ACS Sustainable Chemistry & Engineering

Research Article

Cite This: *ACS Sustainable Chem. Eng.* 2018, 6, 10766−10777

Carbon Footprint Analysis of Gasoline and Diesel from Forest Residues and Algae using Integrated Hydropyrolysis and Hydroconversion Plus Fischer−Tropsch (IH^2 Plus cool GTL)

Olumide Winjobi,[*,†] Hossein Tavakoli,[‡] Bethany Klemetsrud,[§] Robert Handler,[†] Terry Marker,[∥] Michael Roberts,[∥] and David Shonnard[†]

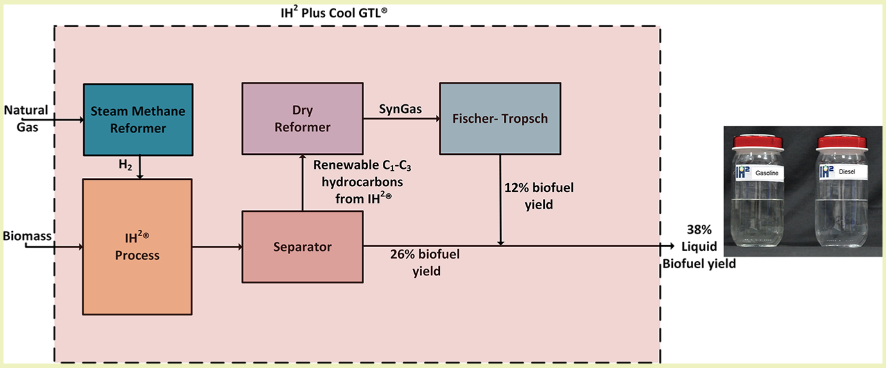
[†]Department of Chemical Engineering and the Sustainable Futures Institute, Michigan Technological University, 1400 Townsend Drive, Houghton, Michigan 49931, United States

[‡]Department of Civil and Environmental Engineering, Michigan Technological University, 1400 Townsend Drive, Houghton, Michigan 49931, United States

[§]Department of Chemical Engineering, University of North Dakota, 243 Centennial Drive, Stop 7101, Grand Forks, North Dakota 58202, United States

[∥]Gas Technology Institute, 1700 South Mount Prospect Road, Des Plaines, Illinois 60018, United States

Supporting Information



ABSTRACT: Life cycle analysis was conducted with a focus on greenhouse gas (GHG) emissions of renewable gasoline and diesel produced by the integrated hydropyrolysis and hydroconversion (IH^2) and the new IH^2 plus Fischer−Tropsch (IH^2 Plus cool GTL) processes. This new process has a primary objective of increasing the yield of biofuel relative to original IH^2 process (increase of 26% to 38% wt) by processing the C1−C3 gas co-products through an integrated Fischer−Tropsch unit to produce liquid-range hydrocarbon biofuel. For both biofuel processes, woody biomass residues (forest logging and saw mills) and algae were investigated as feedstocks. The effect of the electricity generation mix of different states in the U.S. was also examined for algae cultivation. For woody residues as feedstock, life cycle GHG emission savings of about 86.8% and 63.3% were calculated for the IH^2 and optimized-IH^2 Plus cool GTL hydrocarbon biofuel, respectively, relative to fossil-derived fuel. For algae as feedstock, emission increases of about 140% and 103% were calculated for the IH^2 and optimized-IH^2 Plus cool GTL, respectively, relative to fossil-derived fuel. The electricity grid mix of the biorefinery location significantly impacts the GHG emissions of the processes for algae feedstock. GHG savings of about 42% can be potentially achieved if the plant was located in an area with a low GHG intensity grid. This study has shown that a significant biofuel yield boost can be achieved while retaining high GHG savings by using IH^2 Plus cool GTL for a woody feedstock.

KEYWORDS: *Hydropyrolysis, Hydroconversion, Fischer−Tropsch, Forest residue, Algae, Greenhouse gas, Life cycle assessment*

INTRODUCTION

Anthropogenic greenhouse (GHG) emissions are one of the major environmental concerns facing the world today. Biofuels with lower amounts of associated GHG emissions could help to address issues associated with climate change in a sustainable manner.[1] Increased production of biofuels could also address concerns of reliance on imported petroleum, increasing fuel costs, and domestic job creation. This trend in increased biofuels production is being supported at the highest levels of national governments, particularly in the most developed nations. For example, the Energy Independence and Security Act (EISA) of 2007 mandates renewable fuel

Received: May 7, 2018
Revised: June 22, 2018
Published: June 30, 2018

ACS Publications

DOI: 10.1021/acssuschemeng.8b02091

production targets through the year 2022, at which time 36 billion gallons should be produced annually.[2] This quantity would represent approximately 25% of current annual gasoline consumption in the U.S.[2] A report by the U.S. Department of Energy estimated that over 1 billion dry metric tons of biomass are available for collection per year in the U.S. within sustainability constraints and at a price less than $60/dry ton (2011 basis).[2] The majority of this biomass from the domestic U.S. "billion ton vision" is woody (lignocellulosic) as opposed to the current predominant global biomass feedstocks for biofuels, i.e., sugar cane, corn starch, and plant oils. Anticipated conversion technologies for lignocellulosic biomass are either biochemical, including hydrolysis for production of sugars and fermentation production of biofuels, or thermochemical, which includes gasification, pyrolysis, or hydropyrolysis, plus a catalytic upgrading step to convert intermediate synthesis gas or pyrolysis oil to hydrocarbon "drop-in" biofuels.[3] Primarily lignocellulosic materials are being considered for the "billion ton vision"; however, studies are also investigating algae as a viable feedstock for biofuel production. This is due to algae's advantages of higher photosynthetic efficiency, higher per area biomass production, and faster growth compared to lignocellulosic materials.[4−6]

The integrated hydropyrolysis−hydroconversion process (referred to as IH^2 hereafter) developed by Gas Technology Institute (GTI) shown in Figure 2 is a thermochemical process for the conversion of a broad range of biomass types into liquid hydrocarbon biofuels spanning the range of gasoline, jet, and diesel.[7] Compared to other thermocatalytic technologies, the IH^2 process operates at slightly lower temperatures and has a higher yield of hydrocarbons.[8] Relative to fast pyrolysis and upgrading, the hydrocarbon products from the IH^2 process have advantages of higher energy density, low acidity (TAN < 0.05), negligible loss of carbon to water, and high stability.[9] The IH^2process is carried out in two sequential yet integrated stages at moderate pressure (20−35 bar) and temperatures ranging between 350 and 450 °C. The first step involves exothermic catalytic fast hydropyrolysis and hydrodeoxygenation reactions carried out in a fluidized bed reactor at moderate hydrogen pressure. The product vapors from the first step are carried to the second conversion step, an exothermic polishing hydrodeoxygenation and hydroconversion fixed-bed reactor operating at essentially the same pressure as the first reactor. The hydrogen required for the IH^2 process can be either imported from an external source, such as a steam methane reformer, or can be produced in a reformer using internally produced short chain (C1−C3) hydrocarbon co-products. Other co-products from the process are solid char, high-pressure steam, and ammonia/ammonium sulfate. Solid char can be combusted internally to provide heat for feedstock drying and process start-up and electricity for internal process use. Ammonia and hydrogen sulfide in the process condensate from the separator are stripped and oxidized to make an aqueous ammonia/ammonium sulfate product, which can be used as an agricultural fertilizer. Hydrocarbon gasoline produced from the IH^2 process has been shown to have similar properties to petroleum.[10] A more detailed description of the IH^2 process can be found in the works of Fan, Tan, and colleagues.[9,10]

