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# Well-to-Wheels Analysis of Fast Pyrolysis Pathways with GREET

**Energy Systems Division** 

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by

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## NOTATION

C	carbon
CAPDET	calcium carbonate Computer, Assisted Procedure for Design and Evaluation of Wastewater
CAIDEI	Treatment Systems
$CH_4$	methane
CHP	combined heat and power
CO	carbon monoxide
$CO_2$	carbon dioxide
DOE	U.S. Department of Energy
EERE	Office of Energy Efficiency and Renewable Energy (DOE)
EIA	Energy Information Administration (DOE)
EPA	U.S. Environmental Protection Agency
FBR	fluidized-bed reactor
FT	Fischer-Tropsch
gCO <sub>2</sub> -e	gram(s) of CO <sub>2</sub> -equivalent
GHG	greenhouse gas
GREET	Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation
	(model)
H <sub>2</sub>	hydrogen
INL	Idaho National Laboratory
ISU	Iowa State University
К	potassium
K <sub>2</sub> O	potash
LCA	liquefied patroloum gas
LPG	inqueined petroleum gas
mpg	mile(s) per gallon
mmBtu	million Btu
MT	metric ton(s)
Ν	nitrogen
NG	natural gas
NH <sub>3</sub>	ammonia
NH <sub>2</sub> CONH <sub>2</sub>	urea
NH <sub>4</sub> NO <sub>3</sub>	ammonium nitrate

nitrous oxide
National Renewable Energy Laboratory
phosphorus
Pacific Northwest National Laboratory
phosphate
pump to wheels
steam methane reforming
sulfur oxides
weight percent
well to pump
well to wheels

### WELL-TO-WHEELS ANALYSIS OF FAST PYROLYSIS PATHWAYS WITH THE GREET MODEL

by

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#### ABSTRACT

The pyrolysis of biomass can help produce liquid transportation fuels with properties similar to those of petroleum gasoline and diesel fuel. Argonne National Laboratory conducted a life-cycle (i.e., well-to-wheels [WTW]) analysis of various pyrolysis pathways by expanding and employing the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model. The WTW energy use and greenhouse gas (GHG) emissions from the pyrolysis pathways were compared with those from the baseline petroleum gasoline and diesel pathways. Various pyrolysis pathway scenarios with a wide variety of possible hydrogen sources, liquid fuel yields, and co-product application and treatment methods were considered. At one extreme, when hydrogen is produced from natural gas and when bio-char is used for process energy needs, the pyrolysis-based liquid fuel yield is high (32% of the dry mass of biomass input). The reductions in WTW fossil energy use and GHG emissions relative to those that occur when baseline petroleum fuels are used, however, is modest, at 50% and 51%, respectively, on a per unit of fuel energy basis. At the other extreme, when hydrogen is produced internally via reforming of pyrolysis oil and when bio-char is sequestered in soil applications, the pyrolysis-based liquid fuel yield is low (15% of the dry mass of biomass input), but the reductions in WTW fossil energy use and GHG emissions are large, at 79% and 96%, respectively, relative to those that occur when baseline petroleum fuels are used. The petroleum energy use in all scenarios was restricted to biomass collection and transportation activities, which resulted in a reduction in WTW petroleum energy use of 92–95% relative to that found when baseline petroleum fuels are used. Internal hydrogen production (i.e., via reforming of pyrolysis oil) significantly reduces fossil fuel use and GHG emissions because the hydrogen from fuel gas or pyrolysis oil (renewable sources) displaces that from fossil fuel natural gas and the amount of fossil natural gas used for hydrogen production is reduced; however, internal hydrogen production also reduces the potential petroleum energy savings (per unit of biomass input basis) because the fuel yield declines dramatically. Typically, a process that has a greater liquid fuel yield results in larger petroleum savings per unit of biomass input but a smaller reduction in life-cycle GHG emissions. Sequestration of the large amount of bio-char co-product (e.g., in soil applications) provides a significant carbon dioxide credit, while electricity generation from biochar combustion provides a large energy credit. The WTW energy and GHG

emissions benefits observed when a pyrolysis oil refinery was integrated with a pyrolysis reactor were small when compared with those that occur when pyrolysis oil is distributed to a distant refinery, since the activities associated with transporting the oil between the pyrolysis reactors and refineries have a smaller energy and emissions footprint than do other activities in the pyrolysis pathway.

#### **1 INTRODUCTION**

As the global population and economy continue to grow, so, too, will the demand for energy. According to the Energy Information Administration (EIA) in the U.S. Department of Energy (DOE), the worldwide transportation sector has been relying solely on petroleum, consuming more than 50% of global world oil production (EIA 2010). In terms of demand, the United States is the top oil-importing country. Two major issues facing the transportation sector in the United States, as well as in other major countries, are energy security and environmental sustainability. The United States imported about 49% of the crude oil and refined petroleum products that were consumed during 2010 (EIA 2011). Moreover, according to the U.S. Environmental Protection Agency (EPA 2011), greenhouse has (GHG) emissions from the transportation sector represent about 26% of U.S. total GHG emissions. To address these issues, the Energy Independence and Security Act of 2007 (EISA) mandated the production of 21 billion gal of advanced biofuel (whose life-cycle GHG emissions reduction exceeds 50% relative to the total life-cycle emissions of the corresponding baseline petroleum fuel) and the production of 15 billion gal of conventional biofuel (whose life-cycle GHG emissions reduction achieves at least 20% relative to the total life-cycle GHG emissions of baseline petroleum fuel) by 2022 (U.S. Congress 2007).

Fast pyrolysis could play an important role in bio-fuel production because the upgrading and refining of pyrolysis oil produces a mixture of naphtha-range products (gasoline blend stock) and diesel-range products (diesel blend stock) that are compatible with the current transportation fuel distribution infrastructure and current vehicle technologies. Fast pyrolysis is performed under a range of temperatures and short residence times in the reactor to maximize the liquid hydrocarbon yield (Figure 1). This process contrasts with the much slower gasification process, which provides a high yield of fuel gas that can be synthesized into liquid fuel (e.g., via the Fischer-Tropsch [FT] process). In order to fully assess the potential energy and GHG emissions benefits of the fast-pyrolysis-based liquid fuels compared with those benefits from the use of conventional petroleum fuels, this study performs a complete life-cycle analysis (LCA) of the fast pyrolysis pathway, going from the collection of cellulosic biomass feedstock to the production of liquid fuels and their use in vehicles.

Liquid fuel production via the fast pyrolysis of biomass is described in numerous sources. An excellent and extensive review of the fast pyrolysis of biomass and product upgrading is presented by Mohan et al. (2006) and Bridgwater (2011). Bulushev and Ross (2011) reviewed and compared catalytic conversion processes for biomass, such as pyrolysis, gasification, hydrotreating, hydrocracking, and esterification. This report relies on two sources for data on pyrolysis and the upgrading process: (1) a techno-economic analysis of the fast pyrolysis of corn stover to liquid fuels conducted by Iowa State University (ISU), ConocoPhilips, and National Renewable Energy Laboratory (NREL) (Wright et al. 2010) and (2) a design case study of the fast pyrolysis of forest residue to gasoline and diesel fuel conducted by Pacific Northwest National Laboratory (PNNL) (Jones et al. 2009). Both sources offer designs for the complete process, going from cellulosic biomass to ready-to-blend fuels in the gasoline and diesel ranges.



**FIGURE 1** Yields from Fast, Intermediate, and Slow Pyrolysis and Gasification (Bridgwater 2007)

#### 1.1 WELL-TO-WHEELS ANALYSIS WITH THE GREET MODEL

The terms "life cycle," "fuel cycle," and "WTW" are used interchangeably in the LCA literature. The term "life cycle" (or an LCA) typically includes all the stages of a product's life, from the extraction of raw materials through the materials' processing, manufacturing, distribution, use, and disposal or recycling. The term "fuel cycle" accounts for all the stages in the entire fuel cycle, including feedstock recovery and transportation, fuel production and transportation, and fuel consumption at any end use. The term "WTW" is similar to "fuel cycle" but is more pertinent to the assessment of transportation fuels for use in vehicles. The WTW pathway for petroleum, shown in Figure 2, includes exploration and recovery, petroleum transportation and storage, gas venting and flaring, and refining, and it incorporates nonpetroleum inputs to the petroleum life cycle, such as natural gas (NG), methanol, and ethanol. The exploration and recovery activities (from the well) to the fuel production and transportation activities (to the pump) constitute the well-to-pump (WTP) stage. The combustion of fuel for vehicle operation constitutes the pump-to-wheels (PTW) stage. The combination of these two stages constitutes the well-to-wheels (WTW) cycle.

This study employs the GREET (Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation) model developed by Argonne National Laboratory with the support of several programs in DOE's Office of Energy Efficiency and Renewable Energy (EERE). GREET is structured to systematically examine the WTW energy use and emissions associated with a wide range of vehicle technologies and feedstock sources for producing alternative fuels (Brinkman et al. 2005).



FIGURE 2 Well-to-Wheels Pathway for Petroleum Gasoline

## 1.2 STUDY SCOPE AND REPORT ORGANIZATION

This report summarizes the LCA of the pyrolysis of corn stover and forest residue and subsequent upgrading of pyrolysis oil to produce renewable gasoline and diesel fuels. It describes the pathways, feedstock characteristics, and conversion processes; assesses key material inputs and energy efficiencies of conversion processes; addresses co-products and process emissions; and presents WTW results.

The report is organized into seven sections. Following this brief introduction, Section 2 describes the details of pyrolysis and upgrading processes used in this study. Section 3 discusses the availability, characteristics, collection, and transport of biomass feedstock. Section 4 discusses WTW pathways, their key stages, and important features of the WTW analysis. Sections 5 and 6 present results on WTW energy use and GHG emissions, followed by conclusions. Section 7 lists the references. WTW results for pyrolysis-based renewable diesels per million Btu (mmBtu) of fuels are presented in the appendix.

#### 2 PYROLYSIS AND PRODUCT UPGRADING

The production of liquid fuels via fast pyrolysis can be divided into two main processes:

- *Pyrolysis oil production*. In this first step, the incoming biomass undergoes fast decomposition in the absence of oxygen to produce pyrolysis oil. The pyrolysis oil is separated into light and heavy phases.
- *Stable oil upgrading.* The pyrolysis oil is unstable and has a high oxygen and water content. Phase separation and polymerization may occur if it is stored for an extended period of time under wide temperature fluctuations. Thus, stabilization of pyrolysis oil is required. Pyrolysis oil can be stabilized by reducing its oxygen content via hydrotreatment. Further hydroprocessing (upgrading) of the pyrolysis oil, possibly including a hydrocracking step, is necessary to produce liquid fuels, such as gasoline and diesel. When the upgrading process is integrated with the pyrolysis reactor in the same facility, the pyrolysis oil can concurrently be stabilized and upgraded. The final step of the upgrading process is the separation of the liquid product into different fuels with the desired boiling ranges, nominally naphtha-range (gasoline) and distillate (diesel).

