recovery, processing, and transmission and distribution. In particular, a GREET version has been developed through this effort.

The following sections describe each pathway in detail. The first pathway is the biochemical conversion of corn stover to ethanol. In the second process, southern pine tree chips undergo a thermochemical conversion process, indirect gasification, to yield ethanol and mixed alcohols. Finally, the third pathway is pyrolysis of hybrid poplar to hydrocarbon fuels (gasoline or diesel).

## **2 BIOCHEMICAL CONVERSION (BC) OF CORN STOVER TO ETHANOL**

The biochemical route to ethanol from corn stover considered here is similar to the production of corn ethanol. Both processes use enzymes, a fermenting microorganism, and a corn-derived feedstock. Key differences are that the feedstock is a residue of corn agriculture (rather than a main product) and that its structure renders it more challenging to convert to ethanol. The supply chain sustainability analysis for this pathway is discussed in detail in the following sections. Note that energy consumption values for the duration of the report are reported based on lower heating values.

### **2.1 FEEDSTOCK PRODUCTION**

Corn stover is the feedstock for this process. It is a residue of the corn plant left in the field after corn harvest and is made up of the plant's stalks and leaves. Hess et al. (2009) provide a description of corn stover harvesting techniques.

One key issue in the analysis of corn stover as a feedstock is the division of the impacts of corn agriculture inputs between the production of stover versus grain. In this analysis, corn stover is treated as a by-product of corn agriculture and it is burdened only with the incremental energy and fertilizer consumption associated with its collection and production. When corn stover is removed from the field and collected as a biofuel feedstock, the corn field loses nutrients it would otherwise gain from the decomposition of the stover. In this analysis, we assume that these nutrients will be replenished with the supplemental application to the field (above the levels typically applied for corn agriculture without stover removal) of conventional fertilizers. When corn stover decays on the field, it releases  $N_2O$ , a GHG with a global warming potential (GWP) 298 times that of  $CO_2$  (Eggleston et al. 2006). Under a baseline scenario with no corn stover harvested, all the uncollected stover would emit some  $N_2O$  to the atmosphere. Since some stover is removed, direct and indirect  $N_2O$  emissions will decrease. The supplemental fertilizer, however, will increase those emissions. If the N content in the removed stover is equal to the N content of the supplemental conventional fertilizer then the net  $N_2O$  emissions from the baseline scenario will be zero, assuming the same conversion rate from N in stover and N in fertilizer. This analysis assumes that nitrogen fertilizer is applied to corn fields in an amount that exactly replaces the nitrogen content of the harvested stover and therefore no net  $N_2O$  emissions are attributed to the use of corn stover as an ethanol feedstock. Table 1 contains key parameters for corn stover collection as used in the analysis of the BC pathway.

In some supply chain sustainability analyses of biofuels, the impacts of the production of agricultural equipment are considered. However, adding these impacts typically does not significantly influence results. For example, in the case of corn ethanol, the inclusion of agricultural equipment production increased life-cycle GHG emissions by about 1% (Wang et al. 2011).

**TABLE 1 Key Parameters for Corn Stover Agriculture**

Parameter	Value <sup>a</sup>
Corn stover yield	3 dry tons/acre
Dry matter loss during harvesting	24%
Effective corn stover yield	2.28 dry tons/acre
N content of corn stover	(ISU 2002, U.S. DOE 2006)
N removed from field	0.02 tons N/acre 7,264 g N/dry ton stover collected
Supplemental fertilizer application rate	7,264 g N/dry ton stover collected
Increase in N content on corn field	0 g N/dry ton stover collected
P content of corn stover (as P <sub>2</sub> O <sub>5</sub> )	0.3% (ISU 2002)
Application rate of P <sub>2</sub> O <sub>5</sub>	1,088 g/dry ton stover collected
K content of corn stover (as K <sub>2</sub> O)	1.3% (ISU 2002)
Application rate of K <sub>2</sub> O	15,963 g/dry ton stover collected
Farming energy use	136,413 Btu/dry ton stover collected
Dry matter loss during storage as uncovered bales <sup>b</sup>	16%

<sup>a</sup> Values from Tan (2012) unless otherwise noted.

<sup>b</sup> Emery (2013)

## 2.2 FEEDSTOCK TRANSPORTATION

Corn stover is baled at a density of 12 lb/ft<sup>3</sup> and transported to the biorefinery. We assume a transport distance of 36.2 miles (Cafferty 2012) by heavy-duty truck with a fuel economy of 6 miles per diesel gallon and a payload of 20 tons (Tan 2012). At this time, no dry matter loss is assumed to occur between the farm field and the biorefinery. If dry matter loss were included, impacts of feedstock production would rise as more corn stover would need to be harvested to satisfy demand at the biorefinery.

## 2.3 FEEDSTOCK CONVERSION

All parameters for feedstock conversion (Table 2) are based on NREL process modeling. Enzyme production occurs on-site. The process produces surplus electricity that can be exported to the grid. In GREET simulations we assumed that this electricity is displacing electricity from the U.S. average grid, which has the characteristics listed in Table 3. This approach to accounting for the benefit of the co-produced electricity is called displacement. Alternatively, the burdens of the conversion process (e.g., energy consumption and associated emissions) could be divided between the fuel and the co-produced electricity on the basis of their energy content. Ethanol constitutes 89% of the energy in the two products leaving the biorefinery. In general, the displacement technique is more widely accepted and is recommended by ISO 14040 (ISO 1997).

It should be avoided, however, when the co-product makes up a major share of the overall energy (or mass in other cases) output. That is not the case here, so we use the displacement method.

**TABLE 2 Key Parameters for Feedstock Conversion (Tao et al. 2014)**

Parameter	Value <sup>a</sup>	Source of Material and Energy Flow Data for Process Inputs
Yield	71 gal ethanol/dry ton stover	-
Electricity export <sup>b</sup>	34.6 kWh/mmBtu ethanol	-
H <sub>2</sub> SO <sub>4</sub> consumed	4,450 g/mmBtu ethanol	Wang et al., 2003
NH <sub>3</sub> consumed	545 g/mmBtu ethanol	Wang et al., 2003
Corn steep liquor consumed	1,725 g/mmBtu ethanol	Dunn et al., 2012a
Diammonium phosphate consumed	182 g/mmBtu ethanol	Wang et al., 2003
NaOH consumed	1,544 g/mmBtu ethanol	Dunn et al., 2012a
CaO consumed	999 g/mmBtu ethanol	Dunn et al., 2012b
Urea consumed	272 g/mmBtu ethanol	Wang et al., 2003
Enzyme loading	0.16 ton enzyme/ton dry substrate	-
Sugar consumed in enzyme production	0.17 ton/ton enzyme	-
Corn steep liquor consumed in enzyme production	0.01 ton/ton enzyme	-
NH <sub>3</sub> consumed in enzyme production	0.01 ton/ton enzyme	-

<sup>a</sup> The lower heating value of ethanol used in GREET is 76,330 Btu/gal.