The yield of biofuel from the thermochemical conversion of biomass has a significant effect on the economics and biofuel environmental profile. Some suggest that biofuel economics and environmental performance can be significantly improved through production and use of co-products of high value which displace high emission products in the market.[11,12] Arbogast et al. estimated a 6−7% reduction in the production cost of biofuel for a 10% increase in the yield of biofuel from the upgrade of pyrolysis bio-oil (Pyoil).[13] Several approaches are being investigated to increase the yield of the biofuel. One of the approaches being researched is the acid or alkali pretreatment of biomass before the pyrolysis conversion step. Acid or alkali pretreatment is believed to remove alkali earth metals in the biomass, leading to an increase in the bio-oil yield and potentially an increase in the yield of biofuel obtained from the upgrade of the bio-oil.[14−18] Karnjanakom et al. observed an increase in the yield of bio-oil when woody biomass feedstock is subjected to an ultrasonic pretreatment prior to pyrolysis of the biomass.[19] Ultrasonic pretreatment is believed to destroy wax and lignin layers in biomass and break connecting glycosidic bonds, resulting in the increase the yield of bio-oil.[19,20] Changes to the structure of biomass to increase its lignin content are also a suggested method to increase the yield of pyrolysis bio-oil. Fahmi and co-workers observed in their study an increasing yield in pyrolysis bio-oil with increasing lignin content of the biomass feedstock.[14]

The IH^2 plus Fischer−Tropsch process (referred to as IH^2 Plus cool GTL hereafter) recently developed by GTI, as shown in Figure 3, is an alternative approach on the base IH^2 process to increase the yield of liquid hydrocarbon transportation biofuel relative to IH^2. IH^2 Plus cool GTL is an innovation under development that could be applied as an auxiliary addition to base IH^2 in the case of natural gas being available and acceptable as a source of hydrogen. Instead of utilizing the C1−C3 gas co-products for the production of the required hydrogen, in the IH^2 Plus process the C1−C3 gas co-products are sent directly to a dry reforming system that uses CO_2 and steam to generate synthesis gas. The synthesis gas is then processed in an integrated Fischer−Tropsch system to produce additional hydrocarbon liquid biofuels, resulting in an increase in the mass yield of hydrocarbon biofuels. Because the C1−C3 stream is used to generate additional liquid biofuel in the IH^2 Plus cool GTL process, hydrogen required in the IH^2 Plus cool GTL system is produced from the steam reforming of fossil natural gas, instead of being produced internally as in the IH^2 process.

Life cycle assessment (LCA) is a holistic and comprehensive method used in evaluating the environmental impacts and resources used throughout a product's life cycle, i.e., from the raw material acquisition, through production and use phases, to waste management.[21] Several studies have utilized LCA to evaluate the greenhouse gas (GHG) emissions of renewable biofuels. Fan and co-workers estimated GHG emission savings of 67−86% for IH^2 gasoline and diesel compared to fossil-derived gasoline and diesel.[10] Handler and co-workers, in their LCA of algal biofuel produced through fast pyrolysis using rapid thermal processing (RTP) technology, estimated a reduction of 32−87% (depending on the settling method utilized) relative to fossil gasoline when the algal feedstock is cultivated using wastewater effluent.[22] However, an increase in GHG emissions of about 41−81% (depending on the settling method utilized) relative to fossil gasoline was estimated by Handler and co-workers for algal biofuel using the RTP technology when the algal feedstock is raceway-cultivated.[22] Some studies have used LCA to investigate the effect of an increase in the yield of biofuel/bio-oil on GHG emissions using sensitivity analysis in their LCA. Chan and co-workers observed in their study an over 20% potential reduction in GHG emissions for an about 34% increase in the yield of bio-oil produced from the hydrothermal liquefaction of oil palm.[23] Wang and co-workers reported an about 9.9% reduction in GHG emissions for a 15% increase in the yield of bio-oil produced from the fast pyrolysis of municipal solid waste.[24] The sensitivity analyses in these LCAs are typically "first-order" scenario analyses that measure the sensitivity of the LCA results with a change in only the yield of biofuel.

The purpose of this study is to evaluate the effects of increasing IH^2 biofuel yield on life cycle GHG emissions of hydrocarbon biofuel blends (gasoline and diesel) produced by the IH^2 and IH^2 Plus cool GTL processes while also taking into consideration the trade-offs from the process modifications. The feedstocks utilized were woody biomass (forest logging residues, unmarketable roundwood, and mill residues) and algae cultivated in photobioreactors.

■ LCA METHODS

Goal-Scope, Functional Unit, Allocation, and Methods Overview. In this LCA, the system boundary is cradle-to-grave, including feedstock collection and transportation, feedstock processing (size reduction and drying), fuel production, waste treatment, transportation, and use of final fuel product. The functional unit of the study is 1 MJ of final fuel blend used. GHG emissions of GTI renewable fuels are compared to the equivalent petroleum fuel counterparts (gasoline and diesel) based on the daily amount of gasoline and diesel produced in each case. The supply chain inputs for woody biomass were obtained from a previous study by Fan et al.[10] Algae production data was provided from personal communication with Mr. James Winfield (Algae Energy, Cumming, GA.) GTI provided inputs and outputs from the IH^2 and IH^2 Plus cool GTL processes. The inventory data for all of the inputs and outputs were entered into SimaPro 8.0 software by selecting appropriate ecoinvent profiles to represent the inputs of materials and energy for the simulation.[25] Where necessary, such as in the case of electricity grid mix, modifications were made to the ecoinvent profiles to better reflect the input data (this is further discussed later in this study). GHG credits for the co-product ammonia were accounted for using the system expansion method that is recommended by ISO 14041 and the U.S. EPA.[26,27] All of the input data used in this study were processed in SimaPro software on the basis of the functional unit by taking into account the amount of hydrocarbon biofuel produced and the LHV of the biofuel.