The upgrading of pyrolysis oil requires a significant amount of hydrogen for the hydrotreating and hydrocracking process. Hydrogen may come from an external source (e.g., steam methane reforming [SMR] of natural gas) or from an internal source by reforming co-produced fuel gas or a fraction of the pyrolysis oil.

The pyrolysis and subsequent upgrading processes can also be self-sufficient with regard to heat and electricity requirements. The pyrolysis reaction produces other combustible co-products. Examples are fuel gas (a mixture of carbon monoxide [CO] and methane [CH<sub>4</sub>]) and bio-char, both of which can be used to produce combined heat and power (CHP). These co-products can satisfy and often exceed the needs of the upgrading process for heat and power.

### 2.1 FAST PYROLYSIS EXAMINED BY WRIGHT AND COLLEAGUES

Wright et al. (2010) examined a biomass fast pyrolysis plant designed to process 2,000 metric tons per day (MT/d) of dry-conditioned corn stover, as shown in Figure 3. The process inputs include corn stover as the chosen form of biomass, a small amount of electricity, and hydrogen, which can be produced internally or purchased from an external source. The main product is a liquid fuel mixture of naphtha-range and diesel-range materials. The main co-products are the remaining excess solids (bio-char), and fuel gas (CH<sub>4</sub>/CO mixture). The following subsections in Section 2.1 describe the main process and highlight the key data required for the WTW analysis.



FIGURE 3 Block Flow Diagram of Complete Fast Pyrolysis and Pyrolysis Oil Upgrading Process, with Optional Hydrogen Production (Adapted from Wright et al. 2010)

Incoming corn stover is chopped from its initial average size of 10–25 mm to a uniform particle size of 10 mm. Then it is dried from 25% to 7% moisture content and ground to particles that each has a diameter of 3 mm. The drying heat is provided by the combustion of pyrolysis solids (bio-char) and noncondensable gases (fuel gas).

The dried corn stover is pyrolyzed by fluidized bed reactors (FBRs). The combustion of bio-char and fuel gas provides enough process heat for the FBRs, which require 27.5 MJ/kg of dried biomass feed. Fuel gas and bio-char are combusted and recycled to the reactor to provide the necessary heat transfer and to aid in the reactor's fluidization. The material yield distribution after the fast pyrolysis step is complete is summarized in Table 1. Table 2 outlines the process mass balance prior to upgrading.

Compound	Share (%)
Noncondensable gas	13
Pyrolysis oil (15.5% moisture)	71
Char/ash	16
Total	100

-	Input	Product	
Parameter	Dry Biomass (Corn Stover)	Pyrolysis Oil (Wet)	Char
Mass flow (MT/d)	2.000	1.440	301
Carbon (weight % [wt%])	47.3	55.1	51.2

#### TABLE 2 Fast Pyrolysis Section Overall Mass Balance

Hydroprocessing upgrades pyrolysis oil into liquid fuel. The upgrading process described in Wright et al. (2010) is based on a process described in a previous UOP report (Marinangeli 2005) and a subsequent presentation (Holmgren et al. 2008). The original schematic includes in-situ hydrogen production accomplished by reforming the pyrolysis oil's light phase. A modified version is also presented, which is based on a later UOP presentation that describes a process that maximizes liquid fuel yields by using commercially imported hydrogen of undetermined origin. Table 3 shows hydrogen input to and yields from pyrolysis oil upgrading, comparing hydrogen produced in situ via pyrolysis oil reforming versus externally purchased hydrogen.

We have considered two cases for upgrading the pyrolysis oil in our WTW analysis. The first case, defined as the "distributed refinery" approach, represents a scenario in which there is an interest in partial upgrading (stabilization via hydrotreatment) of the pyrolysis oil to a product that is compatible with a refinery product. The second case, defined as the "integrated refinery" approach, represents a scenario in which the hydrocracking process is integrated with the production and hydrotreatment of the pyrolysis oil in a single location.

Inputs and Yields	H <sub>2</sub> Produced In Situ (wt%)	Externally Purchased H <sub>2</sub> (wt%)
Feed		
Pyrolysis oil (dry)	100	100
Hydrogen		3–4.5
Intermediate		
Hydrogen	4–5	
Product		
Light ends	15	0
Naphtha range	30	21
Diesel range	8	21
Water and carbon dioxide (CO <sub>2</sub> )	51-52	60

# TABLE 3 Pyrolysis Oil Upgrading (Hydrotreating/Hydrocracking) Inputsand Yields (Wright et al. 2010)

#### 2.1.1 Distributed Refinery Scenario

Table 4 summarizes the inputs and outputs for the production and partial upgrading (hydrotreatment) of the pyrolysis oil step for the distributed refinery scenario taken from Wright et al. (2010). The inputs and outputs for the subsequent hydrocracking step, also taken from Wright et al. (2010), are presented in Table 5. The process hydrogen can be provided entirely from external (purchased) hydrogen sources or produced locally by reforming a mixed stream of external NG with co-produced fuel gas. In the latter case, it is assumed that the reforming efficiency of the fuel gas and NG mixture to produce hydrogen is 73%. In such a case, the coproduced fuel gas is not available for any other purpose than for hydrogen production.

Modeling the described process as a distributed process requires breaking the pyrolysis oil hydroprocessing section described in Wright et al. (2010) into two separate operations: pyrolysis oil stabilization and pyrolysis oil upgrading. Stabilized pyrolysis oil is obtained by performing the initial pyrolysis oil hydrotreatment to reduce the oil's oxygen content and thus its acidity. This initial hydrotreatment consumes a majority of the total hydrogen needed to upgrade the pyrolysis oil to liquid fuels (i.e., about 85% of the total hydrogen consumed). It is assumed that the bio-oil stabilization consumes a negligible amount of electricity. Therefore, all electricity consumption in the stabilization and upgrading (based on our personal communications with Mark Wright, the lead author of the ISU study) is allocated to the upgrading part in the distributed process.

Inputs and Outputs	External Hydrogen (Purchased) (Btu)	Internal Reforming of NG and Fuel Gas (Btu)
Inputs		
Corn stover biomass [dry lb]	19,851 [2.82]	19,851 [2.82]
Hydrogen (external)	2,976	0
Supplemental NG for H <sub>2</sub> reforming <sup>a</sup>	0	3,390
Electricity	656	656
Outputs		
Hydrotreated pyrolysis oil [dry lb]	14,325 [1.00]	14,325 [1.00]
Bio-char (carbon content: 51.2%) [dry lb]	3,853 [0.41]	3,853 [0.41]
Fuel gas	687	0
Excess heat (steam)	818	818

#### TABLE 4 Inputs and Outputs for Pyrolysis Oil Production and Hydrotreatment (Stabilization)

<sup>a</sup> Since  $H_2$  from reforming the co-produced fuel gas is not sufficient to satisfy the process  $H_2$  supplemental NG is provided externally and reformed into  $H_2$  with the fuel gas.

Inputs and Outputs	External Hydrogen (Purchased) (Btu)	Internal Reforming of NG and Fuel Gas (Btu)
Inputs		
Hydrotreated pyrolysis oil [dry lb]	18,315 [1.28]	18,315 [1.28]
Hydrogen (external)	645	0
Supplemental NG for H <sub>2</sub> reforming <sup>a</sup>	0	575
Heat (steam)	73	73
Electricity	11	11
Outputs		
Liquid fuel [dry lb]	18,315 [1.00]	18,315 [1.00]
Fuel gas	309	0

 TABLE 5 Inputs and Outputs for Hydrotreated Pyrolysis Oil Upgrading (Hydrocracking)

<sup>a</sup> Since  $H_2$  from reforming the co-produced fuel gas is not sufficient to satisfy the process  $H_{2,}$  supplemental NG is provided externally and reformed into  $H_2$  with the fuel gas

#### 2.1.2 Integrated Refinery Scenario

The integrated refinery scenario covers the overall production of liquid fuels from biomass in a single step. The inputs and outputs of the integrated production are provided in Table 6. The process hydrogen can be purchased from external hydrogen sources, from local reforming of a mix of co-produced fuel gas with NG, or from internal reforming of pyrolysis oil. Since the excess heat from the pyrolysis and hydrotreatment is sufficient for the heat required for hydrocracking, no external heat is required for the integrated design. When internal reforming of pyrolysis oil occurs, all the hydrogen necessary for upgrading (hydrotreating and hydrocracking) the pyrolysis oil is internally produced (i.e., no external hydrogen or NG is required), but the liquid fuel yield is greatly reduced.

### 2.2 FAST PYROLYSIS EXAMINED BY JONES AND COLLEAGUES

PNNL conducted a techno-economic analysis of converting hybrid poplar wood chips to liquid fuels via a fast pyrolysis process (Jones et al. 2009). The goal of the PNNL study was to evaluate a pathway for converting biomass feedstock into infrastructure-compatible hydrocarbon liquid fuels through process modeling. The design case investigated the production of fast pyrolysis oil from the biomass feedstock and then upgrading the pyrolysis oil to produce renewable gasoline and diesel. The plant was designed to process 2,000 MT of bone-dry wood each day in order to produce 76 million gal of gasoline and diesel fuel per year. This amount is equivalent to a yield of 105 gal of liquid fuel per dry MT of biomass, or a 32% yield by mass.

Inputs and Outputs	External Hydrogen (Purchased) (Btu)	Internal Reforming of Fuel Gas/NG (Btu)	Internal Reforming of Pyrolysis Oil (Btu)
î	· · · ·	· · · · ·	· · · ·
Inputs			
Corn stover biomass [dry lb]	25,379 [3.61]	25,379 [3.61]	45,698 [6.49]
Hydrogen (external)	4,450	0	0
Supplemental NG for H <sub>2</sub> reforming <sup>a</sup>	0	4,909	0
Electricity	849	849	1,562
Outputs			
Liquid fuel [dry lb]	18,315 [1.00]	18,315 [1.00]	18,315 [1.00]
Char [dry lb]	4,926 [0.52]	4,926 [0.52]	8,869 [0.94]
Fuel gas	1,187	0	8,325
Excess heat (steam)	973	973	1,032

#### TABLE 6 Inputs and Outputs for Integrated Refineries (Wright et al. 2010)

<sup>a</sup> Since H<sub>2</sub> from reforming the co-produced fuel gas is not sufficient to satisfy the process H<sub>2</sub>, supplemental NG is provided externally and reformed into H<sub>2</sub> with the fuel gas

The processing of the biomass to liquid fuels involved four main steps, as follows (see Figure 4, adopted with permission from Jones et. al. 2009):

- Drying the biomass from 50% to 7% moisture content and grinding the biomass until the diameter of the particles was 2–3 mm;
- Fast pyrolysis of the biomass to highly oxygenated pyrolysis oil;
- Hydrotreating of the pyrolysis oil to produce infrastructure-compatible, stable hydrocarbon oil with less than 2% oxygen (significant hydrogen is needed for the deoxygenation process); and
- Hydrocracking of the heavy portion of the stable hydrocarbon oil to produce liquid fuels (gasoline and diesel) through distillation.