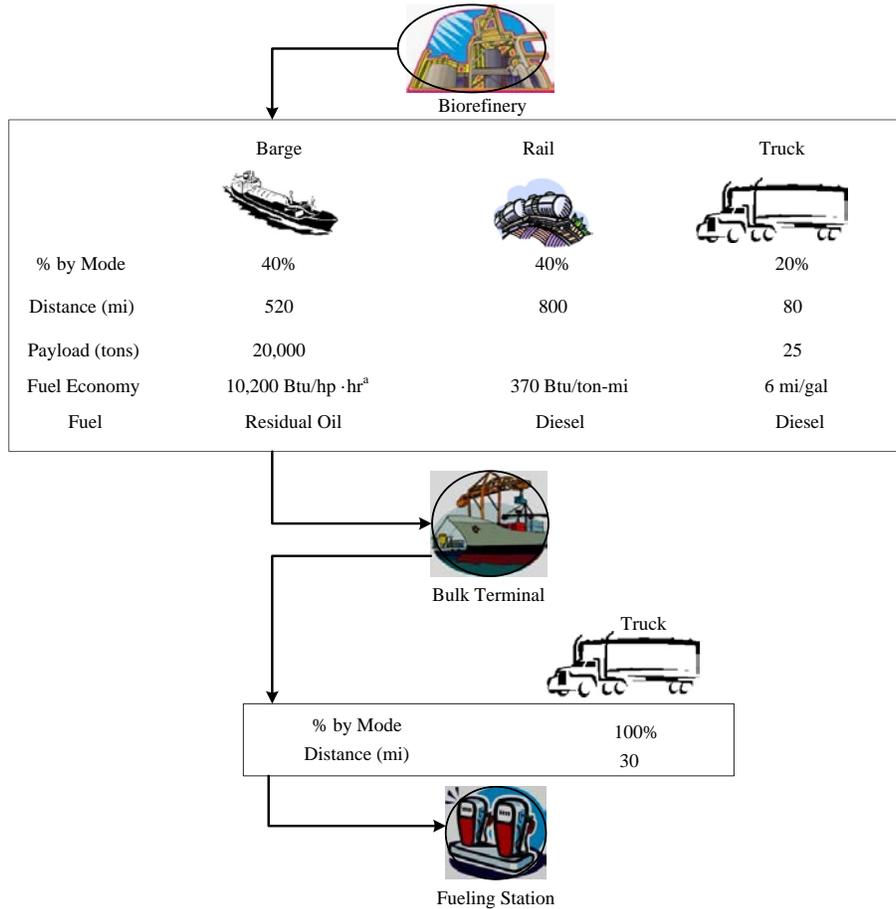
<sup>b</sup> This is the net electricity export. It is the total electricity generated from lignin combustion less electricity for powering the biorefinery, including on-site enzyme production.

**TABLE 3 U.S. Electricity Grid as Modeled in GREET (EIA 2013)**

Energy Source	Share in U.S. Grid
Residual oil	0.9%
Natural gas	22.7%
Coal	46.0%
Nuclear power	20.3%
Biomass	0.3%
Hydroelectric	6.6%
Geothermal	0.38%
Wind	2.4%
Solar photovoltaic	0.03%
Other	0.40%

## 2.4 FUEL TRANSPORTATION, DISTRIBUTION, AND USE

Once produced, ethanol is transported to bulk terminals and then to fueling stations. Key GREET parameters for ethanol distribution are in Figure 2. Additional parameters are found within GREET.



<sup>a</sup> Average of fuel economy for origin-to-destination and return trip values

**FIGURE 2 GREET Parameters for Ethanol Distribution**

Results for this pathway are presented together with those for the indirect gasification pathway to ethanol in Section 4.

### 3 INDIRECT GASIFICATION (IG) OF SOUTHERN PINE TO ETHANOL AND MIXED ALCOHOLS

Indirect gasification, a thermochemical pathway to ethanol, is the indirect application of heat to gasify feedstock. In this process olivine, a magnesium ore, acts as a heat transfer surface to supply the heat in the gasifier. Synthesis gas is reformed into a mixture of alcohols, of which the dominant product is ethanol. In contrast, direct gasification or partial oxidation technologies supply process heat from the feedstock partially combusting with oxygen. The feedstock for this process in this analysis of IG is southern pine.

#### 3.1 FEEDSTOCK PRODUCTION

Southern pine is a long rotation tree that can be farmed with minimal fertilizer inputs. This work modeled the farming process as a 75 year cycle to obtain one crop. At harvest, a total of almost 60 total tons per acre are felled, with a moisture content of 50%. During the felling, debarking, delimiting, piling, and chipping, 39% of the dry matter is lost. The harvesting requires 127,000 Btu of diesel fuel per dry ton felled. The relevant growth and harvest inputs are given in Table 4.

**TABLE 4 Key Parameters for Southern Pine (Johnson 2009)**

Parameter	Value
Felled yield	33.1 dry tons/acre
Dry matter loss during harvesting	39%
Effective biomass yield	20.2 dry tons/acre
Application rate of N	321 g/dry ton felled
Application rate of P <sub>2</sub> O <sub>5</sub>	54.4 g/dry ton felled
Harvest diesel consumption	127,000 Btu/dry ton felled

#### 3.2 FEEDSTOCK TRANSPORTATION

Pine chips are transported directly to the biorefinery via truck. During transport, 5% of the dry matter from the landing is lost. The chipped wood moisture content is still 50%. Heavy-duty trucks transport a distance of 50 miles at 6 miles per gallon of diesel with a payload of 12 dry tons of chips.

#### 3.3 FEEDSTOCK CONVERSION

All parameters for feedstock conversion (Table 5) are based on NREL process modeling. In the process, olivine serves as the heat transfer medium for the indirect gasification of the

biomass. Syngas (CO and H<sub>2</sub>) forms along with char and tar, which adhere to the olivine. The olivine is recovered and the char and tar are burned off with oxygen to reheat the olivine substrate. The syngas is converted to yield ethanol and mixed alcohols through a catalytic alcohol synthesis step. Table 5 details process inputs, including catalysts.

Mixed alcohols are separated in the plant into two products: a concentrated ethanol stream and a higher alcohol stream. Process energy and materials burdens are allocated between these two products in this analysis with the energy allocation method. This method was chosen because of the presence of multiple co-products in the higher alcohol stream (ethanol, propanol, butanol), for which it would be difficult to construct material and energy profiles to use in displacement allocation calculations. Additionally, the mixed alcohol co-product and ethanol have similar properties and end uses. These similarities make the energy allocation method attractive. For each product stream, the total process energy and materials consumption was multiplied by the fraction of the total energy content of biorefinery products in that stream. For example, the ethanol stream constitutes 88.3% of energy in biorefinery products and is assigned that percent of total process energy and materials inputs. The parameters in Table 6 are the gross inputs to the process, before allocation.

**TABLE 5 Key Parameters for Feedstock Conversion before Allocation (Tan 2012)**

Parameter	Value
Ethanol yield	82.9 gallons of ethanol/dry ton chips
Diesel consumed	2,190 Btu/mmBtu
NaOH consumed	309 g/mmBtu
Alcohol synthesis catalyst consumed	14.2 g/mmBtu
Tar reforming catalyst consumed	13.2 g/mmBtu
Olivine consumed	410 g/mmBtu
DEPG <sup>b</sup> consumed	1.3 g/mmBtu

<sup>a</sup> Dimethyl ether of polyethylene glycol

Many of the process inputs from Table 5 were not previously available in GREET. Material and energy flow data for these inputs were developed based on first principles and available data for catalysts, olivine, and DEPG. Material and energy data are in Table 6.