Inventory. *Inventory-Feedstocks. Woody Biomass.* A plant size of 500 tonnes per day was evaluated for a Memphis, Tennessee location. A previous forest feedstock supply study to understand the economic feasibility of supplying woody biomass to an IH^2 processing facility next to an existing refiner determined the Memphis, Tennessee, location as a suitable location that can support the scale of residues required for the IH^2 facility.[10] The feedstock includes forest residues, unmarketable roundwood, and mill residues. Forest residues are collected using conventional logging equipment, converted roadside into chips, and hauled to the receiving location with a semitruck and trailer rig. Roundwood is processed into 0.2 m and tree length logs using conventional logging equipment, which are transported to the receiving facility and then converted into chips. Mill residues are collected in a sawmill facility, which includes bark from round logs and pulpwood, sawdust and sawmill chips, and slabs. All feedstock is delivered to Memphis where it is processed and dried. A hauling distance of 117 km was utilized in this study for the transport of woody feedstock. The inputs of woody biomass feedstock supply are tabulated in Table 1. In this study, woody biomass is assumed to be transported about 117 km by truck, assuming a fuel efficiency of 2.13 km/L diesel and a load capacity of 12 bone dry metric ton per truck to the GTI processing facility.[10] Inventory inputs for a round-trip truck transport are shown in Table 1

Table 1. Inputs for Woody Biomass Collection, Transport, and Processing[10,a]

processing stage	item	input amount[b]
raw material processing in woods (harvesting, forwarding, chipping, loading, and unloading)	diesel	4860
	lubricating oil	38
	hydraulic fluid	42
	grease (tubes)[d]	29
	gasoline	110
trucking (round trip)	diesel	4187
	lubricating oil	8
	grease (tubes)[d]	1
yard equipment	diesel	689
	lubricating oil	30
	hydraulic fluid	30
	grease (tubes)[d]	21
feedstock processing and drying (TN electricity grid)[e]	energy in kWh (size reduction)	14920
	energy in kWh (drying)[c]	12757

[a] Basis: 500 metric tons per day feedstock input. [b] In liters unless otherwise noted. [c] Feedstock drying uses excess heat from the IH^2 process, so these values do not represent actual inputs. [d] Value of 400 g/tube. [e] TN = Tennessee.

Algae. There are two basic ways to cultivate algae on a commercial scale, open pond systems and enclosed photobioreactor (PBR) systems. PBRs are closed systems with controlled environments that typically facilitate higher growth rates of algae. One of the advantages of using closed systems is that it is easier to define optimal growth requirements of algae (e.g., nutrient supply, water supply, temperature, light, density, pH, avoiding contamination, and mixing rate) and control them accordingly. The cultivation of algae in this study was done utilizing a PBR as described by Algae Energy.

Algae Energy's PBR cultivation technology is based on a series of acrylic rectangular boxes, stacked side-by-side to cultivate algae. Between each PBR unit there is an LED light panel that runs the entire height of the PBR to shine light on each PBR as shown in Figure 1. The PBRs are run in parallel, and the modules have two distinct sides to offer the capacity to grow two types of algae at once, as well as to prevent total system collapse if one side has issues. High-efficiency LEDs are used that provide a complete wavelength spectrum (white light), along with bonus light in red and blue wavelengths that algae are particularly attuned to use. The algae cultivation medium is supplemented by nutrients which have been added to meet the stoichiometric requirements of the algae. The medium is based on the Guillard's (F/2) Marine Enrichment medium, which is an enriched seawater medium for growing costal marine algae. The recipe of major nutrients, trace metals, and vitamins for the medium can be found in section B of the Supporting Information (SI).[28−30]

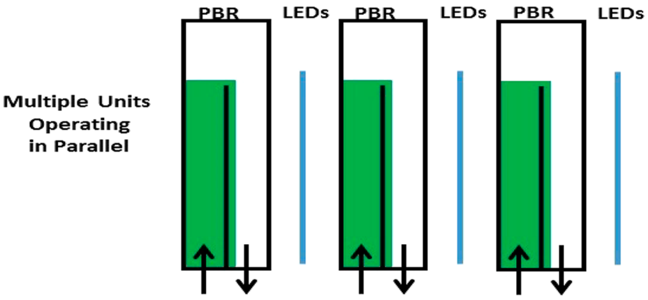


Figure 1. Schematic of the Algae Energy PBR.

After cultivation, algae must be harvested and subsequently dewatered before further processing. A hollow fiber membrane filter system is used to harvest the algae, followed by two sequential centrifugation steps to bring the water content below 20%. Algae biomass is then crushed in a bead mill and dried to a moisture content of less than 10%.

Algae often has a high lipid content, and the algae oil could be isolated for use as fuel precursors, chemical feedstocks, or food ingredients. If oil extraction is required, it may be accomplished while the algae is still fairly moist, depending on the technique used. Chemical oil extraction is the most common method, using a solvent like hexane to attract the lipids after cell disruption. In this study, whole algae biomass is used for the GTI process, although potential variations on that scenario are discussed in later sections. Table 2 presents more details of the inputs and outputs of algae cultivation and processing. It should be noted that the algae cultivation data was collected from a system that was not operating at a full commercial scale. It was assumed that algae would be processed in the same place it was cultivated, in Georgia, and that transportation requirements would be negligible.

Table 2. Inputs and Outputs of Algae Cultivation and Processing[a]

process stage	item[b]	amount
cultivation	electricity (pumping, lighting) in kWh	2.11×10^6
	water in MT	3.83×10^2
	CO_2-containing gas stream in MT	1.20×10^3
	nutrients[c] in MT	5.47×10^1
	salt in percent	2.4
processing	electricity in kWh (hollow fiber membrane filter)	4.26×10^4
	electricity in kWh (centrifuge)	3.20×10^5
	electricity in kWh (rack dryer)	6.40×10^4
outputs	algae (dry wt) in MT	500
	oil content	50%

[a] Basis: 500 dry metric tons per day feedstock input. [b] MT is metric tons. GA (= Georgia) electricity grid is assumed. [c] Nutrients are based on Guillard's (F/2) Marine Enrichment medium shown in the SI.[28,29]

Inventory-Processes. IH^2 Process. The IH^2 processing data were provided by GTI. The process is carried out at mild conditions with temperatures varying in the hydropyrolysis stage from about 340 to 470 °C and 370 to 400 °C in the hydroconversion stage, with pressures ranging from 20 to 35 bar.[10] Integrated hydropyrolysis and hydroconversion steps convert the biomass to an IH^2 fuel blend of gasoline and diesel hydrocarbon species. The cases analyzed assume a stand-alone integrated IH^2 facility, where H_2 is produced internally by reforming C1−C3 co-products made in the process with steam. Biogenic CO_2 is also produced from the process, which is shown in Figure 2. The biomass processing shown in Figure 2 for woody residue includes the collection of residues, transportation of residues to the processing facility, and drying of the woody residues, while processing for algae is the algae cultivation using a PBR. Burdens from provision and any pretreatment of the flue gas (CO_2 source) prior to being available for algae cultivation are not included in this study. Prior modeling efforts focused on flue gas utilization by algae cultivation systems have assumed that the gas pretreatment or conditioning burdens are negligible.[31]

The char produced from the process is used internally to produce steam and electricity. Electricity from the grid is used to supplement electricity demand not met by the internally generated electricity.