Although the fast pyrolysis produces significant amounts of char and fuel gas co-products, these co-products are consumed as process fuels for drying the feed and heating the pyrolysis reactor.



FIGURE 4 Block Diagram of the Overall PNNL Design Case (Adopted from Jones et al. 2009)

The hydrotreatment of the highly oxygenated pyrolysis oil is necessary to avoid possible phase separation and polymerization and to produce hydrocarbon oil that is ready for transportation in existing infrastructure and for upgrading in conventional petroleum refineries. If the stable pyrolysis oil is shipped into an existing petroleum refinery, then the last process step (hydrocracking) will take place in that refinery. We examine these two cases separately in the LCA of the pyrolysis pathways. Note that PNNL's design case evaluates technology that has been demonstrated at the laboratory scale but includes advances that are potentially achievable by 2015.

The properties of feedstock in the PNNL study are different from those in the GREET model. The moisture content and lower heating value of biomass feedstock (hybrid poplar) in the original PNNL study are 50% and 7,603 Btu/lb, while those of the comparable feedstock in GREET (forest residue) are 20% and 6,622 Btu/lb. To resolve the differences in biomass feedstock properties, updated process assumptions for biomass feedstock with 30% moisture were obtained through a personal communication with Sue Jones (the lead author of the PNNL study). The increase in energy use and emissions associated with biomass freedstock input rate in the PNNL study was adjusted to account for the energy difference between the two feedstock heating values.

As described earlier, we consider two scenarios for the WTW analysis of pyrolysis pathways: the distributed refinery scenario and the integrated refinery scenario. The energy use, as extracted from the PNNL analysis, is shown in Tables 7 and 8 for the distributed scenario and in Table 9 for the integrated scenario. Note that bio-char from pyrolysis is used internally to provide process electricity and heat. In the internal reforming case, moreover, fuel gas from the hydrotreating and hydrocracking processes are used as supplements to NG for producing hydrogen in the steam reformer. The PNNL analysis did not investigate the pyrolysis oil reforming case. The units adopted in these tables are compatible with the units typically used in the GREET model.

Inputs and Outputs	External Hydrogen (Purchased) (Btu)	Internal Reforming of NG and Fuel Gas (Btu)
Inputs		
	01 111 [2 10]	01 111 [2 10]
Forest residue biomass [dry lb]	21,111 [3.19]	21,111 [3.19]
Hydrogen (external)	5,068	0
Supplemental NG for H2 reforming <sup>a</sup>	0	2,871
Electricity	736	737
Outputs		
Hydrotreated pyrolysis oil [dry lb]	17,450 [1.00]	17,450 [1.00]
Fuel gas	4,201	0

### TABLE 7 Inputs and Outputs for Pyrolysis Oil Production and Hydrotreatment (Stabilization)

<sup>a</sup> Since  $H_2$  from reforming the co-produced fuel gas is not sufficient to satisfy the process  $H_{2,}$  supplemental NG is provided externally and reformed into  $H_2$  with the fuel gas.

TABLE 8 Inputs and Outputs for Hydrotreated Pyrolysis Oil Upgr	ading
--	-------

Inputs and Outputs	External Hydrogen (Purchased) (Btu)	Internal Reforming of NG and Fuel Gas (Btu)
Inputs		
Hydrotreated pyrolysis oil [dry lb]	17,230 [0.99]	17,230 [0.99]
Hydrogen (external)	847	0
Supplemental NG for H <sub>2</sub> reforming <sup>a</sup>	0	1,182
Electricity	51	62
Outputs		
Liquid fuel [dry lb]	17,756 [1.00]	17,756 [1.00]
Fuel gas	0	0

<sup>a</sup> Since  $H_2$  from reforming the co-produced fuel gas is not sufficient to satisfy the process  $H_2$ , supplemental NG is provided externally and reformed into  $H_2$  with the fuel gas.

Inputs and Outputs	External Hydrogen (Purchased) (Btu)	Internal Reforming of NG and Fuel Gas (Btu)
Inputs		
Forest residue biomass [dry lb]	20,845 [3.15]	20,845 [3.15]
Hydrogen (external)	5,851	0
Supplemental NG for H <sub>2</sub> reforming <sup>a</sup>	0	4,017
Electricity	777	790
Outputs		
Liquid fuel [dry lb]	17,756 [1.00]	17,756 [1.00]
Fuel gas	4,148	0

## **TABLE 9** Inputs and Outputs for Integrated Refineries

<sup>a</sup> Since  $H_2$  from reforming the co-produced fuel gas is not sufficient to satisfy the process  $H_2$ , supplemental NG is provided externally and reformed into  $H_2$  with the fuel gas.

#### **3 BIOMASS FEEDSTOCK FOR PYROLYSIS**

This analysis considers corn stover and forest residue as feedstocks for producing liquid fuels via fast pyrolysis. This section describes the key parameters that affect the feedstock's role in the WTW of pyrolysis-based renewable fuels.

#### 3.1 CORN STOVER

#### 3.1.1 Feedstock Availability

Oak Ridge National Laboratory estimates that in 2012, at a price of less than \$60 per dry ton, 153 million dry tons of corn stover will be available (DOE 2011). Considering the yield of liquid fuel for the integrated process outlined in Table 6 and assuming it is entirely gasoline, this production of corn stover could supply about 10% (with external  $H_2$ ) or 6% (with internal  $H_2$  from pyrolysis oil reforming) of the U.S. annual demand for gasoline.<sup>1</sup> As shown in Figure 5, corn stover is mainly available in the Midwest. Therefore, this study assumes that corn stover collected and pyrolysis facilities are in the Midwest.



FIGURE 5 Corn Stover Resources of the United States (Adapted from DOE 2011)

<sup>&</sup>lt;sup>1</sup> U.S. consumption of gasoline in 2009 was 135,379 million gal (EIA 2010).

#### 3.1.2 Corn Stover Carbon Content and Moisture Content at Harvest

GREET simulations of biofuel pathways employ values for corn stover carbon and moisture content. The former is used for carbon calculations, and the latter is used for making payload assumptions that are needed to calculate the energy consumption associated with the transportation of corn stover. Table 10 lists literature values for these parameters and the values that have been selected for use in this study.

Source	Carbon Content (%)	Moisture Content at Harvest (%)
Birrell <sup>a</sup>	46.68	24
Hess et al. (2009a)	Not reported	20-64
Hoskinson et al. (2007)	44	24
This study	45	24

#### **TABLE 10** Corn Stover Carbon and Moisture Content

<sup>a</sup> Based on a personal communication with Stuart Birrell from ISU.

#### 3.1.3 Energy Consumed during Corn Stover Harvest

The harvesting and collection of corn stover involve gathering the residual stalks, cobs, and husks left in the field after the grain from the corn plants (called stover) has been harvested. Per a model developed at Idaho National Laboratory (INL), the stover is consolidated into windrows to be dried, baled, and moved to a roadside location (Hess et al. 2009a). Table 11 outlines the equipment that performs each of these steps and the resulting energy consumption.

Logistics Process	Equipment	Energy Use (1000 Btu/ton of dry matter)
Condition/windrow	Tractor and 15-ft flail shredder with windrow	91.2
Bale	Tractor and baler	77.3
Roadside	Stacker	20
Total		188.5

**TABLE 11 Energy Consumption during Corn Stover Harvest** 

INL specifies windrow size as 1.04 tons of harvested material/1,000 windrow-ft. The baler in this study formed  $4 \times 4 \times 8$ -ft rectangular stover bales with a density of 8–9 dry matter bulk lb/ft<sup>3</sup>. Hess et al. (2009a) specified that prior to baling, the stover must dry in the field to moisture content of less than 15–20% so that it can be aerobically stable once it is baled

In the future, more efficient methods of windrowing and baling and techniques to minimize dry matter loss from the bales may increase the harvest yield (Hess et al. 2009a).

#### 3.1.4 Corn Stover Yield

Collection rates of corn stover are a function of the mechanical capabilities of existing machinery and the impact from removing the stover on soil quality. Hess et al. (2009a) explains that existing harvesting equipment may be capable of collecting about 30% of available stover for a scenario in which common tillage practices are used. That fraction may increase to 54% or 68% on farms that follow increased no-till and all no-till crop management practices. To maintain soil quality and functioning, it may be best to remove no more than 33% of the available stover, although the exact sustainable removal rate is highly dependent on local factors. Garlock et al. (2009) reviewed the available literature and provided a range of 20–80% for the sustainable stover removal rate. Table 12 contains values for the yield of corn stover from the literature, which range from 1.52 to 3.6 dry tons/acre. In simulations of stover to biofuels via pyrolysis, we use a value of 2.1 dry tons/acre, the average of the values in Table 12.

Source	Yield of Stover (dry tons/acre)	Notes
Avila-Segura et al. (2011)	$3.22 \pm 0.49$	Uncertainty is the standard deviation from the mean based on 68 measurements. The research site is in south central Wisconsin.
Hess et al. (2009a)	3.6	Based on U.S. Department of Agriculture grain production data.
Hoskinson et al. (2007)	2.27	Actual yields were obtained with an experimental single-pass harvester. The study examined three scenarios—high, normal, and low cut—which left 10, 40, and 75 cm of stubble in the field, respectively. The yield was 2.27 dry tons of stover/acre when the normal-cut approach was used.
Karlen (2010)	1.52–2.19	The values, based on field trials in six states, represent harvestable dry stover—the amount that could be collected mechanically with available machinery.
This study	2.1	Average of literature values.

#### **TABLE 12** Stover Yield

#### 3.1.5 Fertilizer Replacement Rates

Traditionally, the bulk of corn stover has been left on corn fields to replenish the soil with nitrogen (N), phosphorus (P), and potassium (K), which reintegrate into the soil and nourish the next season's crops. Stover harvesting as part of the biofuel supply chain will certainly require farmers to supplement the nutrient content in harvested stover with fertilizer. Recent studies provide new insight into the fertilizer replacement levels that are needed as a result of stover harvesting. Table 13 summarizes these studies' replacement rates, which assume the removed nutrients are replenished pound for pound. The nitrogen fertilizer replacement rate was increased by a factor of 10% to account for nitrogen fertilizer volatilization. It is important to note that fertilizer application rates exhibit great variability with geography and other factors; thus, choosing a single value to represent replacement ratios for national corn stover production may not be representative. As a result, we chose conservative, round values for N, phosphate (P<sub>2</sub>O<sub>5</sub>), and potash (K<sub>2</sub>O) replacement rates. Although we convey the reported calcium carbonate (CaCO<sub>3</sub>) value from Avila-Segura et al. (2011), we do not include a CaCO<sub>3</sub> replenishment rate in GREET at this time.