GREET contains material and energy data for the catalyst metals, with the exception of molybdenum. Copper and molybdenum are frequently co-mined, so the copper oxide data were used as a proxy for molybdenum oxide. The catalysts were assumed to be composed of the oxide form of the mineral. A processing step is constructed to transform the metal to the requisite catalyst, which usually consists of calcining. The energy consumed in this step was estimated based on a method from Dunn et al. (2012b) for heating where the acid synthesis catalyst was heated to 500°C and the tar reforming catalyst to 600°C.

The composition of the acid synthesis catalyst was approximated from U.S. Patent 4,882,360 (Stevens 1989). The acid synthesis catalyst was assumed to be composed (all percentages given by weight) of 12% molybdenum oxide, 2% potassium oxide, 11% cobalt oxide, and 68% carbon support. The remaining weight was assumed to be sulfur from hydrogen sulfide which displaces oxygen during chemical reduction of the surface. The structure of the tar reforming catalyst in Magrini-Bair, et al. (2007) was adopted. It was assumed to be composed of 5% nickel oxide, 4% potassium oxide, and 8% magnesium oxide on an 84% aluminum support (all percentages given by weight).

Olivine is a mineral form of magnesium-iron silicates. The raw ore needs very little processing to convert to olivine, so only inputs for mining, size reduction, and transportation are included. The energy data are summarized in Table 6.

DEPG is a specific form of polyethylene glycol with functional end groups that aid in capturing CO<sub>2</sub>. Energy data from an American Chemistry Council-sponsored life cycle assessment of polymers were used in this study for ethylene and the conversion of ethylene to ethylene oxide (Franklin Associates 2011). Ethylene production consumes oil and natural gas as feedstocks, the energy content of which is taken into account in the analysis. Ethylene oxide is then polymerized into polyethylene glycol. The processing energy for polymerization of polyethylene terephthalate was used as a representative example of this step.

**TABLE 6 Material and Energy Requirements for IG Process Inputs**

	Alcohol Synthesis Catalyst	Tar Reforming Catalyst	Olivine	DEPG <sup>a</sup>
Coal (mmBtu/ton)	0.06	4.21	0	0.96
Diesel (mmBtu/ton)	0.79	0.50	0.73	0.01
Residual oil (mmBtu/ton)	7.05	14.7	0.05	0
Electricity (mmBtu/ton)	4.38	2.44	2.43	1.23
Natural gas (mmBtu/ton)	15.7	22.9	0	18.0
Natural gas as feed (mmBtu/ton)				28.6
Oil as feed (mmBtu/ton)				5.80

<sup>a</sup> Cumulative inputs to make DEPG as the final product, with upstream production of ethylene, ethylene oxide, and processing energy to make each intermediate and the final product included.

### 3.4 FUEL TRANSPORTATION, DISTRIBUTION, AND USE

Parameters for the transportation, distribution, and use of the ethanol product in the IG pathway are identical to those for ethanol produced via the BC pathway as described in Section 2.4.

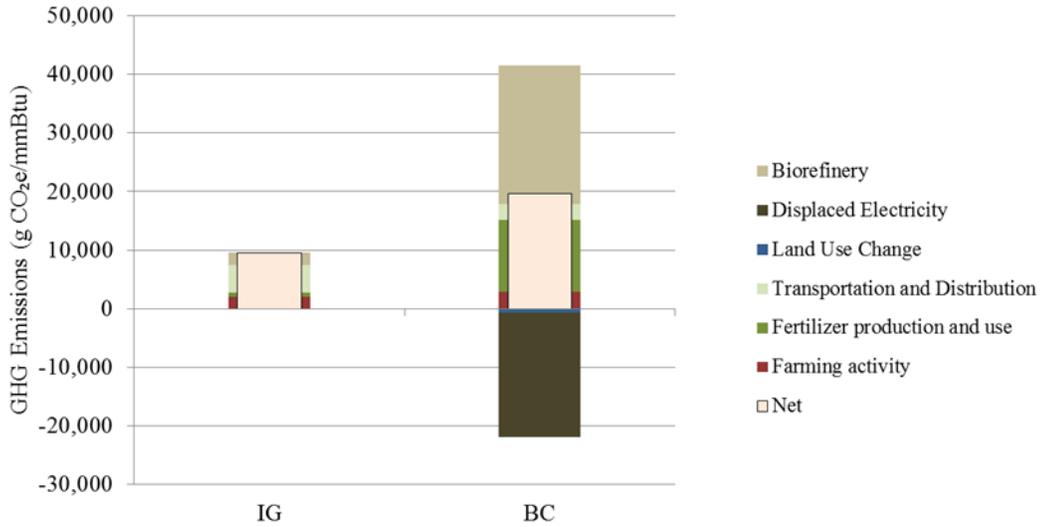
## 4 COMPARISON OF IG AND BC PATHWAYS TO ETHANOL

This report contains two routes to ethanol as described in Sections 2 and 3. In this section, we compare the GHG emissions of these two pathways from farm-to-pump. In addition, we examine fossil energy consumption, GHG emissions, and key air emissions of these routes over the full supply chain.

Figure 3 illustrates the contribution of individual steps to the farm-to-pump GHG emissions of the IG and BC pathways. The net GHG emissions for the IG and BC pathways are 9,527 and 19,631 g CO<sub>2</sub>e/mmBtu ethanol, respectively. Converted to a per MJ basis, these results are 9 and 19 g CO<sub>2</sub>e/MJ for the IG and BC pathways, respectively. GHG emissions in each step in the farm-to-pump stage of the supply chain are influenced by key activities or inputs. For example, results for the farming activity category in Figure 3 reflect GHG emissions from the combustion of fuel at the farming site. In the case of corn stover, this category includes land-use change (LUC) GHG emissions of -638 g CO<sub>2</sub>e/mmBtu (Dunn et al. 2013a, Dunn et al. 2013b). LUC GHG emissions associated with the production of farmed trees are not included in this analysis. There is some indication, however, that conversion of lands (specifically native forest or pastures) to pine plantations may decrease soil carbon by between 12-15% (Guo and Gifford 2002). Yet, the soil carbon impacts of pine plantations are strongly influenced by a number of variables including soil type, prior land use, and climate making a prediction of pine production's impact on soil carbon quite difficult without further research.

Fertilizer production and use has a minor impact on farm-to-pump GHG emissions in the case of the IG pathway because the southern pine trees used as a feedstock have minimal fertilizer inputs. In the case of the BC pathway, emissions from fertilizer production are the second largest source of emissions.

The biorefinery category in Figure 3 represents emissions that occur in the conversion facility from the combustion of process fuels and from the production of process inputs (e.g., chemicals such as H<sub>2</sub>SO<sub>4</sub>). Biorefinery emissions are greater for the BC pathway, in large part because more process inputs (9,807 g/mmBtu ethanol) are consumed in this pathway than in the IG pathway (2,938 g/mmBtu). For the BC pathway, the contribution of process inputs (including enzymes) dominates the GHG emissions from the biorefinery (71%). NaOH, CaO, and NH<sub>3</sub> make up 40% of the process input contribution to biorefinery GHG emissions, while enzymes make up 33% of the process input contribution. This result is logical because NH<sub>3</sub> is very carbon-intensive to produce and NaOH and CaO are among the process inputs with the highest consumption rates. The BC pathway includes the provision of surplus electricity to the grid, which is modeled as displacing the equivalent amount of electricity as provided by the U.S. grid (Table 3). The CO<sub>2</sub> credit attributed to the displacement of conventional electricity is -21,235 g CO<sub>2</sub>e/mmBtu.