IH^2 Plus cool GTL Process. The IH^2 Plus cool GTL processing data were provided by GTI. The H_2 required in the IH^2 Plus cool GTL process is generated from steam reforming of fossil natural gas, while the C1−C3 co-products are dry-reformed to produce synthesis gas, as shown in Figure 3. The synthesis gas is then processed through a Fischer−Tropsch (F-T) system to produce additional hydrocarbon transportation fuel. With this configuration, the mass yield of biofuel is boosted relative to the base IH^2 process from 26% to 38% wt. Similar to the IH^2 process, the char produced from the process is used internally to produce steam and electricity, while unmet electricity demand is satisfied from external electricity from the grid. The system flow diagrams of the IH^2 Plus cool GTL process for biomass conversion to fuel is illustrated in Figure 3. GHG emissions of fossil natural gas were evaluated in this study using appropriate life cycle inventory data in SimaPro software (natural gas, from medium network (0.1−1 bar), at service station (RoW)).

To illustrate the potential differences in GHG emissions associated with different feedstocks and different processing platforms, four primary cases in this study were designed to reflect this range of options and are outlined in Table 3.

Table 4 shows some of the collected inputs and outputs of all cases at the fuel production stage. All scenarios were developed using a basis of 500 tonnes per day of feedstock input. Onsite IH^2 processing utilities required for processing algae biomass are expected to be about the same as the woody biomass processing, except the amounts of electricity required from external sources differ between the two feedstocks due to the amount of electricity that can be produced internally from char in each situation, as shown in Table 4 (utilities subsection). The char produced from woody residue feedstock (cases 1 and 2) is significantly more than that produced from algae feedstock (cases 3 and 4). In a measure to check data quality for inputs in Table 4, we computed biogenic carbon balances utilizing ultimate analyses of woody residue, algae, and biofuels (gasoline and diesel), shown in Table S4. Biogenic carbon balances of approximately 106, 110, 103,

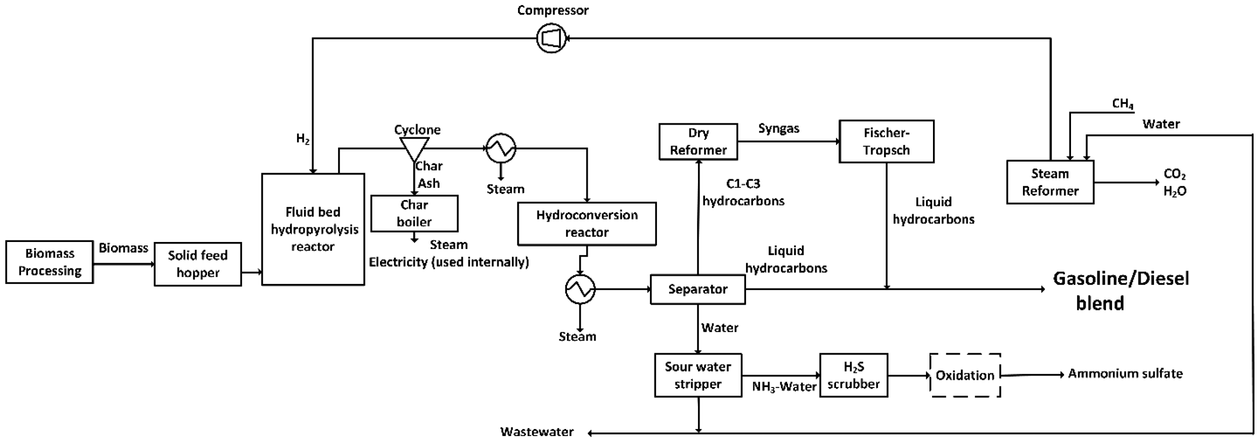


Figure 2. Schematic of the IH^2 process.

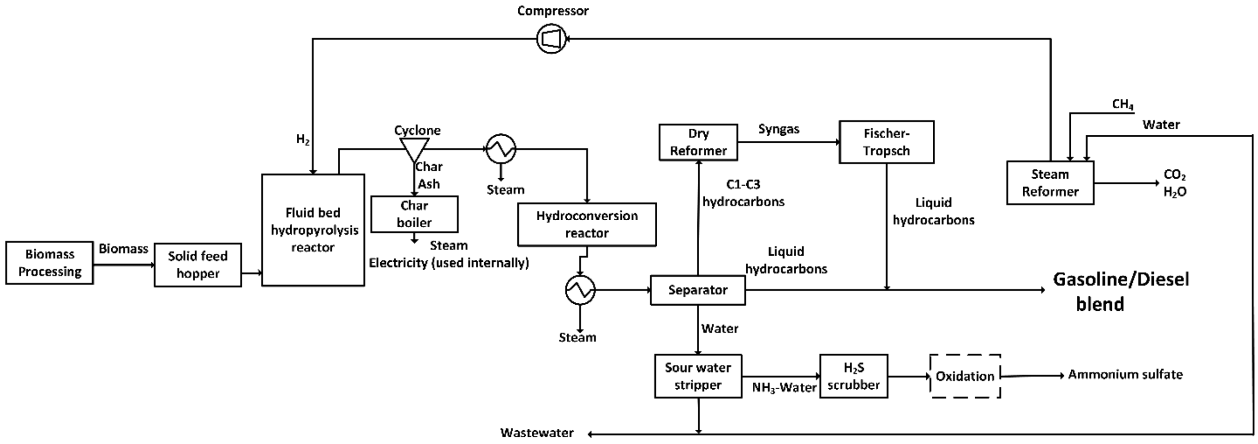


Figure 3. Schematic of the IH^2 Plus cool GTL process.