Source	Ν	Р	K	CaCO <sub>3</sub>
Avila-Segura et al. (2011)	6,504	755	10.190	29.158
Karlen (2010)	10,097	1,093	9,835	-,
Hess et al. (2009b)	6,719	2,315	12,349	
Fixen (2007)	8,626	2,588	14,528	
Lang (2002)	6,810	2,679	11,350	
Petrolia (2006)		2,815	14,987	
Nielsen (1995)	6,174	1,634	8,944	
O'Brien et al. (2010)	7,718	1,816	22,700	
This study	7,700	2,000	12,000	

 TABLE 13 Replacement Rates for Nitrogen, Phosphorus, Potassium, and Calcium Carbonate after Corn Stover Harvesting (g fertilizer/dry ton stover harvested)

#### **3.1.6 Corn Stover Transport**

Hess et al. (2009a) provides a detailed analysis of bale handling and transportation. Standard 8-ft-wide by 53-ft-long semi-tractor trailers transport the bales, which have dimensions of  $4 \times 4 \times 8$  ft. Key parameters from Hess et al. (2009a) are provided in Table 14.

Parameter	Value
Bale moisture content	12%
Bale bulk density	8.55 lb/ft <sup>3</sup>
Payload	34,000 lb (15 dry matter tons)
Transportation speed	50 miles per hour
Loader energy use	4,200 Btu/dry matter ton

# TABLE 14 Bale Handling and Transportation KeyParameters (Hess et al. 2009a)

#### **3.2 FOREST RESIDUE**

#### 3.2.1 Feedstock Availability

It is estimated that in 2012, at a price of less than \$60 per dry ton, 97 million dry tons of forest residue and other wood wastes will be available (DOE 2011). This estimate includes wood supplies on federal lands and urban wood waste. Considering the yield of liquid fuel for the integrated process outlined in Table 9 and assuming it is entirely gasoline, this production of forest residue could supplant about 8% of the U.S. annual demand for gasoline.

As shown in Figure 6, forest residue is mainly available in the South, Southeast, Northwest, North, and Northeast in the United States. This study assumes that forest residue is collected and pyrolysis facilities are located in the Southeast.

#### 3.2.2 Energy Consumed during Forest Residue Collection and Transport

GREET simulations of biofuel pathways employ values for the carbon and moisture contents of woody biomass. The new GREET version (GREET 1\_2011) uses values of 47% for carbon content and 50% for moisture content at harvest. During transport, the moisture content of forest residue is reduced to 20% (assuming natural drying before transport).

To calculate the energy consumption of forest residue harvesting, we adopt a forest residue yield of 12 dry tons of residue produced per acre (Elsayed et al. 2003). The rotation length of trees producing forest residue is assumed to be 66 years (Oneil et al. 2010). We assume no fertilizer or agrochemical input for the production of forest residue. The resulting requirement for forest residue stumping and collection of 230,000 Btu/dry ton is based on calculations that use data from Elsayed et al. (2003). This energy includes that expended for forest maintenance activities, harvesting, collecting residues, bailing, and extracting the residues. It also includes milling and chipping of the wood. All energy consumption is allocated to the production of forest residue from the total production of forest products (including saw logs and round wood) based on mass fractions.



FIGURE 6 Forest Residue Resources of the United States (Adapted from DOE 2011)

#### **4 WELL-TO-WHEELS ANALYSIS OF PYROLYSIS PATHWAYS**

In our WTW analysis of pyrolysis-based renewable fuels, we include fertilizer production (for corn stover), biomass collection and transportation, pyrolysis of biomass, hydrotreating of pyrolysis oil, pyrolysis oil transportation, pyrolysis oil refining to gasoline and diesel, and transportation and distribution of gasoline and diesel as well as fuel consumption during vehicle operation. Figure 7 shows the stages included in our study for the corn-stover-based and forest-residue-based pathways. For forest residue, the fertilization step is not applicable. Hydrotreated pyrolysis oil can be (1) refined by an on-site-hydrocracker, (2) transported and refined at a distributed standalone bio-refinery, or (3) transported and refined at a conventional petroleum refinery. The refined renewable gasoline and diesel are then transported and distributed to refueling stations.



FIGURE 7 Fuel Cycle Stages of Pyrolysis Pathways

As discussed in Section 2, process  $H_2$  for hydroprocessing can be provided from pyrolysis oil reforming, fuel gas and external NG reforming, or external sources. This analysis also evaluates different possibilities for co-product applications, including the use of bio-char and fuel gas for process heat and soil applications. More details on the evaluation of co-products are provided in Section 4.3.3.

#### **4.1 FERTILIZER PRODUCTION**

As discussed in Section 3.1.5, additional fertilizers (N,  $P_2O_5$ , and  $K_2O$ ) need to be applied when corn stover is removed in order to supplement the nutrient loss due to corn stover removal. Nitrogen fertilizer consists of ammonia (NH<sub>3</sub>), urea (NH<sub>2</sub>CONH<sub>2</sub>), and ammonium nitrate (NH<sub>4</sub>NO<sub>3</sub>), with shares of 70.7%, 21.1%, and 8.2%, respectively. Since NH<sub>3</sub> requires a large amount of NG (26.4 mmBtu/ton of NH<sub>3</sub>) and since the other nitrogen fertilizers need a notable amount of NH<sub>3</sub> for their production (0.57 ton of NH<sub>3</sub>/ton of urea and 0.53 ton of NH<sub>3</sub>/ton of NH<sub>4</sub>NO<sub>3</sub>), nitrogen fertilizer is both energy-intensive and GHG-intensive (Wang et al. 2003; Wu et al. 2006).

#### 4.2 BIOMASS COLLECTION AND TRANSPORTATION

Table 15 summarizes the assumptions made about the collection and transportation of corn stover and forest residue discussed in Section 3. Biomass transportation includes both transporting biomass to pyrolysis facilities and backhaul travel. The diesel fuel economy of heavy-duty truck (Class 8 trucks) is assumed to be 5 miles per gallon (mpg) for transporting both feedstocks.

Activity and Usage	Corn Stover	Forest Residue	
Biomass collection			
Diesel (Btu/dry ton)	188,500	230,000	
Electricity (kWh/dry ton)	0	0	
N (g/dry ton)	7,700	0	
$P_2O_5$ (g/dry ton)	2,000	0	
$K_2O$ (g/dry ton)	12,000	0	
Transportation			
Payload (tons)	15	17	
Fuel economy (mi/gal diesel)	5	5	
Roundtrip energy use for integrated plants (Btu/dry ton)	156,000	321,000	
Roundtrip energy use for distributed plants (Btu/dry ton)	79,000	161,000	
Load energy use (Btu/dry ton)	4,200	0	

TABLE 15	Assumptions for the	<b>Collection and</b>	Transportation	of Corn	Stover	and
Forest Resid	due					
Transportation distances depend on the size of the pyrolysis plant. Integrated plants are expected to be larger than distributed plants in order to compensate for their large capital investment. Therefore, we assume that the distances for transporting corn stover for the integrated and distributed plants are 80 and 40 mi, respectively, while those for transporting forest residue are 150 and 75 mi, respectively.

Because of the longer transportation distances, more petroleum is used for the collection and transportation of forest residue than for corn stover. On the other hand, due to the N fertilizer inputs for corn stover, the total amount of energy and NG used for the collection and transportation of corn stover is more than for forest residue.

## 4.3 PYROLYSIS AND UPGRADING

#### 4.3.1 Distributed Refineries

Table 16 summarizes and compares the inputs and outputs for the distributed refinery scenario for corn stover and forest residue previously discussed in Section 2. The yields of hydrotreated pyrolysis oil are similar, but the process using corn stover described in Wright et al. (2010) uses a smaller amount of hydrogen for stabilization and produces a larger amount of bio-char. The hydrogen requirements could depend not only on the feedstock but also on the process design. The dependencies of yield, process energy, and product slates on feedstock and process design have yet to be investigated.

For upgrading at standalone bio-refineries, the process described in Wright et al. (2010) requires a much larger amount of hydrotreated pyrolysis oil but a smaller amount of hydrogen per unit of liquid fuel produced than does the process described in Jones et al. (2009). The differences could result from pyrolysis oil properties (affected by the feedstock and process design of pyrolysis and stabilization) and upgrading process designs. Wright et al. (2010) specifies the heat requirement for the upgrading process, which is assumed to be provided by (1) the combustion of co-produced fuel gas at 90% boiler efficiency for the external hydrogen case or (2) the excess heat from internal reforming of fuel gas and NG for the internal hydrogen case.

This study also examines a case where the hydrotreated pyrolysis oil is transported and refined at a distant conventional petroleum refinery. In such cases, hydrotreated pyrolysis oil is assumed to be inserted in the refining process after distillation to avoid the front end of the refinery (air and vacuum distillation columns that consume a large amount of energy). Because of the lack of information on this particular scenario, the process assumptions for conventional petroleum refining are adjusted by the relative energy intensities of conventional refineries and standalone bio-refineries with internal reforming of fuel gas and NG. The upgrading processes with internal reforming are selected because they are more comparable to a conventional refinery because they still consume gas internally. For example, when the conventional refineries' efficiency is 89.4% and the NG share 27%, the NG consumption per mmBtu of gasoline is

	Reference Source, Feedstock, and Hydrogen Source						
	Wright	et al. (2010)	Jones	et al. (2009)			
	Cor	n Stover	Fore	st Residue			
		Internal		Internal			
Inputs and Outputs	External	(Fuel Gas/NG)	External	(Fuel Gas/NG)			
Pyrolysis and stabilization							
Inputs							
Biomass (dry lb/lb pyrolysis oil)	2.82	2.82	2.61	2.61			
Electricity (Btu/lb pyrolysis oil)	656	656	1,078	1,078			
NG (Btu/lb pyrolysis oil)	0	3,390	0	5,170			
H <sub>2</sub> (Btu/lb pyrolysis oil)	2,976	0	5,156	0			
Outputs							
Char (Btu/lb pyrolysis oil)	3,853	3,853	0	0			
Fuel gas (Btu/lb pyrolysis oil)	687	0	1,825	0			
Upgrading at standalone bio-refineries							
Pyrolysis oil (dry lb/lb liquid fuel)	1.28	1.28	1.04	1.04			
Electricity (Btu/lb liquid fuel)	11	11	56	56			
NG (Btu/lb liquid fuel)	0	575	0	498			
$H_2$ (Btu/lb liquid fuel)	645	0	902	0			
	040	5	202	0			
Fuel gas (Btu/lb liquid fuel)	228	0	738	0			

#### **TABLE 16 Inputs and Outputs for Distributed Refineries Scenario**

32,000 Btu. The efficiency of the upgrading process examined by Wright et al. (2010) is 96.5% with internal reforming of fuel gas and NG. Thus, the adjusted NG consumption for conventional refineries is calculated as  $32,000 \times (1/0.965 - 1)/(1/0.894 - 1) = 9,800$  Btu/mmBtu.