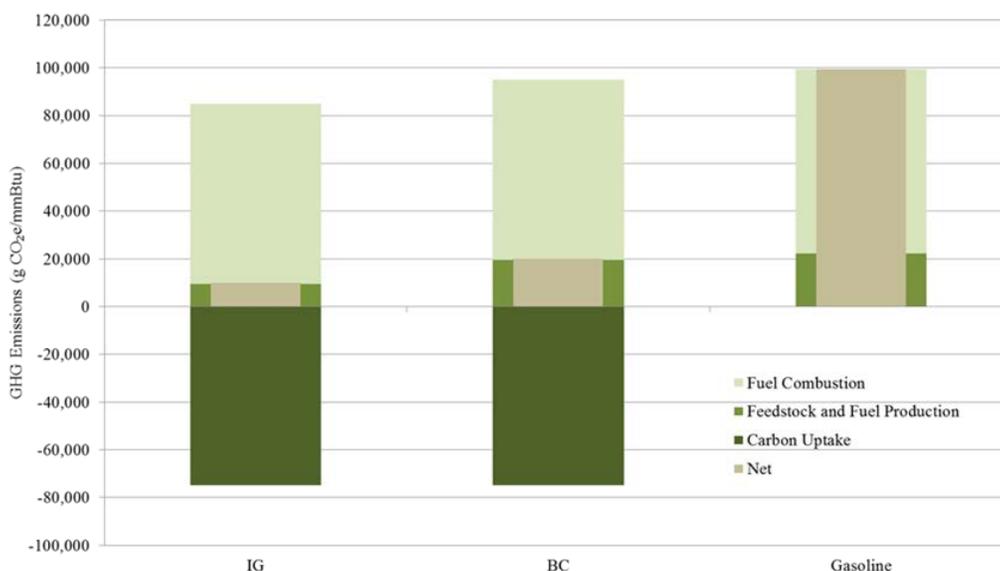


**FIGURE 3 Breakdown of Farm-to-Pump GHG Emissions in the BC and IG Pathways**

The transportation and distribution category in Figure 3 is comprised of two steps, the transport of feedstock to the biorefinery and the transportation and distribution of the final ethanol product to fueling stations. Compared to the BC pathway, the feedstock transportation step for the IG pathway is more GHG-intensive because of a longer transport distance and a lighter payload.

From an examination of Figure 3 it is clear that the main drivers of the farm-to-pump GHG results are the biorefinery and fertilizer production and use in the BC pathway. The production of cellulosic feedstocks is a relatively new endeavor and appropriate fertilizer application rates are still under development (e.g., Avila-Segura et al. 2011, Karlen 2010). It is possible that optimization of fertilizer use will reduce application rates for both corn stover production and tree production. Likewise, energy and material inputs to biorefineries may decrease as these technologies mature.

Figure 4 contains the full supply chain GHG emissions for the BC and IG pathways and compares them to supply chain results for gasoline production. In this figure, the feedstock and fuel production bars represent all supply chain stages up to delivering the fuel to a fueling station (see Figure 1). The fuel combustion bars represent the pump-to-wheels, or use stage, of the fuel. The CO<sub>2</sub> consumed by feedstocks during growth is represented by the carbon uptake bars. The figure also shows the net GHG emissions for each fuel. The BC and IG pathways achieve 80% and 90% reductions, respectively, in comparison to baseline gasoline. For the BC pathway, if the grid displaced were the California grid, which, with only 8% coal, is less carbon-intensive than the national average grid, the BC pathway would achieve a 73% reduction against conventional gasoline.

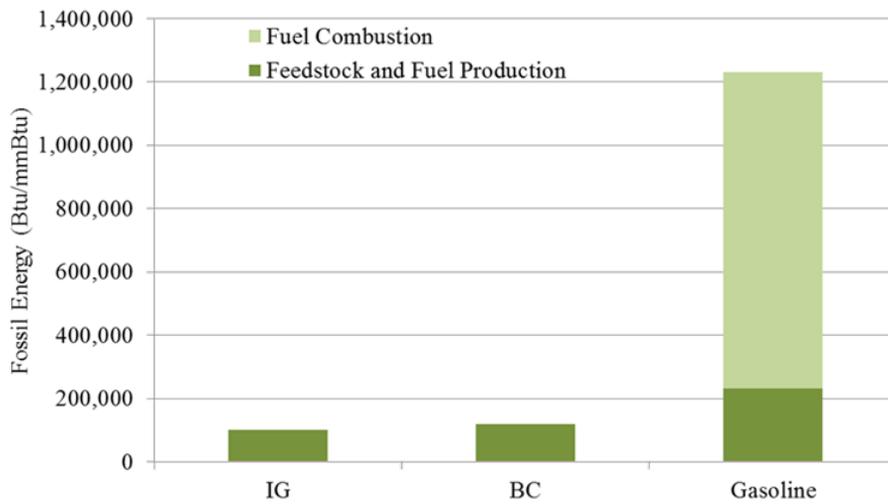


**FIGURE 4 Supply Chain and Use Stage GHG Emissions for IG, BC, and Gasoline Pathways**

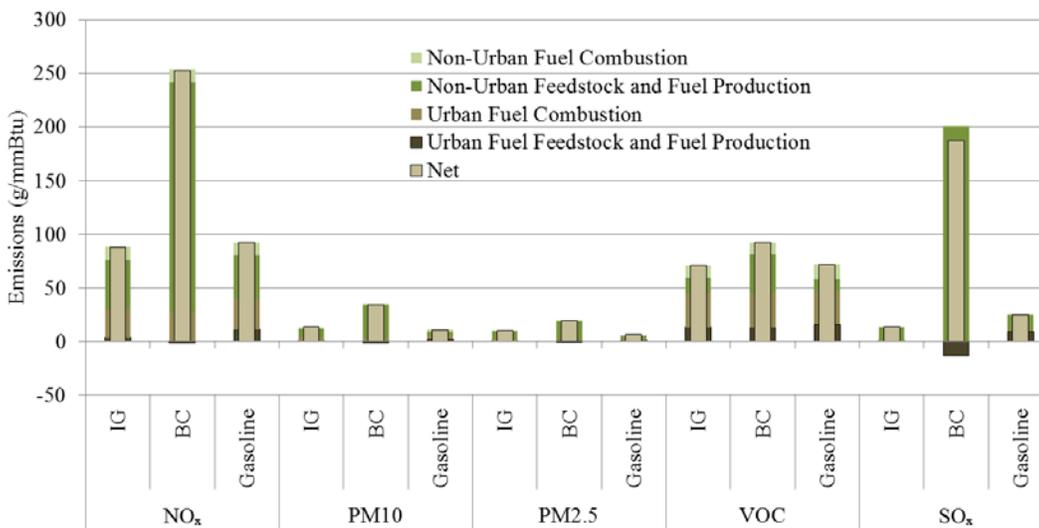
As expected, Figure 5 illustrates that the supply chains for both ethanol pathways, which start with non-fossil feedstocks, consume less fossil energy than the gasoline supply chain.