Table 3. Summary of Primary Cases in This LCA Study

	case 1	case 2	case 3	case 4
feedstock	wood	wood	algae	algae
conversion technology	IH^2	IH^2 Plus	IH^2	IH^2 Plus

Table 4. Comparison of Selected Inputs and Outputs in Primary Cases[a]

	case 1	case 2	case 3	case 4
input, MT/d				
biomass	500[b]	500[b]	500[c]	500[c]
oxygen in air (used to combust char and in the H_2 plant furnace)	317	458	138	125
natural gas	0	70	0	70
output, MT/d				
gasoline	90	120	112.5	152
diesel	40	70	112.5	152
total fuel produced	130	190	225	304
ammonia in sour water	0.25	0.25	9.06	9.06
ash	1.5	1.5	66.5	66
water, process	12	12	76	66
water, burning char + reformer gas, MT/d	103	103	82	82
water, burning F-T waste gas	0	78	0	28
water total	115	193	194	176
CO_2 (from IH^2 process)	95[d]	0	74[d]	0
CO_2 (from H_2 plant reformer process)	171[d]	171	171[d]	171
CO_2 (from H_2 plant reformer burning)	53[d]	53	53[d]	53
CO_2 (from F-T process)	0	100[d]	0	7[d]
CO_2 (from F-T waste gas burning)	0	66[d]	0	100[d]
CO_2 (from char burning)	257[d]	257[d]	37[d]	29[d]
CO_2 total	576	647	335	360
utilities				
electricity, MW	2	2	11	11
raw makeup water, L/s	17.9	17.9	17.9	17.9
wastewater out, L/s	7.1	7.1	7.1	7.1
nitrogen, kg/h	2.5	2.5	2.5	2.5

[a] MT = metric ton. [b] 12% moisture content. [c] MAF = moisture and ash free. [d] Biogenic carbon.

and 109% were calculated for cases 1, 2, 3, and 4, respectively. Considering potential uncertainty in ultimate analyses of biomass feedstocks and biofuels, we considered the closure of biogenic C satisfactory.

The electricity generated internally in all four cases through the combustion of char was not sufficient to fully offset the electricity required by the processes. The remaining electricity needed was purchased from the grid.

The final fuel products (renewable diesel and gasoline blend) are "drop-in" fuels that are considered to be direct replacements for petroleum gasoline and diesel. Although biofuel transportation assumptions could be changed to more accurately model specific commercial locations, we will see that fuel distribution has a minimal impact compared to other items in the biofuel pathway.

The IH^2 and IH^2 Plus cool GTL processes also produce a water−ammonia stream, which can be converted to fertilizer as described by Fan, Tan, and their colleagues.[9,10] The ammonia co-produced from the processes is assumed to be similar to the ammonia produced from the conventional pathway. Displacement credits as recommended by ISO 14040 were assigned to the ammonia in the water−ammonia stream based on the environmental burden of synthetic N fertilizer on a 1:1 basis of N content. Ammonia is modeled in SimaPro using the inventory "Ammonia, as 100% NH_3 (NPK 82−0−0) at regional house" in this study. Ash is trucked and disposed of in a local landfill with an assumed transportation distance of 80 km one way. The mass yield of ash produced from the processes is approximately less than 0.1% for woody biomass, while for algae it is about 12% relative to the input biomass, as shown in Table 4. Cooling tower blowdown and wastewater are treated at the refinery wastewater treatment plant. GHG emissions of waste treatment are determined in SimaPro by selecting an appropriate industrial wastewater treatment ecoprofile (Wastewater, average (CH), treatment of, capacity 1E9l/year).

Impact Assessment. Life cycle impacts were determined using the IPCC 2013 GWP 100a method for GHG emissions, most notably including CO_2, CH_4, and N_2O but also including climate-active refrigerants and solvents in the full list of emissions inventories from each LCA case. Net CO_2 emissions of renewable fuel blend at all stages, including the combustion stage, are considered carbon neutral because CO_2 is sequestered by photosynthesis during the growth of biomass. The C neutrality assumption is further supported by recent studies demonstrating relatively small direct and indirect land use change effects when logging and mill residues are utilized and similarly minimal soil C reduction for algae production systems.[2,32,33] Thus, only fossil CO_2 is accounted for in this life cycle C footprint analysis. GHG emissions of GTI renewable fuels are compared to the equivalent petroleum fuel counterparts (gasoline and diesel) based on the amount of gasoline and diesel produced in each case. GHG emissions for fossil fuel were obtained from a study from the National Energy Technology Laboratory.[34] A sample calculation for the petroleum fuel counterpart for case 1 can be found in section C of the SI. Energy impacts were also determined using the Cumulative Energy Demand method in SimaPro.

DOI: 10.1021/acssuschemeng.8b02091
ACS Sustainable Chem. Eng. 2018, 6, 10766−10777

Table 5. Summary of Scenario Analysis Scenarios for Case 2

	case 2a	case 2b	case 2c	case 2d
feedstock	woody biomass	woody biomass	woody biomass	woody biomass
conversion technology	IH^2 Plus cool GTL (energy optimized)	IH^2 Plus cool GTL (energy optimized)	IH^2 Plus cool GTL	IH^2 Plus cool GTL (energy optimized)
other changes (relative to base case)	lower natural gas input	lower natural gas input more diesel, less gasoline catalyst modifications	lower biofuel yield	lower natural gas input more electricity required[a]

[a] More electricity required for the IH^2 Plus conversion step only.

Table 6. Summary of Scenario Analysis Scenarios for Case 4

	case 4a	case 4b	case 4c	case 4d
feedstock	algae	algae	algae	algae
conversion technology	IH^2 Plus cool GTL (energy optimized)	IH^2 Plus cool GTL (energy optimized)	IH^2 Plus cool GTL	IH^2 Plus cool GTL (energy optimized)
other changes (relative to base case)	lower natural gas input	lower natural gas input more gasoline, less diesel catalyst modifications	lower yield	lower natural gas input more electricity required[a]

[a] More electricity required for the IH^2 Plus conversion step only.

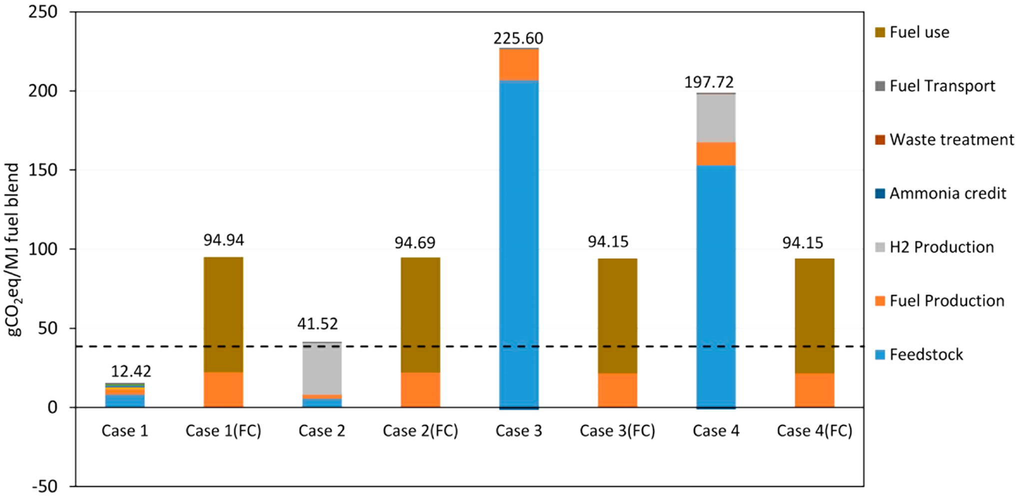


Figure 4. Life cycle GHG emissions of IH^2 and IH^2 Plus cool GTL fuel blends. The dashed line represents a 60% reduction in GHG emissions from petroleum gasoline. FC represents the fossil counterpart calculated based on the weighted average of gasoline and diesel in the fossil fuel blend and their emissions. Fossil fuel emissions data from Cooney et al. (2016).[34]