Transportation distances for hydrotreated pyrolysis oil also depend on the feedstock source, since the locations of the closest refineries from the various feedstock sources are different. As shown in Figures 5 and 6, corn stover is usually produced in the Midwest states, while forest residue is widely available in the South and Southeast. This study assumes that pyrolysis oil from corn stover is transported from Des Moines, Iowa, to Chicago, Illinois, via rail for 300 mi and via truck for 50 mi (to collect the pyrolysis oil from individual facilities and get it to Des Moines). Pyrolysis oil from forest residue, on the other hand, is transported from Texarkana, Arkansas, to Port Arthur, Texas, or Lake Charles, Louisiana, via rail for 225 mi and via truck for 50 mi (again, for local collection).

#### 4.3.2 Integrated Refinery

Table 17 summarizes and compares the assumptions for the integrated refinery scenario for corn stover and forest residue, as discussed earlier in Section 2. The liquid oil yields predicted by Jones et al. (2009) are significantly higher than those predicted by Wright et al. (2010). Notably, the internal reforming of pyrolysis oil in Wright et al. (2010) reduces the liquid fuel yield sharply (or requires a much larger amount of biomass per unit of liquid fuel product). Note that pyrolysis of forest residue usually shows higher yields than pyrolysis of corn stover because of its lower ash content (Bridgwater 2011). However, for smaller fuel yields, a smaller amount of process fuel (especially H<sub>2</sub>) is required, and a larger amount of co-products is produced.

	Reference Source, Feedstock, and Hydrogen Source							
		Wright et al. (2010	0)	Jones et al. (2009)				
		Corn Stover		Forest Residue				
Inputs and Outputs	External	Internal (Fuel Gas/NG)	Internal (Pyrolysis Oil)	External	Internal (Fuel Gas/ NG)			
Pyrolysis and stabilization		· · · · · · · · · · · · · · · · · · ·	,		,			
Inputs								
Biomass (dry lb/lb liquid fuel)	3.61	3.61	6.49	2.73	2.73			
Electricity (Btu/lb liquid fuel)	849	849	1,562	1,182	1,182			
NG (Btu/lb liquid fuel)	0	4,909	0	0	5,866			
H <sub>2</sub> (Btu/lb liquid fuel)	4,450	0	0	6,232	0			
Outputs								
Char (Btu/lb liquid fuel)	4,926	4,926	8,869	0	0			
Fuel gas (Btu/lb liquid fuel)	1,187	0	8,325	2,643	0			

#### **TABLE 17** Parametric Assumptions for Integrated Pyrolysis Processes

On the basis of Tables 16 and 17, the pyrolysis processes examined by Jones et al. (2009) show higher yields than those examined by Wright et al. (2010). With the correlations between yields, process design, and feedstock unknown, this study calls the processes examined by Jones et al. "high-yield" processes and those examined by Wright et al. "low-yield" processes.

## 4.3.3 Co-Products from Pyrolysis

A large amount of co-products (including fuel gas, steam and bio-char) are generated from the pyrolysis and upgrading processes. The co-products can be used in various applications, as shown in Figure 7. For example, fuel gas and bio-char can be combusted to generate electricity. In such a case, the generated electricity is used to satisfy the process needs, and the surplus is assumed to be exported and to displace the electricity produced by the average U.S. generation mix. If electricity is generated internally, the external electricity requirements and the fuel gas outputs shown in Tables 16 and 17 will be reduced accordingly. Excess steam may be used and displace conventional steam generation if there are nearby demands. However, this study assumes that all excess steam is discarded.

Bio-char can be exported and applied to soil as a means of soil amendment and carbon sequestration. Because of its high stability, the majority of carbon in bio-char is assumed to remain in solid form for a long period. Gaunt and Lehmann (2008) assumes no carbon loss in 10 years, while Roberts et al. (2010) uses a conservative assumption in which 20% of the carbon is liberated to the atmosphere. The percent of carbon sequestration from bio-char is quite uncertain; it depends on the feedstock source and environmental conditions. This study uses the same conservative assumption as those used in Roberts et al. (2010).

In addition to sequestering carbon, bio-char is reported to reduce other GHG emissions from soils. For example,  $CH_4$  emissions can be completely suppressed, and nitrous oxide (N<sub>2</sub>O) emissions can be reduced by 50–80% depending on soil conditions (Lehmann et al. 2006). Bio-char adsorbs  $NH_3$ , dissolved ammonium, nitrate, and  $P_2O_5$ , which reduces leaching and runoff losses of N and P and improves the fertilizer utilization. Bio-char application may also affect crop yield. Crop yield could decrease because smaller amounts of N are available to the soil as a result of the carbon-to-nitrogen (C/N) ratio of bio-char (Lehmann and Rondon 2006), or crop yield could increase as a result of the higher fertilizer efficiency, especially for highly degraded soils (Roberts et al. 2010). Because of this uncertainty, the effects of bio-char on GHG emissions (other than C sequestration), fertilizer utilization, and crop yields are not taken into account in this analysis. However, the energy and emissions associated with transporting biochar to farms by truck are included; distances are set at 40 mi for distributed refineries and 80 mi for integrated refineries.

#### 4.3.4 Handling of Co-Products

Because pyrolysis and upgrading processes produce large amounts of co-products, the co-product credit method chosen can significantly influence the WTW results for bio-fuels (Wang et al. 2011). To calculate the impact of the co-products, two methods—the allocation method and the displacement method—are commonly applied.

The displacement method assumes that a co-product from a given process displaces a similar conventional product. The life-cycle energy use and emissions of the displaced product are taken as credits for the fuel product, which are subsequently subtracted from the life-cycle energy use and emissions associated with all products of the given process. The displacement method is data-intensive and dynamic, requiring a detailed understanding of the displaced product's life cycle, which might change depending on economic and market conditions. Moreover, the displacement method may not be reliable if a large amount of co-products is produced in a fuel facility because the co-product credit may dominate the LCA results.

The allocation method, in contrast, allocates the life-cycle energy burdens and emissions associated with both the main product and the co-products among the products according to their energy output shares, mass shares, or market revenue shares. The allocation method is easy to use and does not require frequent updates for a mature industry. However, the energy allocation may not be entirely accurate when a product is used for nonfuel applications. Also, the market revenue allocation is subject to price variations for different products. Therefore, this study uses a hybrid approach, in which the energy allocation method is applied to energy co-products (e.g., fuel gas and electricity) and bio-char is always used for carbon sequestration.

# 4.4 TRANSPORTATION, DISTRIBUTION, AND VEHICLE USE OF PYROLYSIS GASOLINE AND DIESEL

Pyrolysis gasoline and diesel fuel are transported from refineries to distribution terminals by mixed transportation modes (i.e., barges, pipelines, and rail) and then distributed to refueling stations via trucks. The properties of pyrolysis-based gasoline and diesel are assumed to be identical to those of their petroleum-based counterparts. Therefore, the same fuel economies that are assumed for both petroleum-based and pyrolysis-based gasoline and diesel fuel. The baseline fuel economy of gasoline passenger cars (which are assumed for this analysis) is set at 23.4 mpg, while the fuel economy of diesel cars is assumed to be 20% higher (on a per volume basis) than that of gasoline cars. Similarly, the same vehicle emission factors are applied to petroleum fuels and pyrolysis fuels, except in the case of sulfur oxides  $(SO_x)$ ; these emissions are calculated on the basis of sulfur content, and pyrolysis gasoline and diesel have zero sulfur content (Mohan et al. 2006).

# **5 WELL-TO-WHEELS ANALYSIS RESULTS**

Functional units are critical when LCA results of various alternative products are being compared. For energy products, a common functional unit is a "unit of delivered energy" (e.g. million Btu); this metric can be considered to be based on an "energy functional unit." When fuels that are used in similar combustion technologies with similar end-use efficiencies (e.g., petroleum diesel, biodiesel, renewable diesel) are compared, the energy functional unit is transparent and reliable, because complications due to the differences in end-use efficiencies are avoided. When fuels are used in different combustion technologies with different end-use efficiencies but similar functions, the energy functional unit may not be appropriate. For example, diesel vehicles are typically more efficient than gasoline vehicles. In such cases, a "service function unit" (e.g., vehicle mile traveled) could be a more reliable metric, even though the results would depend on fuel economy, which varies depending on many factors (vehicle type, powertrain technology, driving cycle, time). Moreover, for biofuels, a "unit of biomass input" (e.g., ton of dry biomass) is a meaningful functional unit because the rate of biomass input is constrained by the technology and scale of the facility (e.g., 2000 MT/d). Therefore, a unit of biomass input can be useful when different fuel production technologies are being compared because it shows the extent of energy and emissions savings compared with those of the reference case.

This study, therefore, provides WTW results for the pyrolysis-based renewable fuel pathways incorporated into the GREET model by using three functional units: one million Btu (mmBtu) of fuel, vehicle mile driven, and ton of biomass feedstock.

#### 5.1 WELL-TO-WHEELS ENERGY AND EMISSIONS PER MILLION BTU OF FUEL

Depending on factors related to co-product application (e.g., how much bio-char is used for electricity generation or soil application; how much fuel gas is combusted for electricity generation, converted into hydrogen, or exported to displace liquefied petroleum gas [LPG]), many scenarios for pyrolysis pathways are available. Therefore, for this study, 12 cases, which are listed in Table 18, were chosen. They are compared according to their hydrogen sources in Section 5.1.1, system configurations in Section 5.1.2, and bio-char applications in Section 5.1.3. The last three columns in Table 18 indicate whether the scenario is included in the corresponding section.

						Section	Section	Section
Yield	Feedstock	Upgrading	Hydrogen Source	Bio-Car	Fuel Gas	5.1.1	5.1.2	5.1.3
Low	Corn stover	Integrated	Ext. H <sub>2</sub> from NG	Elec. gen.	Export	0	0	0
Low	Corn stover	Integrated	Ext. H <sub>2</sub> from NG	C seq.	Export			0
Low	Corn stover	Integrated	Ref. fuel gas/NG	Elec. gen.	Int. H <sub>2</sub>	0		0
Low	Corn stover	Integrated	Ref. fuel gas/NG	C seq.	Int. H <sub>2</sub>			0
Low	Corn stover	Integrated	Ref. pyrolysis oil	Elec. gen.	Export	0		0
Low	Corn stover	Integrated	Ref. pyrolysis oil	C seq.	Export			0
Low	Corn stover	Distributed	Ext. H <sub>2</sub> from NG	Elec. gen.	Export		0	
Low	Corn stover	Conventional	Ref. pyrolysis oil	Elec. gen.	Export		0	
High	Forest residue	Integrated	Ext. H <sub>2</sub> from NG	Elec. gen.	Export	0	0	
High	Forest residue	Integrated	Ref. fuel gas/NG	Elec. gen.	Int. H <sub>2</sub>	0		
High	Forest residue	Distributed	Ext. H <sub>2</sub> from NG	Elec. gen.	Export		Ο	
High	Forest residue	Conventional	Ext. H <sub>2</sub> from NG	Elec. gen.	Export		0	

TABLE 18 Scenario Selection for Pyrolysis-Based Renewable Gasoline and Diesel<sup>a</sup>

<sup>a</sup> Integrated process; distributed process with standalone biorefinery; conventional = distributed process with conventional petroleum refinery; ext.  $H_2$  from NG = external  $H_2$  from NG reforming; Ref. fuel gas/NG = internal reforming of fuel gas and NG; ref. pyrolysis oil = internal reforming of pyrolysis oil; elec. gen. = electricity generated from bio-char combustion; C seq. = bio-char applied to soil for carbon sequestration; export = export fuel gas to displace LPG; int.  $H_2$  = internal reforming of fuel gas for  $H_2$ .