Figure 6 contains supply chain emissions of NO<sub>x</sub>, PM<sub>10</sub>, PM<sub>2.5</sub>, VOC, and SO<sub>x</sub> for biofuel pathways and gasoline. Negative emissions are essentially a credit for the displacement of NO<sub>x</sub> and SO<sub>x</sub> emissions associated with conventional electricity. Total biofuel supply chain PM<sub>10</sub>, PM<sub>2.5</sub>, and VOC emissions are slightly higher than those for gasoline although urban emissions are lower for the two biofuel pathways. Urban emissions are a key metric because they indicate levels of pollutants that densely-populated areas will experience. Total NO<sub>x</sub> and SO<sub>x</sub> emissions are notably higher for the BC pathway. For both pathways, urban NO<sub>x</sub> and SO<sub>x</sub> emissions are lower than the conventional fuel pathway.

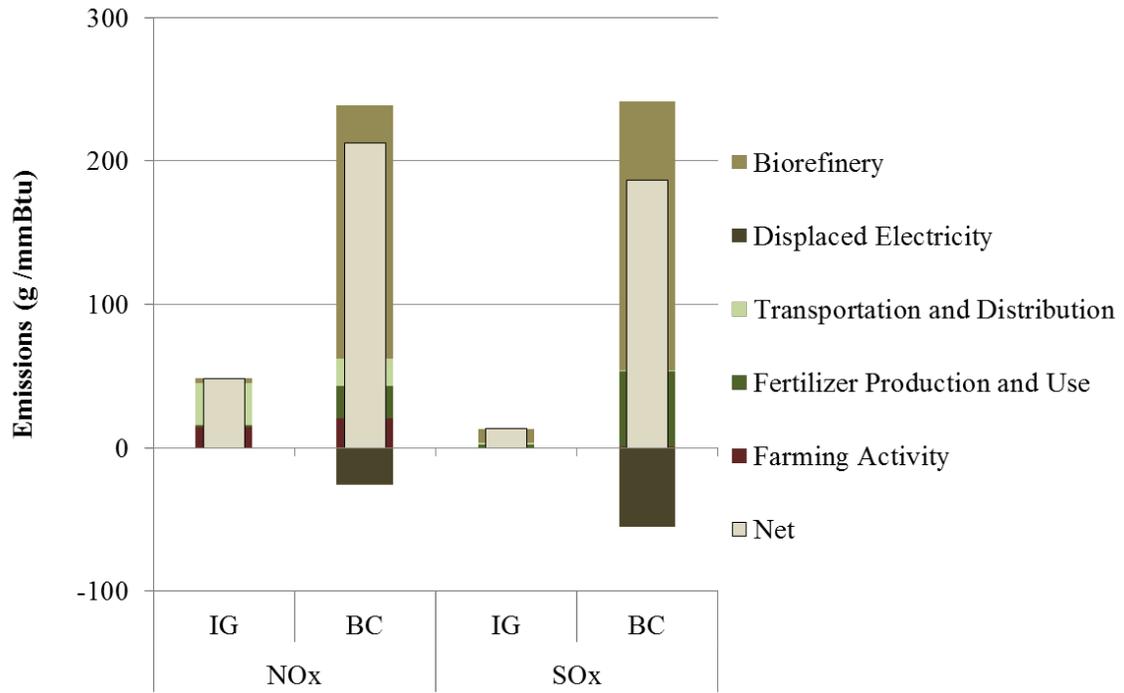
Figure 7 shows the contributions of steps in the biofuel pathways to supply chain NO<sub>x</sub> emissions. For the BC pathway, NO<sub>x</sub> emissions at the biorefinery are the most significant contributor. 82% of BC ethanol biorefinery NO<sub>x</sub> emissions are from combustion of lignin to generate steam and power. The bulk of biorefinery NO<sub>x</sub> emissions in the IG pathway come from combustion of woody feedstock. For this pathway, SO<sub>x</sub> emissions are slightly less than those for gasoline. In contrast, BC total SO<sub>x</sub> emissions, the bulk of which occur in non-urban areas, exceed those for gasoline. 69% of these emissions stem from process inputs, with sulfuric acid as the most SO<sub>2</sub>-intensive. The combustion of lignin contributes 31% of biorefinery SO<sub>x</sub> emissions. It is possible biorefinery air emissions could be reduced through additional air pollution control devices. Operation of these devices consumes energy and material inputs (Kaliyan et al. 2011), however, so the full supply chain impacts of these air pollution control strategies must be integrated into the analysis before their merits can be accurately assessed. Further, air emissions from biomass combustion and gasification are subject to ongoing research. Air emissions results should therefore be considered preliminary.



**FIGURE 5 Supply Chain Fossil Energy Consumption in the IG, BC, and Gasoline Pathways**



**FIGURE 6 Supply Chain Air Pollutant Emissions in the IG, BC, and Gasoline Pathways**



**FIGURE 7 Breakdown of Farm-to-Pump NO<sub>x</sub> and SO<sub>x</sub> Emissions in the IG and BC Pathways**

## 5 PYROLYSIS OF HYBRID POPLAR TO HYDROCARBON FUELS

The third pathway in this analysis produces a hydrocarbon fuel rather than ethanol. The feedstock is a short rotation woody crop (SRWC), hybrid poplar. Pyrolysis of the feedstock results in a bio-oil which is then upgraded to gasoline and diesel. The following sections outline the pathway and key inputs to the supply chain sustainability analysis.

### 5.1 FEEDSTOCK PRODUCTION

The feedstock for this pathway is hybrid poplar, a SRWC. Table 7 contains the key parameters for the feedstock production stage. The nitrogen fertilizer application rate reflects an amortization of the annual application rate (9,300 g/acre) over six years. The analysis accounts for direct and indirect N<sub>2</sub>O emissions from fertilizer application to soil. A herbicide, glyphosate, is applied at a level of 430 g/acre in the first year of the production cycle. Diesel fuel is consumed during poplar harvest. Although some dry matter loss may occur during chipping or other processing of the poplar at the production site, the impacts of this dry matter loss are not included in the analysis. 5% dry matter loss during storage is included, however, and increases the amount of poplar that must be harvested to meet biorefinery demand, augmenting the impacts of fertilizer application and harvest energy consumption on the supply chain.

**TABLE 7 Key Parameters for Hybrid Poplar Agriculture (Volk 2010, Searcy and Hess 2010)**

Parameter	Value
Production cycle	7 years
Yield in 7 <sup>th</sup> year	39 dry tons/acre
Amortized nitrogen fertilizer application rate	1,431 g/dry ton
N <sub>2</sub> O conversion rate of N fertilizer	1.525% (Wang et al. 2012)
Herbicide application rate	11 g/dry ton
Harvest energy consumption	337,440 Btu/dry ton
Dry matter loss during storage	5%

### 5.2 FEEDSTOCK TRANSPORTATION

Key parameters associated with feedstock transportation are summarized in Table 8. At this time, no dry matter loss is assumed to occur between the farm field and the biorefinery.