Scenario Analysis. *Effect of Changes in Process Inputs on GHG Emissions.* Many processing decisions or assumptions surrounding the process will have an impact on the final LCA results, and therefore, several additional scenarios were investigated. Case 2a evaluates how optimizing the process affects the GHG emissions from the IH^2 Plus cool GTL process relative to the unoptimized baseline case 2. Compared to the base case 2 where the heat for the H_2 plant is generated by burning natural gas, in case 2a, waste gas from the Fischer−Tropsch process is utilized to provide some of the heat. As a result, case 2a results in a lower natural gas requirement for process heat.

Case 2b investigates how, by catalyst modifications, increasing the yield of diesel while reducing the yield of gasoline from the optimized IH^2 Plus cool GTL process affects the GHG emissions of the mixed biofuel product. The lower natural gas requirement for process heat (as in case 2a) also applies for 2b. The yield of gasoline biofuel decreased by 21% relative to the base case, while the yield of diesel biofuel increased by 36% relative to the base case, as shown in Table S1. However, the overall yield of biofuel is the same as the yield obtained in the base case.

Case 2c examines how a lower yield of fuel, about 11% reduction in the yield of gasoline relative to the base case (about 7% reduction in overall biofuel yield relative to the base case), affects the GHG emissions. Like the base case, the IH^2 Plus cool GTL process is also not energy optimized, as shown in Table S1. The main reason for the lower yield here could be a result of any potential inefficiency of the IH^2 Plus cool GTL process. In this scenario, reduction in liquid fuel blend is not compensated for with increases in either char or other co-products containing carbon. Therefore, this is only a "first-order" scenario analysis that measures the sensitivity of the LCA result with a change in only one process variable.

In case 2d, the effect of higher electricity demand from the energy optimized IH^2 Plus cool GTL process was examined. The electricity input rate increased from 2 MW to 4 MW. The higher electricity demand can result from the use of electric heaters in the IH^2 Plus cool GTL process instead of heat exchangers. The scenarios involving woody biomass feedstock are summarized in Table 5. These same scenario ideas presented for woody biomass in cases 2a−d were also tested for the algae feedstock, and those cases, labeled 4a−d in a similar fashion, are summarized in Table 6. Input and output data for the scenario analysis at the fuel production stage are found in Tables S1 and S2 for woody residue and algae feedstock, respectively.

Effect of Biorefinery Location on GHG Emissions. For this study, the electricity mix profile of the base locations, Tennessee (TN) and

Table 7. Life Cycle GHG Emissions of IH^2 Renewable Fuel Blend

$g\ CO_{2eq}/MJ$	case 1 wood IH^2	case 2 wood IH^2 Plus	case 3 algae IH^2	case 4 algae IH^2 Plus	petroleum diesel[34]	petroleum gasoline[34]
feedstock	7.96	5.45	206.77	154.16	19.40	23.50
fuel production	3.65	2.49	19.57	14.49	–	–
H_2 production	0.00	32.75	0.00	30.51	–	–
ammonia credit	−0.08	−0.05	−1.63	−1.21	–	–
waste treatment	0.04	0.04	0.06	0.06	–	–
fuel transport	0.85	0.85	0.85	0.85	–	–
fuel use	0.00	0.00	0.00	0.00	72.70	72.70
total ($g\ CO_{2eq}/MJ$)	12.42	41.52	225.63	198.87	92.10	96.20
GHG reduction[a] (%)	86.8	55.8	−140.0	−112.0		

[a] GHG reductions are compared to petroleum gasoline.

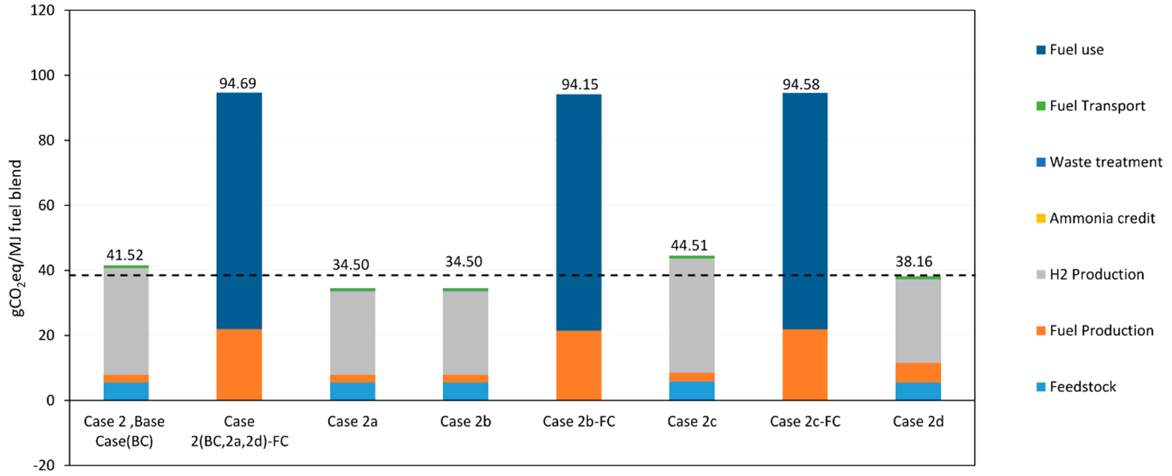


Figure 5. Life cycle GHG emissions scenario analysis of IH^2 Plus cool GTL renewable fuel blend for woody biomass (case 2). The dashed line represents a 60% reduction in GHG emissions from petroleum gasoline. FC represents the fossil counterpart calculated based on weighted average of gasoline and diesel in the fossil fuel blend and their emissions. Fossil fuel data from Cooney et al. (2014).[34]

Georgia (GA) for wood and algae, respectively, was updated using more recent literature data based on electricity generation (eGRID) statistics from 2014, the most recent available year.[35] A scenario analysis to investigate the effect of electricity mix profiles was carried out, looking at other states in the U.S. besides the base locations. Four states, Washington (northwest), Oklahoma (southwest), Florida (southeast), and Vermont (northeast), were considered in this analysis. It must, however, be noted that several other factors beyond the electricity mix, such as capital and operating costs, proximity to allied industries, and light and temperature conditions (especially for algae), among others, are important in the siting of such biorefineries. The effect of electricity profile mix of different locations was investigated only for algae feedstock because electricity use in the woody biomass case was found to be insignificant. The inventory inputs for the electricity generation mix of these locations and the base locations are tabulated in Table S3.