#### 5.1.1 Hydrogen Sources

Figure 8 presents pathways representing WTW total energy use for pyrolysis-based renewable gasoline with different sources of  $H_2$  and compares them with petroleum gasoline pathways. For the pyrolysis pathways, the integrated process design is used, and the bio-char co-product is combusted to generate electricity. In Figure 8, "Pyro-Oil, "Fuel Gas/NG," and "External" represent the pathways with  $H_2$  from pyrolysis oil reforming,  $H_2$  from a mixture of fuel gas and NG reforming, and  $H_2$  from external sources, respectively. Depending on the  $H_2$  sources, pyrolysis-based renewable gasoline requires 32–43% more total energy (including renewable and fossil energy) than does conventional gasoline. Moreover, external  $H_2$  from central SMR takes less total energy, because the feedstock for external  $H_2$  is less energy intensive than the feedstock for internal reforming (e.g., fuel gas from biomass).



FIGURE 8 WTW Total Energy Use for Pyrolysis-Based Renewable Gasoline Pathways with Different H<sub>2</sub> Sources Compared to the Petroleum Gasoline Pathway (Btu/mmBtu)

Figure 9 compares WTW fossil fuel use for pyrolysis-based renewable gasoline pathways with the petroleum gasoline pathways. Since pyrolysis-based renewable gasoline is produced from biomass feedstock sources, no fossil fuels are used in the PTW stage, which results in 52–90% reduction in fossil fuel consumption when compared with petroleum gasoline scenario. The lower end of the fossil fuel reduction corresponds to the H<sub>2</sub> production from NG (external H<sub>2</sub> case). Reduced fossil fuel use is associated with internal H<sub>2</sub> production because renewable fuel gas displaces a significant portion of fossil NG for H<sub>2</sub>. Moreover, pyrolysis oil reforming for H<sub>2</sub> production reduces WTW fossil fuel use further, because no fossil fuels except those used to generate the small amount of electricity are used in the fuel production pathway.

Figure 10 compares WTW petroleum use for pyrolysis-based renewable gasoline pathways with the petroleum gasoline pathway. In a fashion similar to that of the fossil fuel case just mentioned, pyrolysis-based renewable gasoline pathways consumes no petroleum in the PTW stage, while almost all of reformulated gasoline PTW is from petroleum sources. Therefore, pyrolysis gasoline pathway reduces petroleum consumption by 92–95% relative to the petroleum gasoline pathway. The pathway with pyrolysis oil reforming shows slightly larger petroleum consumption because the sharply reduced liquid fuel yield requires significantly more biomass per unit energy of biomass, whose collection energy is mainly from petroleum.



FIGURE 9 WTW Fossil Fuel Use for Pyrolysis-Based Renewable Gasoline Pathways with Different H<sub>2</sub> Sources Compared to the Petroleum Gasoline Pathway (Btu/mmBtu)



FIGURE 10 WTW Petroleum Use for Pyrolysis-Based Renewable Gasoline Pathways with Different H<sub>2</sub> Sources Compared to the Petroleum Gasoline Pathway (Btu/mmBtu)

Figure 11 presents WTW GHG emissions for pyrolysis-based renewable gasoline and petroleum gasoline pathways; the figure shows a trend similar to that of WTW fossil fuel uses. Since the CO<sub>2</sub> emissions are biogenic, a large CO<sub>2</sub> credit is applied to WTP stage for the biogenic carbon absorbed during biomass growth. Depending on the H<sub>2</sub> source for the pyrolysis oil upgrading, the pyrolysis-based renewable gasoline pathways reduce GHG emissions by 54–86% relative to the petroleum pathways. The lower end of the GHG emissions reduction corresponds to the case of H<sub>2</sub> production from NG. When H<sub>2</sub> is produced from fuel gas reforming, GHG emissions are reduced, because less NG is required to process H<sub>2</sub> inputs. Furthermore, pyrolysis oil reforming reduces GHG emissions further by removing fossil H<sub>2</sub> inputs completely from the fuel production pathway.

Table 19 summarizes WTW results for pyrolysis-based renewable gasoline and petroleum gasoline pathways per mmBtu of fuel. WTW results for diesel fuels are virtually identical to those for gasoline because the only differences between the two pathways are the small amount of blended ethanol for petroleum gasoline and the transportation and distribution of gasoline and diesel due to the energy allocation at the final refining. WTW results for pyrolysis-based renewable diesel and petroleum diesel pathways per mmBtu of fuel are summarized in Appendix Section A.1.



FIGURE 11 WTW GHG Emissions for Pyrolysis-Based Renewable Gasoline Pathways Compared to the Petroleum Gasoline Pathway (grams of CO<sub>2</sub>-equivalent per million Btu [gCO<sub>2</sub>-e/mmBtu])

		Pyrolysi	s Gasoline (Low	Yield)	Pyrolysis G (High Yi		
Use and Emissions	Cycle	Pyrolysis Oil	Fuel Gas/NG	External	Fuel Gas/NG	External	Gasoline
Lillissions	Cycle	1 91019313 011	1 401 043/110	External	1 461 643/110	External	Gusonne
Total energy (Btu)	WTP	749,320	707,242	678,187	784,487	648,349	246,590
	PTW	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000
	WTW	1,749,320	1,707,242	1,678,187	1,784,487	1,648,349	1,246,590
Fossil fuel (Btu)	WTP	121,290	379,949	428,027	456,866	581,969	225,240
	PTW	0	0	0	0	0	979,201
	WTW	121,290	379,949	428,027	456,866	581,969	1,204,441
Petroleum (Btu)	WTP	64 925	55 180	52.644	89 774	74 192	80 462
redoledin (Brd)	PTW	01,25	00,100	02,011	0	0	979 201
	WTW	64,925	55,180	52,644	89,774	74,192	1,059,664
GHGs (gCO <sub>2</sub> -e)	WTP	-62,034	-44,031	-41,364	-38,228	-30,689	21,429
	PTW	75,947	75,947	75,947	75,947	75,947	77,594
	WTW	13,913	31,916	34,584	37,719	45,258	99,024

# TABLE 19 WTW Results for Pyrolysis-Based Renewable Gasoline and Petroleum Gasoline Pathways with Different H<sub>2</sub> Sources per mmBtu of Fuel

## 5.1.2 Distributed Versus Integrated Refineries

Figures 12–15 present WTW total energy use for pyrolysis-based renewable gasoline pathways with different pyrolysis oil upgrading scenarios compared with the petroleum gasoline pathway. The WTW results for pyrolysis-based renewable gasoline and petroleum gasoline pathways per mmBtu of fuel are summarized in Table 20. For the pyrolysis pathways, hydrogen is supplied by external SMR of NG, and bio-char is combusted to generate electricity. In the figures and tables, "INT," "SA," and "Conv" mean an integrated process with an on-site bio-refinery, a distributed process with a standalone bio-refinery and a distributed process with a conventional petroleum refinery, respectively.

Depending on the pyrolysis oil upgrading scenario, pyrolysis-based renewable gasoline uses 32–36% more total energy than does gasoline. However, the fossil fuel use, petroleum use, and GHG emissions are reduced by 50–65%, 91–95%, and 51–65%, respectively. Among the pathways with the same feedstock, the differences between the two upgrading scenarios with a bio-refinery ("INT" and "SA") are negligible, or less than 1%. The small impact of the upgrading scenario on the WTW total energy use results from small contribution of the pyrolysis oil transportation activities to the entire WTW energy use and emissions. Also, the energy benefits from system integration (heat) are estimated to be small in the ISU and PNNL studies (Wright et al. 2010; Jones et al. 2009).

The scenario of pyrolysis-based renewable gasoline production in a conventional petroleum refinery consumes slightly more petroleum, since a conventional petroleum refinery consumes other petroleum products (e.g., crude oil, petroleum coke, refinery gas, unfinished oil).

The WTW results for renewable and petroleum diesel are presented in Appendix Section A.2; they are virtually identical to those of renewable and petroleum gasoline per unit energy.

The WTW results for renewable and petroleum diesel are presented in Appendix Section A.3; they are virtually identical to those of renewable and petroleum gasoline per unit energy.



FIGURE 12 WTW Total Energy Use for Pyrolysis-Based Renewable Gasoline Pathways with Different Upgrading Plant Options Compared to the Petroleum Gasoline Pathway (Btu/mmBtu)



FIGURE 13 WTW Fossil Fuel Use for Pyrolysis-Based Renewable Gasoline Pathways with Different Upgrading Plant Options Compared to the Petroleum Gasoline Pathway (Btu/mmBtu)



FIGURE 14 WTW Petroleum Use for Pyrolysis-Based Renewable Gasoline Pathways with Different Upgrading Plant Options Compared to the Petroleum Gasoline Pathway (Btu/mmBtu)



FIGURE 15 WTW GHG Emissions for Pyrolysis-Based Renewable Gasoline Pathways with Different Upgrading Plant Options Compared to the Petroleum Gasoline Pathway (gCO<sub>2</sub>-e/mmBtu)

Pathways with	Differen	t Upgradi	ng Plant C	)ptions per r	nmBtu of Fu	uel		
	_	Pyrolysis	Gasoline (L	low Yield)	Pyrolysis	Gasoline (H	ligh Yield)	_
Use and Emissions	Cycle	INT	SA	Conv	INT	SA	Conv	Gasoline

TABLE 20WTW Results for Pyrolysis-Based Renewable Gasoline and Petroleum GasolinePathways with Different Upgrading Plant Options per mmBtu of Fuel

Use and								
Emissions	Cycle	INT	SA	Conv	INT	SA	Conv	Gasoline
Total energy	WTP	678,187	696,655	691,028	648,349	648,807	693,316	246,590
(Btu)	PTW	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000
	WTW	1,678,187	1,696,655	1,691,028	1,648,349	1,648,807	1,693,316	1,246,590
Fossil fuel (Btu)	WTP	428,027	431,237	421,824	581,969	578,843	602,482	225,240
	PTW	0	0	0	0	0	0	979,201
	WTW	428,027	431,237	421,824	581,969	578,843	602,482	1,204,441
Petroleum (Btu)	WTP	52,644	49,574	66,221	74,192	59,077	97,685	80,462
	PTW	0	0	0	0	0	0	979,201
	WTW	52,644	49,574	66,221	74,192	59,077	97,685	1,059,664
GHGs (gCO <sub>2</sub> -e)	WTP	-41,364	-41,135	-41,063	-30,689	-31,086	-27,842	21,429
	PTW	75,947	75,947	75,947	75,947	75,947	75,947	77,594
	WTW	34,584	34,812	34,884	45,258	44,861	48,106	99,024

#### 5.1.3 Bio-Char Application

Figures 16–19 present WTW total energy use for pyrolysis-based renewable gasoline pathways with different bio-char applications (e.g., electricity generation and carbon sequestration) compared with the petroleum gasoline pathway. The WTW results for pyrolysis-based renewable gasoline and petroleum gasoline pathways per mmBtu of fuel are shown in Table 21. For the pyrolysis pathways, the integrated refinery scenario is used. Since the high-yield processes examined in Jones et al. (2009) use all of the bio-char to produce heat and power for fuel production internally, only WTW results for the low yield processes examined in Wright et al. (2010) are presented in this section. In the figures and table, "Gen." and "Seq." mean bio-char combustion for electricity generation and soil application for carbon sequestration, respectively.