**TABLE 8 Feedstock Transportation Key Parameters**

Parameter	Value
Transportation distance	50 miles
Heavy-duty truck fuel economy	6 miles/diesel gallon
Payload	9.9 dry tons <sup>a</sup>

<sup>a</sup> 30% moisture content

### 5.3 FEEDSTOCK CONVERSION

The feedstock conversion stage consists of three integrated steps: pyrolysis, hydrotreating, and hydrocracking. The high-temperature pyrolysis step produces bio-oil and biochar. When the biochar is combusted, heat and electricity are produced and used within the process. The hydrotreating step reduces the oxygen content in the bio-oil, rendering it stable. The gasoline and diesel fractions are then separated from the hydrotreated bio-oil and the heavies are cracked into diesel range components using a conventional hydrocracking process. Both the hydrotreating and hydrocracking steps consume hydrogen which is obtained from steam reforming of offgas from hydrocracking and supplementary natural gas.

Table 9 contains key parameters used in the analysis of this supply chain step, including process air emissions (e.g., air emissions from sources other than combustion) of CO and CH<sub>4</sub>. These process emissions are very small when compared to emissions of these compounds from combustion. It should be noted that hydrotreating, hydrocracking, and reforming catalysts are also used in the conversion process. Of these, the process consumes the hydrotreating catalyst at the highest rate (0.02 lb catalyst/lb main product). In the petroleum refining industry, hydrotreating catalysts are often composed of cobalt, nickel, and/or molybdenum oxides (Lloyd 2011). The composition of hydrotreating catalysts used in the upgrading of bio-oils is subject to ongoing research, in large part because a stable, effective catalyst for this key process stage is one major factor that will determine the economic success of the technology (Arbogast et al. 2013). Recent reports of catalysts used to upgrade bio-oils to hydrocarbon fuels report use cobalt- and nickel-molybdenum catalysts (Wright et al 2010, Jones et al. 2009).

To include catalysts in the SCSA, the cradle-to-gate impacts of preparing the catalyst must be calculated from the intensity of preparing the catalyst from its component parts. For example, if the catalyst contains nickel, its cradle-to-gate energy consumption would include the energy consumed to mine and smelt the nickel. Importantly, the net consumption rate of the catalyst must be known. This rate will be influenced by the lifetime of the catalyst as well as its ability to be regenerated and/or recycled. Catalyst regeneration and recycling consume energy and materials that must also be included in the analysis. For example, the regeneration of hydrotreating catalysts at petroleum refineries consumes hydrogen (Lloyd 2011). These catalysts can become contaminated with metal deposits such as vanadium and nickel that could be recovered through hydrometallurgical, pyrometallurgical, or other process that could consume significant amounts of energy and materials such as sulfuric acid. If metals recovered from catalysts can be used elsewhere, they could displace the production of virgin materials, which

would influence SCSA results. At this time, these aspects of the hydrotreating catalyst are uncertain and so it is excluded from the SCSA. It is expected that as research continues on catalyst development for the upgrading of bio-oils, future SCSAs will include hydrotreating catalyst impacts. Impacts for the other catalysts are likely small because they are consumed at rates several orders of magnitude below that of the hydrotreating catalyst. These catalysts may also be incorporated in future SCSAs of pyrolysis pathways to hydrocarbon fuels.

Prior to being fed to the pyrolysis reactor throat, the woody feedstock undergoes grinding and drying at a site adjacent to the conversion facility. The analysis includes the electricity consumed in this feedstock processing step. Conversion step impacts are divided between gasoline and diesel biorefinery products with the energy allocation method because the two products have similar end uses.

**TABLE 9 Pyrolysis Process Key Parameters (Snowden-Swan 2012)**

Parameter	Value
Electricity consumed during feedstock production	330 Btu/lb main product
Mass dry feedstock/mass main product	4.11
Electricity consumed in pyrolysis process	630 Btu/lb main product
Natural gas consumed to produce hydrogen	1,840 Btu/lb main product
Volumetric share of gasoline produced	53%
Volumetric share of diesel produced	47%
Process emissions of CO	0.0003 g/lb liquid fuel
Process emissions <sup>a</sup> of CH <sub>4</sub>	0.04 g/lb liquid fuel
Process emissions of CO <sub>2</sub> from methane reforming <sup>b</sup>	134 g/lb liquid fuel

<sup>a</sup> From wastewater stream in hydrotreating step

<sup>b</sup> Stoichiometric amount

## 5.4 FUEL TRANSPORTATION, DISTRIBUTION, AND USE

The distribution stage for hydrocarbon fuels differs slightly from ethanol distribution. Hydrocarbon fuels are compatible with existing infrastructure and can be transported via pipeline. Key parameters for this stage that are unique to the pyrolysis pathway are in Table 10.

**TABLE 10 GREET Parameters for Renewable Hydrocarbon Fuel Distribution**

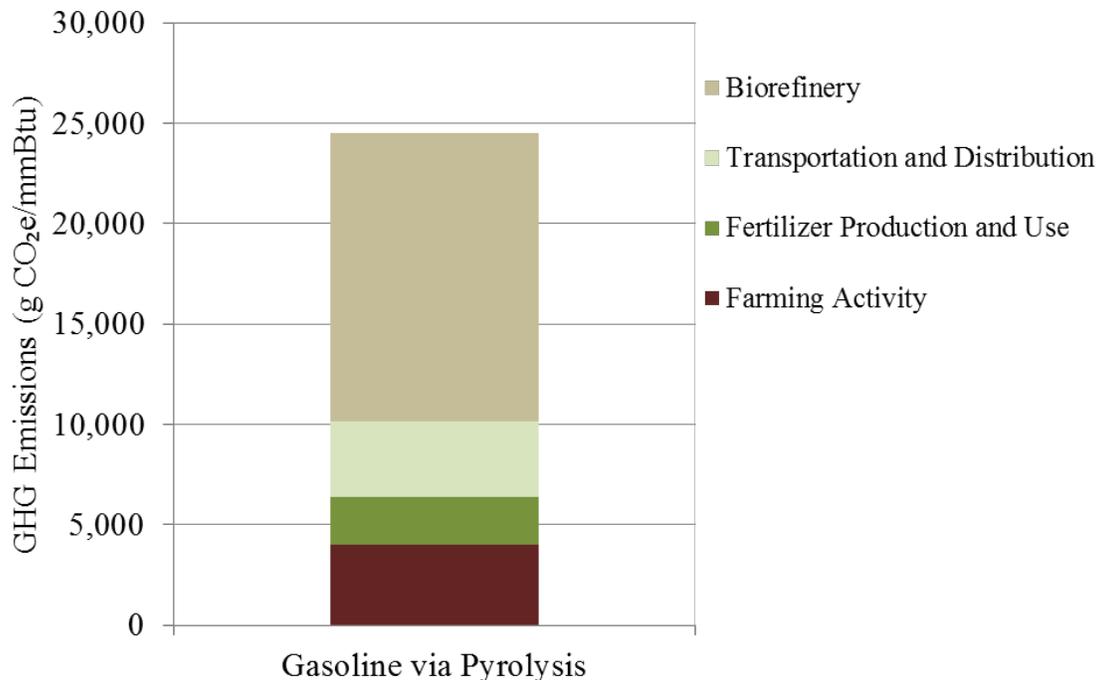
Parameter	Pyrolysis Gasoline or Diesel		
	Barge	Pipeline	Rail
Share of mode for transportation to terminal	8.0%	63%	29%
Transport distance for transportation to terminal	520 miles	400 miles	800 miles
Payload	20,000 tons	NA	NA
Energy intensity of pipeline transportation <sup>b</sup>	253 Btu/ton-mile		
Transportation distance between bulk terminal and fueling station, traveled by truck	30 miles		