■ RESULTS AND DISCUSSION

GHG emissions from the four cases investigated and their paired fossil counterparts are shown in Figure 4 and Table 7. For case 1, the main sources of GHG emissions are from wood feedstock provision and fuel production (IH^2 inputs). For case 2, H_2 production was the overwhelming source of emissions. It can be observed that cases 1 and 2, utilizing woody biomass feedstock in the IH^2 and IH^2 Plus cool GTL processes, respectively, resulted in much lower GHG emissions relative to petroleum-derived diesel and gasoline. The dashed line on Figure 3 shows the GHG emissions that provide 60% savings compared to petroleum gasoline, which is the benchmark to qualify as a "cellulosic biofuel" under the Renewable Fuel Standard 2 (RFS2).[36]

The IH^2 Plus cool GTL process (case 2) resulted in GHG emissions (41.5 $g\ CO_{2eq}/MJ$) that were higher than those of the IH^2 process (case 1) (12.4 $g\ CO_{2eq}/MJ$) for woody feedstock. This is mainly due to the anthropogenic CO_2 emissions from the reforming of natural gas to produce the hydrogen in the IH^2 Plus cool GTL process (case 2) relative to the biogenic CO_2 from the same step for the IH^2 process where hydrogen was produced by reforming the C1−C3 hydrocarbon co-products from the process (case 1).

The range of 56−87% reduction in GHG emissions evaluated for the IH^2 Plus cool GTL (case 2) and the IH^2 (case 1) processes relative to fossil-derived fuel agrees with what other studies have observed. Fan and co-workers estimated an 86% reduction in GHG emissions in their study that investigated hydrocarbon biofuel production from an IH^2 process that processes 500 metric tonnes of wood feedstock.[10] Zaimes and co-workers estimated an 80% reduction in GHG emissions in their study that investigated a multistage torrefaction and catalytic upgrading process that converts 2000 dry metric tonnes of short rotation woody crops to hydrocarbons.[37] Winjobi and co-workers estimated a 56−265% reduction in GHG emissions relative to fossil-derived fuels in their study that investigated a one- and two-step torrefaction and fast pyrolysis of pine that processes 1000 dry metric tonnes of feed through the pyrolysis unit.[38] Iribarren and co-workers estimated a 72% reduction in their study that

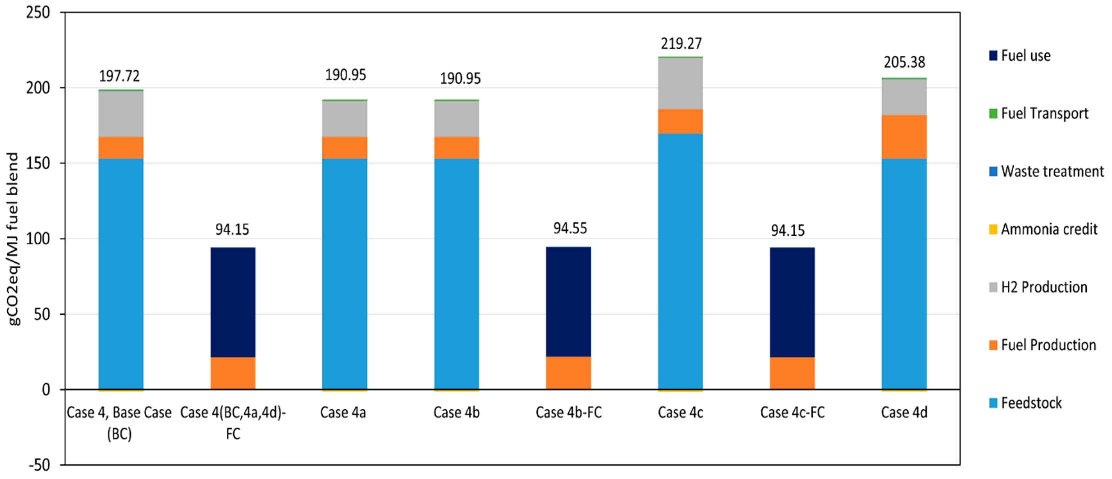


Figure 6. Life cycle GHG emissions scenario analysis of IH^2 Plus cool GTL renewable fuel blend for algae biomass (case 4). FC represents the fossil counterpart calculated based on the weighted average of gasoline and diesel in the fossil fuel blend and their emissions. Fossil fuel emissions data from Cooney et al. (2014).[34]

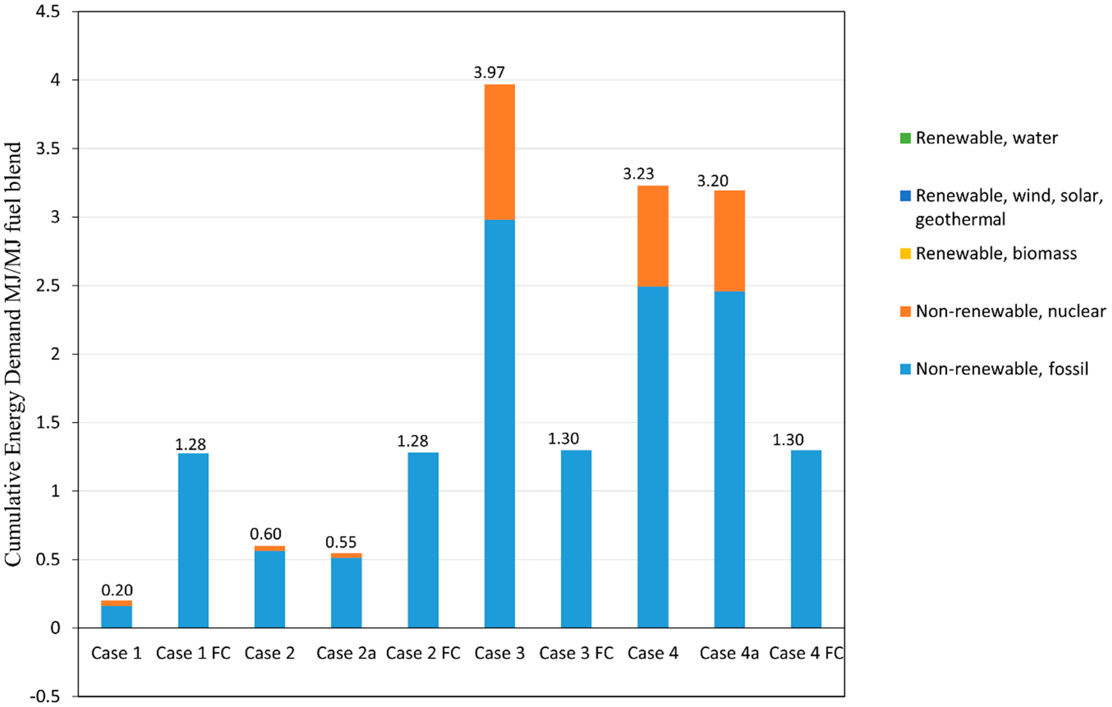


Figure 7. Cumulative energy demand of IH^2 and IH^2 Plus fuel blends (minus biomass feedstock). FC represents the fossil counterpart calculated based on the weighted average of gasoline and diesel in the fossil fuel blend and their fossil energy demand. Fossil fuel CED data obtained from SimaPro.