FIGURE 16 WTW Total Energy Use for Pyrolysis-Based Renewable Gasoline Pathways with Different Bio-Char Applications Compared to the Petroleum Gasoline Pathway (Btu/mmBtu)

Power generation from bio-char combustion shows a significant energy benefit (15–20% for total energy, 10–11% for fossil energy, and 1% for petroleum) when compared with carbon sequestration by applying bio-char to soil. The benefit is larger for the pyrolysis-oil-reforming case because it has larger bio-char co-products. However, the results for the GHG emissions benefit are the opposite. When carbon is sequestered in the soil, GHG emissions are reduced significantly, by 7–11%. This is particularly true in the pyrolysis-oil-reforming case, in which the WTW GHG emissions are near zero due to the net sequestration of carbon.



FIGURE 17 WTW Fossil Fuel Use for Pyrolysis-Based Renewable Gasoline Pathways with Different Bio-Char Applications Compared to the Petroleum Gasoline Pathway (Btu/mmBtu)



FIGURE 18 WTW Petroleum Use for Pyrolysis-Based Renewable Gasoline Pathways with Different Bio-Char Applications Compared to the Petroleum Gasoline Pathway (Btu/mmBtu)



FIGURE 19 WTW GHG Emissions for Pyrolysis-Based Renewable Gasoline Pathways with Different Bio-Char Applications Compared to the Petroleum Gasoline Pathway (gCO<sub>2</sub>-e/mmBtu)

		H <sub>2</sub> from Pyrolysis Oil Reforming		H <sub>2</sub> from Fu Refor	H <sub>2</sub> from Fuel Gas/NG Reforming		External H <sub>2</sub> from Central SMR	
and Emissions	Cycle	Gen.	Seq.	Gen.	Seq.	Gen.	Seq.	Gasoline
		- / 0 0						
Total energy	WTP	749,320	996,085	707,242	903,888	678,187	861,625	246,590
(Btu)	PTW	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000
	WTW	1,749,320	1,996,085	1,707,242	1,903,888	1,678,187	1,861,625	1,246,590
Fossil fuel (Btu)	WTP	121.290	257.768	379.949	499.854	428.027	542.682	225.240
~ /	PTW	0	0	0	0	0	0	979 201
	WTW	121,290	257,768	379,949	499,854	428,027	542,682	1,204,441
Petroleum (Btu)	WТР	64 925	74 806	55 180	62 720	52 644	50 617	80 462
Tenoleum (Dtu)		04,925	74,000	55,100	02,720	52,044	59,017	00,402
	PTW	0	0	0	0	0	0	979,201
	WTW	64,925	74,806	55,180	62,720	52,644	59,617	1,059,664
GHGs (gCO <sub>2</sub> -e)	WTP	-62,034	-72,465	-44,031	-51,847	-41,364	-48,590	21,429
	PTW	75,947	75,947	75,947	75,947	75,947	75,947	77,594
	WTW	13,913	3,482	31,916	24,100	34,584	27,357	99,024

 TABLE 21
 WTW Results for Pyrolysis-Based Renewable Gasoline and Petroleum Gasoline

 Pathways with Different Bio-Char Applications per mmBtu of Fuel

#### 5.1.4 Detailed Greenhouse Gas Emission Sources and Sinks

Figure 20 presents the details of GHG emission sources and sinks for the pathway scenarios discussed in Sections 5.1.1 and 5.1.3. The pathway scenarios discussed in Section 5.1.2 are not included because the impact from upgrading plant options is so small. Biogenic CO<sub>2</sub> credit (CO<sub>2</sub> absorbed during growth of biomass that is converted into fuel) and GHG emissions from vehicle operation almost cancel each other out, because the biomass feedstock for pyrolysis discussed in this study is carbon-neutral. In addition to the biogenic CO<sub>2</sub> credit and vehicle operations, the production of fuel emits the most GHGs for all pathway scenarios except those with pyrolysis oil reforming. As discussed earlier, GHG emissions from fuel production decrease as the amount of H<sub>2</sub> from internal reforming increases, because renewable H<sub>2</sub> displaces fossil H<sub>2</sub>. For low-yield scenarios, supplemental fertilizers are a significant source of GHG emissions because they use corn stover as their feedstock. Large GHG emission credits are obtained if biochar is applied to soil. Even though the application of bio-char to soil eliminates GHG emission credits for co-produced electricity, the CO<sub>2</sub> sequestration credit is much greater than the GHG emission credit for co-produced electricity. Therefore, net GHG benefits are shown in the carbon sequestration option for bio-char. Transportation is the source of relatively fewer GHG emissions, even for high-yield scenarios with forest residue as the feedstock. Moreover, biomass collection is not an important GHG source for all scenarios.



FIGURE 20 Details of Greenhouse Gas Emission Sources and Sinks (gCO<sub>2</sub>-e/mmBtu)

# 5.2 WELL-TO-WHEELS ENERGY AND EMISSIONS PER VEHICLE MILE TRAVELED

As shown in Section 5.1.1, WTW results of gasoline and diesel are virtually identical on an energy basis. Since diesel vehicles are typically more energy efficient than are gasoline vehicles, WTW results for diesel vehicles per vehicle mile traveled show larger energy and emission benefits. Figures 21–24 present WTW total energy, fossil fuel, and petroleum use and GHG emissions of pyrolysis-based renewable gasoline and diesel and compare them with petroleum gasoline and diesel pathways. Table 22 also summarizes WTW results for pyrolysisbased renewable gasoline and diesel and compares them with petroleum gasoline and diesel. For pyrolysis-based renewable fuels, the following pathways are selected: a low-yield process with an integrated refinery scenario and H<sub>2</sub> from reforming pyrolysis oil ("Pyro-Oil Ref."), a lowyield process with an integrated refinery scenario and H<sub>2</sub> from reforming fuel gas and NG ("Fuel Gas/NG Ref."), and a high-yield process with an integrated refinery scenario with H<sub>2</sub> from fuel gas and NG reforming ("Fuel Gas/NG Ref.").



FIGURE 21 WTW Total Energy Use for Pyrolysis-Based Renewable Gasoline and Diesel Pathways Compared to the Petroleum Gasoline and Diesel Pathways (Btu/mi)



FIGURE 22 WTW Fossil Fuel Use for Pyrolysis-Based Renewable Gasoline and Diesel Pathways Compared to the Petroleum Gasoline and Diesel Pathways (Btu/mi)



FIGURE 23 WTW Petroleum Use for Pyrolysis-Based Renewable Gasoline and Diesel Pathways Compared to the Petroleum Gasoline and Diesel Pathways (Btu/mi)



FIGURE 24 WTW GHG Emissions for Pyrolysis-Based Renewable Gasoline and Diesel Pathways Compared to the Petroleum Gasoline and Diesel Pathways (gCO<sub>2</sub>-e/mi)

		Pyrc	olysis Gaso	line Car	Pyrolysis Diesel Car				
		Low	Yield	High Yield		Low	Yield	High Yield	
<b>TT</b> 1		<b>D</b> 1 ·	F 1	<b>F</b> 1	Petrol.	D 1 .	<b>F</b> 1	<b>F</b> 1	Petrol.
Use and	<b>C</b> 1	Pyrolysis	Fuel	Fuel	Gasoline	Pyrolysis	Fuel	Fuel	Diesel
Emissions	Cycle	Oıl	Gas/NG	Gas/NG	Car	Oıl	Gas/NG	Gas/NG	Car
Total energy (Btu)	WTP	3,678	3,471	3,850	1,210	3,064	2,892	3,208	896
	PTW	4,908	4,908	4,908	4,908	4,090	4,090	4,090	4,090
	WTW	8,586	8,379	8,758	6,118	7,154	6,982	7,298	4,986
Fossil fuel (Btu)	WTP	595	1,865	2,242	1,105	496	1,554	1,868	881
	PTW	0	0	0	4,806	0	0	0	4,090
	WTW	595	1,865	2,242	5,911	496	1,554	1,868	4,971
Petroleum (Btu)	WTP	319	271	441	395	267	228	369	326
	PTW	0	0	0	4,806	0	0	0	4,090
	WTW	319	271	441	5,201	267	228	369	4,416
GHGs (gCO <sub>2</sub> -e)	WTP	-304	-216	-188	105	-260	-186	-162	88
	PTW	373	373	373	381	317	317	317	327
	WTW	68	157	185	486	57	131	155	416

TABLE 22WTW Results for Pyrolysis-Based Renewable Gasoline and Diesel Pathways Comparedwith Petroleum Gasoline and Diesel Pathways per Vehicle Mile Traveled

Because of their high efficiency, diesel cars may receive more attention in the U.S. market. However, there are concerns about the criteria pollutants emitted by diesel cars, especially  $NO_x$  and particular matter. These emissions can be addressed by advanced emission control technologies, such as selective catalytic reduction and diesel particulate filters. Along with the use of advanced emission control technologies, the high level of purity and the low sulfur content of pyrolysis-based renewable diesel fuel may decrease the level of criteria pollutant emissions to a level similar to that of F-T diesel.

#### 5.3 PETROLEUM SAVINGS AND GREENHOUSE GAS EMISSION SAVINGS PER TON OF BIOMASS USED

Petroleum and GHG emission savings per ton of biomass are useful metrics, since the productivity of biofuels is often constrained by the availability of feedstock. Petroleum and GHG emission savings are obtained by multiplying petroleum and GHG emission reductions per mmBtu by the liquid fuel yields (in mmBtu per ton of biomass) for each of the cases examined. Figures 25 and 26 present the petroleum and GHG emission savings per ton of biomass, respectively. For the pyrolysis-based renewable fuel pathways, integrated refineries with H<sub>2</sub> from pyrolysis oil reforming, fuel gas/NG reforming, and external sources, as well as a distributed refinery case with an external source of H<sub>2</sub>, are selected.

As shown in Figure 25, pathways with higher yields as feedstock show larger petroleum savings because their liquid fuel yields are much higher, while the reduction in petroleum use per mmBtu of fuel is similar among the different pathways. In particular, if  $H_2$  is supplied internally by reforming pyrolysis oil, petroleum savings are reduced even more because of the sharply reduced liquid fuel yields. Also, the pathways with external  $H_2$  show less WTW petroleum use than do those with internal  $H_2$  reforming, because upstream activities for external  $H_2$  use a significantly smaller amount of petroleum than do the activities for biomass.