<sup>a</sup> Energy intensity of other modes of transportation discussed in Section 2.4

## 5.5 PYROLYSIS PATHWAY RESULTS

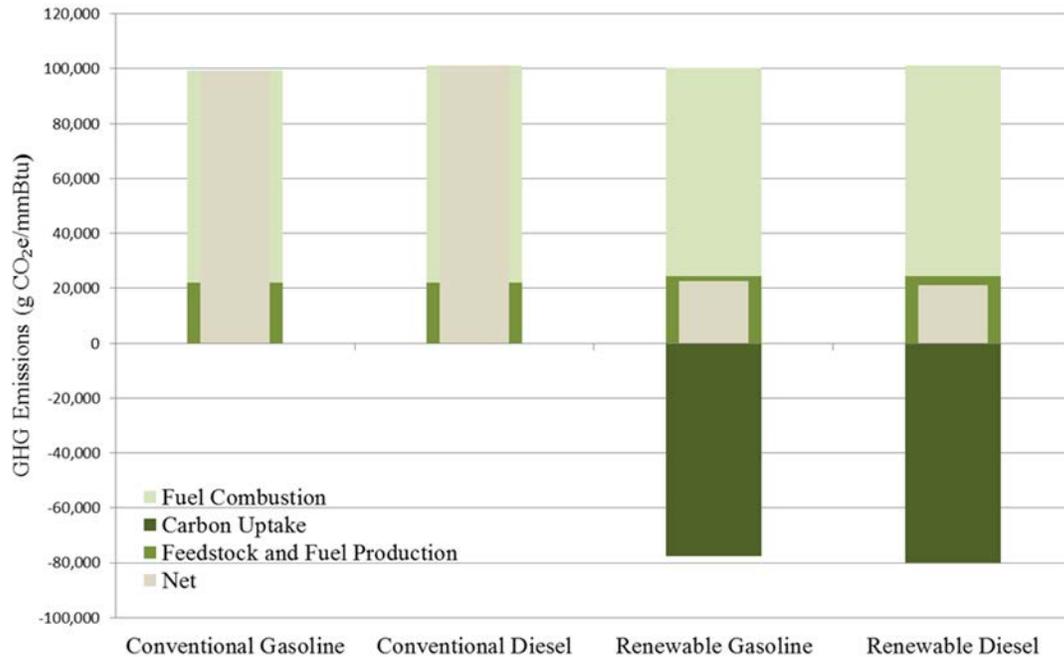
Figure 8 shows the contribution of four steps in the supply chain of pyrolysis-derived gasoline to farm-to-pump GHG emissions. (The breakdown is nearly identical for pyrolysis diesel.) The largest contributor (59%) is emissions from the biorefinery. 44% of biorefinery CO<sub>2</sub> emissions are from the steam methane reforming process, which produces CO<sub>2</sub> in addition to H<sub>2</sub> from methane and steam. 45% of the biorefinery CO<sub>2</sub> emissions are from electricity consumption at the biorefinery. The balance of CO<sub>2</sub> emissions are from natural gas production before delivery to the biorefinery. Feedstock production also is a significant contributor (16%) to farm-to-pump GHG emissions.

LUC GHG emissions are not included for this pathway. Guo and Gifford (2002), from a meta analysis of land use change impacts on soil carbon stocks, conclude that converting cropland to SRWC plantations can increase soil carbon by approximately 10% to 22%. Arevelo et al. (2011) report that land previously used to grow canola that was converted to poplar production returned to its pre-conversion carbon level after seven years. Other studies have found this break-even point to lie between 8 and 15 years depending on prior land use, climate, and other factors. Guo and Gifford (2002) concluded, however, that conversion of forest or pasture land to SRWC plantations can decrease soil carbon by up to -22%. Further analysis is necessary to quantify direct LUC GHG emissions from the production of hybrid poplar as a pyrolysis feedstock.



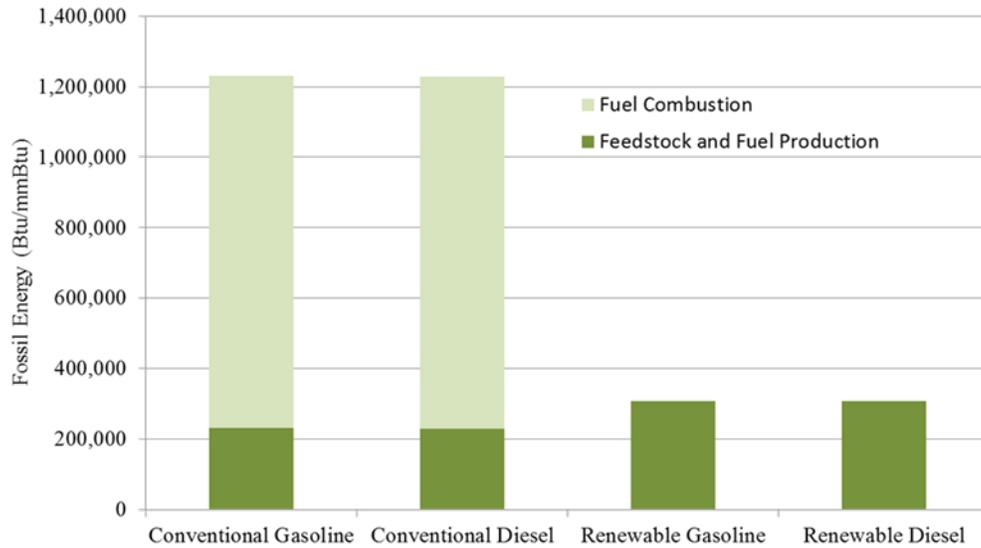
**FIGURE 8 Breakdown of Farm-to-Pump GHG Emissions in the Pyrolysis-Derived Gasoline Pathway**

Figure 9 displays the supply chain GHG emissions for pyrolysis gasoline and diesel, which, as a result of calculating impacts with the energy allocation method, are essentially identical, in comparison to supply chain GHG emissions for conventional gasoline and diesel. The pyrolysis-derived gasoline and diesel achieve a 77% and a 79% reduction in GHG emissions, respectively, as compared to the conventional fuels.

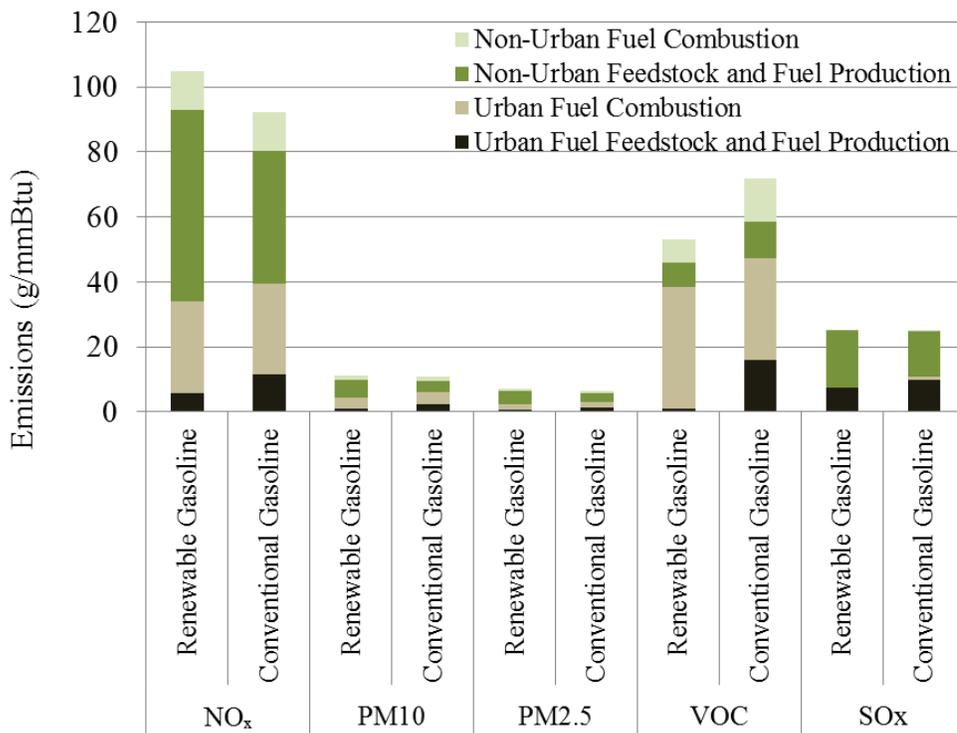


**FIGURE 9 Supply Chain GHG Emissions for Pyrolysis-Derived and Conventional Gasoline and Diesel**

As expected, the supply chain of pyrolysis-derived fuels consumes less fossil energy because the feedstock is non-fossil (Figure 10). As in the case of the ethanol pathways, an analysis of supply chain air emissions (Figure 11) reveals that total NO<sub>x</sub> emissions are higher in the case of the biofuel than for the conventional fuel, although urban emissions are lower. Total supply chain emissions of VOC and SO<sub>x</sub> are lower in the case of the biofuel. Total PM<sub>10</sub> and PM<sub>2.5</sub> emissions are slightly higher through the supply chain for pyrolysis gasoline than for conventional gasoline. For both of these pollutants, urban PM emissions are lower.

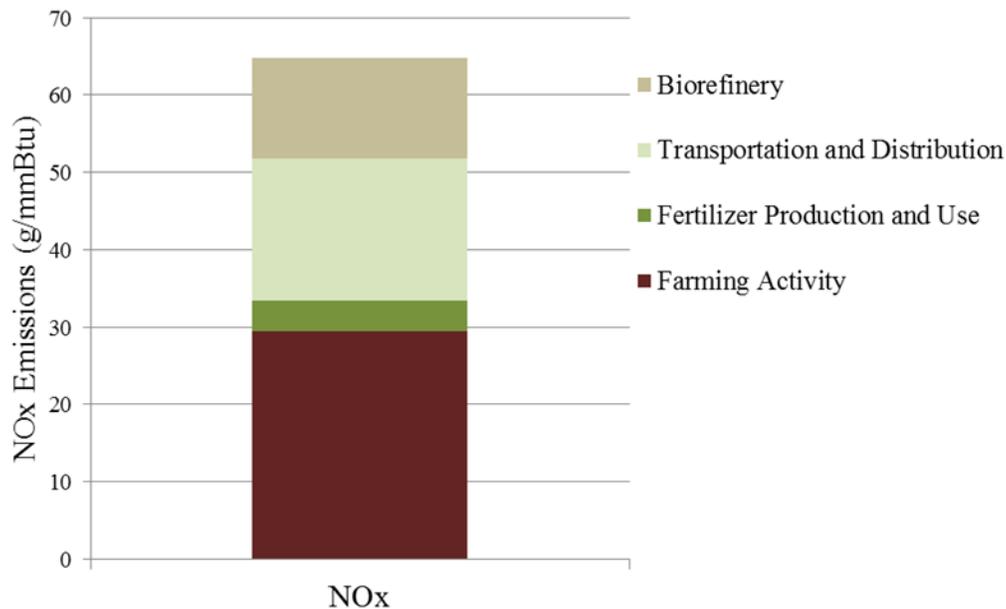


**FIGURE 10 Supply Chain Fossil Fuel Consumption for Pyrolysis-Derived and Conventional Gasoline and Diesel**



**FIGURE 11 Air Pollutant Emissions in the Pyrolysis-Derived and Conventional Gasoline Pathways**

Supply chain NO<sub>x</sub> emissions for pyrolysis gasoline are broken down in Figure 12. The main contributor (45%) is the feedstock production stage, due to combustion of diesel fuel. Transportation and distribution of feedstock and fuels is the second largest contributor (28%). It should be noted that at this time, air emissions from the pyrolysis pathway do not include NO<sub>x</sub> or other emissions from biochar combustion. Emissions from biochar combustion have not been studied beyond a handful of biochar model compound combustion studies (Darvell et al. 2013, Williams et al. 2012). No NO<sub>x</sub> emissions factors for biochar combustion have been published although Darvell et al. (2013) report a NO emissions:biochar N content ratio ranging between 0.22 and 0.60. The authors state, however, that these values are not absolute, but rather for comparison among the studied model compounds. Biochar likely has an N content of about 0.5 wt% (Han et al. 2013). If half of biochar NO<sub>x</sub> were to convert to NO upon combustion, NO<sub>x</sub> emissions would be nearly 70 g NO/mmBtu, which would effectively double the result in Figure 12. It is premature to assign a value to these emissions, which are dependent on feedstock composition and reaction conditions, in this analysis but it will be important to evaluate them in the future.



**FIGURE 12 Breakdown of NO<sub>x</sub> Emissions in the Pyrolysis Gasoline Pathway**

## 6 CONCLUSIONS

The three pathways considered in this report offer significant GHG emissions and fossil energy consumption reductions from a supply chain perspective when compared to their fossil fuel counterparts. Research and development efforts to further reduce life-cycle GHG emissions from these processes could focus on reduced consumption of process inputs, especially  $\text{NH}_3$ , in the case of the BC pathway. More efficient agriculture that requires lower nitrogen fertilizer input would also benefit that pathway's GHG emissions. For the IG pathway, efforts to improve transportation and distribution of the feedstock in addition to optimizing farming energy usage in feedstock (southern pine) production will serve to reduce life-cycle GHG emissions. Finally, research and development efforts to reduce life-cycle GHG emissions from the pyrolysis process should focus on reducing  $\text{H}_2$  demand and electricity consumption in the conversion stage to the extent possible.

Considering air pollutant emissions, biofuel pathways do not always offer reductions in total  $\text{NO}_x$  and  $\text{SO}_x$  emissions as compared to conventional gasoline. Urban air pollutant emissions, however, are consistently lower in biofuel pathways than in conventional fuel pathways. The main source of  $\text{NO}_x$  and  $\text{SO}_x$  emissions for both ethanol pathways is the biorefinery and it is possible that pollution control technologies implemented at these refineries could significantly reduce these emissions. The pyrolysis pathway has supply chain GHG emissions slightly exceeding those for the ethanol pathway. Its  $\text{NO}_x$  and  $\text{SO}_x$  emissions, however, are comparable to the IG pathway and lower than the BC pathway.

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