Figure 26 shows different levels for GHG emissions savings. The GHG savings for lower-yield cases are greater than those for higher-yield cases because the impact from the GHG emission reductions per unit of energy dominates the impact from the higher liquid fuel yields. The pyrolysis-oil-reforming scenarios for the lower-yield cases especially show significant GHG savings, but their petroleum savings are much smaller than they are in the other cases.

The results per ton of biomass used show a clear trade-off between oil displacement and GHG emission reductions among different pyrolysis pathways. With higher liquid fuel yields, oil savings are increased, but GHG emission reductions become smaller. Furthermore, the economics associated with pyrolysis pathways may be in favor of higher liquid fuel yields. Thus the pyrolysis design scenario may be chosen on the basis of multiple factors.



FIGURE 25 WTW Petroleum Savings per Ton of Biomass for Different Pyrolysis-Based Renewable Fuel Pathways



FIGURE 26 WTW GHG Emission Savings per Ton of Biomass for Different Pyrolysis-Based Renewable Fuel Pathways

# 6 CONCLUSIONS AND DISCUSSION

This study investigates pyrolysis-based renewable gasoline and diesel fuel on the basis of two case studies: Wright et al. (2010) and Jones et al. (2009). The information from the two studies was used to add a pyrolysis module with several pathway options to the GREET model. Results show:

- Pyrolysis-based renewable fuels can reduce WTW fossil fuel use, petroleum energy use, and GHG emissions by 50–90%, 92–95%, and 51–96%, respectively, depending on the feedstock, process design, fuel yields, H<sub>2</sub> sources, and co-product applications.
- Internal H<sub>2</sub> production from pyrolysis oil reforming reduces fossil fuel use and GHG emissions significantly, but it also reduces petroleum savings because the liquid fuel yield declines dramatically.
- Because of the large bio-char co-products, soil application of bio-char provides significant CO<sub>2</sub> credits, and the electricity generated from its combustion provides a large energy credit.
- Typically, a process with a higher liquid fuel yield results in greater petroleum savings but also more life-cycle GHG emissions.
- The upgrading scenario for pyrolysis oil (distributed versus integrated) affects WTW energy use and GHG emissions only minimally, since transportation activities have smaller energy and emission footprints than do other WTW activities, and since the benefits from system integration are small (on the basis of the two case studies considered for this analysis).

Although the upgrading scenario for pyrolysis oil (distributed versus integrated) had only a small impact on WTW energy use and emissions, it might be critical for the economic viability and operation of pyrolysis-based renewable fuel pathways. Moreover, the benefit from system integration has not been fully examined because related information is so limited. Thus further research needs to be done in order to compare the environmental and economic benefits from full upgrading to drop-in-ready liquid fuels (gasoline, diesel) versus those benefits from partial upgrading to refinery intermediate (naphtha, distillate) quality.

This study did not address several issues and concerns. Chief among them is the feedstock dependency of pyrolysis and upgrading processes. For example, it has been reported that wood chip has the potential of producing higher fuel yields than herbaceous biomass does (Bridgwater 2011). The choice of feedstock also affects the quality of pyrolysis oil. The quality of pyrolysis oil, in turn, influences the process fuel inputs and the product outputs of the subsequent upgrading processes.

As described in Section 3.1.5, the impact of bio-char as a soil amendment beyond carbon sequestration is not taken into account because of the large uncertainty associated with bio-char

behavior, even though many argue that bio-char would reduce  $N_2O$  emissions and improve fertilizer utilization. Because of the high global warming potential of  $N_2O$  and the high energy and emission intensity of nitrogen fertilizers, the impact of bio-char as a soil amendment could be significant. Further research on the soil application of bio-char is needed in order to gain a better understanding of the potential environmental benefits from pyrolysis-based renewable fuels.

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# APPENDIX: WELL-TO-WHEELS RESULTS FOR PYROLYSIS-BASED RENEWABLE DIESELS AND PETROLEUM-BASED FOSSIL DIESELS PER MILLION BTU OF FUEL



# A.1 HYDROGEN SOURCES

FIGURE A-1 WTW Total Energy Use for Pyrolysis-Based Renewable Diesel Pathways with Different Hydrogen Sources Compared to the Petroleum Diesel Pathway (Btu/mmBtu)

		Pyrolysis	s Diesel (Lov	w Yield)	Pyrolysis (High )		
Use and Emissions	Cycle	Pyrolysis Oil	Fuel Gas/NG	External	Fuel Gas/NG	External	Diesel
Total energy (Btu)	WTP	749,189	707,111	678,056	784,356	648,218	219,180
	PTW	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000
	WTW	1,749,189	1,707,111	1,678,056	1,784,356	1,648,218	1,219,180
Fossil fuel (Btu)	WTP	121,193	379,852	427,931	456,770	581,873	215,385
	PTW	0	0	0	0	0	1,000,000
	WTW	121,193	379,852	427,931	456,770	581,873	1,215,385
Petroleum (Btu)	WTP	65,404	55,658	53,123	90,252	74,671	79,679
· · ·	PTW	0	0	0	0	0	1,000,000
	WTW	65,404	55,658	53,123	90,252	74,671	1,079,679
GHGs (gCO <sub>2</sub> -e)	WTP	-63,511	-45,508	-42,840	-39,705	-32,166	21,632
	PTW	77,503	77,503	77,503	77,503	77,503	79,961
	WTW	13,992	31,995	34,663	37,798	45,337	101,593

# TABLE A-1WTW Results for Pyrolysis-Based Renewable Diesel and Petroleum Diesel Pathwayswith Different Hydrogen Sources per mmBtu of Fuel







FIGURE A-3 WTW Petroleum Energy for Pyrolysis-Based Renewable Diesel Pathways with Different Hydrogen Sources Compared to the Petroleum Diesel Pathway (Btu/mmBtu)



FIGURE A-4 WTW GHG Emissions for Pyrolysis-Based Renewable Diesel Pathways with Different Hydrogen Sources Compared to the Petroleum Diesel Pathway (gCO<sub>2</sub>-e/mmBtu)



# A-2 DISTRIBUTED VERSUS INTEGRATED REFINERIES





FIGURE A-6 WTW Fossil Fuel Use for Pyrolysis-Based Renewable Diesel Pathways with Different Upgrading Plant Options Compared to the Petroleum Diesel Pathway (Btu/mmBtu)



FIGURE A-7 WTW Petroleum Use for Pyrolysis-Based Renewable Diesel Pathways with Different Upgrading Plant Options Compared to the Petroleum Diesel Pathway (Btu/mmBtu)



FIGURE A-8 WTW GHG Emissions for Pyrolysis-Based Renewable Diesel Pathways with Different Upgrading Plant Options Compared to the Petroleum Diesel Pathway (gCO<sub>2</sub>-e/mmBtu)

		Pyrolysis	Diesel (Low	VYield)	Pyrolysis			
Use and Emissions	Cycle	INT	SA	Conv.	INT	SA	Conv.	Diesel
Total energy (Btu)	WTP	678,056	678,434	690,897	648,218	648,677	693,185	219,180
	PTW	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000
	WTW	1,678,056	1,678,434	1,690,897	1,648,218	1,648,677	1,693,185	1,219,180
Fossil fuel (Btu)	WTP	427,931	431,140	421,727	581,873	578,747	602,386	215,385
	PTW	0	0	0	0	0	0	1,000,000
	WTW	427,931	431,140	421,727	581,873	578,747	602,386	1,215,385
Petroleum (Btu)	WTP	53,123	50,052	66,700	74,671	59,556	98,163	79,679
	PTW	0	0	0	0	0	0	1,000,000
	WTW	53,123	50,052	66,700	74,671	59,556	98,163	1,079,679
GHGs (gCO <sub>2</sub> -e)	WTP	-42,840	-42,610	-42,540	-32,166	-32,563	-29,318	21,632
	PTW	77,503	77,503	77,503	77,503	77,503	77,503	79,961
	WTW	34,663	34,893	34,963	45,337	44,940	48,185	101,593

# TABLE A-2WTW Results for Pyrolysis-Based Renewable Diesel and Petroleum Diesel Pathwayswith Different Upgrading Plant Options per mmBtu of Fuel

<sup>a</sup> INT = integrated process with an on-site bio-refinery, SA = distributed process with a standalone bio-refinery, Conv. = distributed process with a conventional petroleum refinery.

# A-3 BIO-CHAR APPLICATIONS



FIGURE A-9 WTW Total Energy Use for Pyrolysis-Based Renewable Diesel Pathways with Different Bio-Char Applications Compared to the Petroleum Diesel Pathway (Btu/mmBtu)



FIGURE A-10 WTW Fossil Fuel Use for Pyrolysis-Based Renewable Diesel Pathways with Different Bio-Char Applications Compared to the Petroleum Diesel Pathway (Btu/mmBtu)



FIGURE A-11 WTW Petroleum Use for Pyrolysis-Based Renewable Diesel Pathways with Different Bio-Char Applications Compared to the Petroleum Diesel Pathway (Btu/mmBtu)



FIGURE A-12 WTW GHG Emissions for Pyrolysis-Based Renewable Diesel Pathways with Different Bio-Char Applications Compared to the Petroleum Diesel Pathway (gCO<sub>2</sub>-e/mmBtu)
		H <sub>2</sub> from Pyrolysis Oil Reforming		H <sub>2</sub> from Fuel Gas/ NG Reforming		External H <sub>2</sub> from Central SMR		
Use and Emissions	Cycle	Gen.	Seq.	Gen.	Seq.	Gen.	Seq.	Diesel
Total energy	WTP	749,189	995,954	707,111	903,757	678,056	861,494	219,180
(Btu)	PTW	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000	1,000,000
	WTW	1,749,189	1,995,954	1,707,111	1,903,757	1,678,056	1,861,494	1,219,180
Fossil fuel (Btu)	WTP	121,193	257,671	379,852	499,758	427,931	542,585	215,385
	PTW	0	0	0	0	0	0	1,000,000
	WTW	121,193	257,671	379,852	499,758	427,931	542,585	1,215,385
Petroleum (Btu)	WTP	65,404	75,285	55,658	63,198	53,123	60,096	79,679
	PTW	0	0	0	0	0	0	1,000,000
	WTW	65,404	75,285	55,658	63,198	53,123	60,096	1,079,679
GHGs (gCO <sub>2</sub> -e)	WTP	-63,511	-73,941	-45,508	-53,324	-42,840	-50,067	21,632
	PTW	77,503	77,503	77,503	77,503	77,503	77,503	79,961
	WTW	13,992	3,562	31,995	24,179	34,663	27,436	101,593

TABLE A-3 WTW Results for Pyrolysis-Based Renewable Diesel and Petroleum Diesel Pathwayswith Different Bio-Char Applications per mmBtu of Fuel



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