investigated conversion of short-rotation poplar to hydrocarbon biofuel.[39]

Cases 3 and 4 using algae feedstock for the IH^2 and IH^2 Plus cool GTL processes, respectively, resulted in much higher GHG emissions relative to the petroleum-derived fuels. For the algae feedstock cases (3 and 4), the major contributor to the GHG emissions is algae cultivation. This is due to the high electricity consumption during the algae cultivation process for pumping, lighting, and dewatering unit operations. In opposition to the wood case, for algae GHG emissions from IH^2 Plus cool GTL are lower than those from IH^2 because the increase in biofuel yield offered through the IH^2 Plus cool GTL process (case 4) more than made up for the burdens imposed by the requirements for natural gas−H_2.

Scenario analysis results for life cycle GHG emissions of IH^2 Plus cool GTL renewable fuel blend for woody biomass cases 2a−d and algae cases 4a−d are presented in Figures 5 and 6, respectively. In the woody biomass scenarios presented in Figure 5, it is observed that case 2a with minimized external energy consumption through use of F-T off-gases within the system can achieve a lower life cycle GHG emissions value compared to the baseline case 2 (34.5 vs 41.5 g CO_{2eq}/MJ, respectively). This improvement is enough to make the IH^2 Plus processing platform achieve a 63% GHG emissions reduction compared to fossil gasoline, which exceeds the 60% threshold to qualify this biofuel as a “cellulosic biofuel” under EPA standards.[36] Case 2b results in a nearly identical result to case 2a because the overall distribution of fuel products does

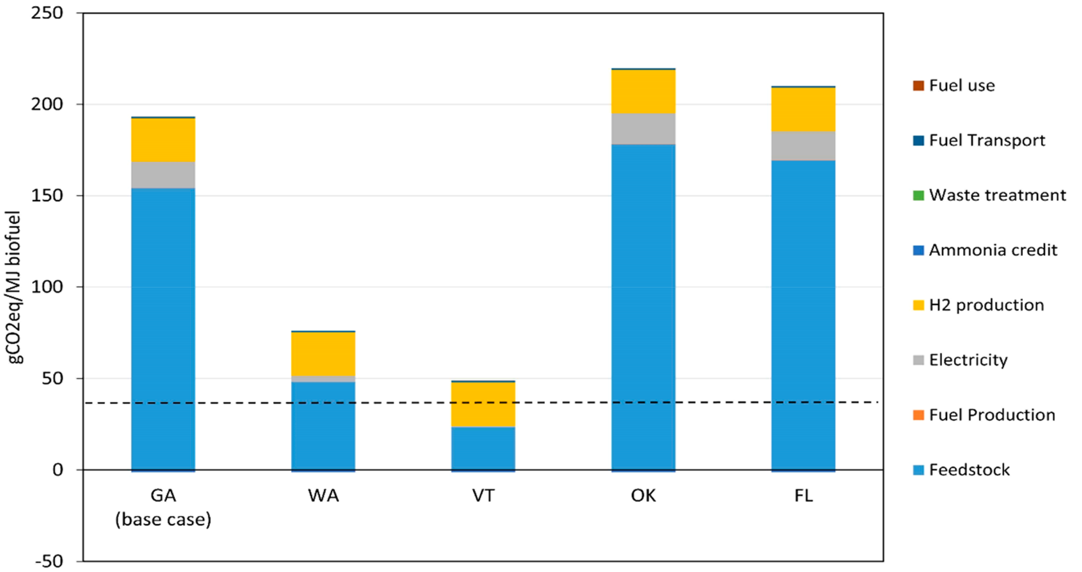


Figure 8. Effect of location electricity mix on GHG emissions from the optimized IH^2 Plus renewable fuel blend for algae feedstock (case 4a). The dashed line represents a 60% reduction in GHG emissions from petroleum gasoline.

not significantly alter the environmental impacts when normalized to a per MJ basis. Case 2c, representing an approximately 7% lower yield of fuel per unit input of biomass, resulted in a slightly higher life cycle GHG emissions value compared to the case 2 baseline (44.5 vs 41.5 g CO_{2eq}/MJ, respectively). Increasing electricity requirements in case 2d resulted in an increase of roughly 4 g CO_{2eq}/MJ compared to case 2a, which illustrates the importance of power usage at the fuel conversion stage. Similar trends can be observed in Figure 6 for algae cases.

Cumulative fossil energy demand (CED) for the cases evaluated using SimaPro are shown in Figure 7. IH^2 and IH^2 Plus cool GTL fuel blends with woody residue feedstock (cases 1 and 2) have significantly lower CED values relative to their fossil-derived counterparts, while cases 3 and 4 with algae feedstock for the IH^2 and IH^2 Plus cool GTL processes, respectively, have the highest CED (ecoprofiles from the U.S. LCI were selected in SimaPro for gasoline and diesel, "Gasoline and Diesel, at refinery/l/US", respectively). From Figure 7, it can be observed that the processes with woody residue feedstock (cases 1 and 2) are more efficient in the use of fossil energy relative to their fossil-derived counterpart while processes with algae feedstock (cases 3 and 4) are significantly less efficient in the use of fossil energy. The high CED for cases 3 and 4 is due to the high energy demands in algae cultivation.

A scenario analysis for the effect of the electricity mix of the plant location on the GHG emissions for the optimized IH^2 Plus cool GTL (case 4a) for algae feedstock is shown in Figure 8. Significant reduction can be expected if the facility is located in low GHG-intensity electricity grid states such as Vermont or Washington relative to the base case of Georgia. Higher GHG emissions are however observed if the process is in high GHG-intensity electricity grid states, for example either Oklahoma or Florida, relative to Georgia. Vermont has the lowest emissions with an about 73% reduction in GHG emissions relative to the base location of Georgia, while Oklahoma has the highest emissions with an about 13% increase in GHG emissions relative to Georgia. Though a significant reduction in GHG emissions is observed for a plant located in Vermont, the reduction does not meet the 60% reduction threshold compared to fossil gasoline to qualify this biofuel as a "cellulosic biofuel" under the EPA RFS2 standards.[36] About 72% of the electricity mix for Vermont is from nuclear (a low GHG source) compared to Oklahoma which has about 43% from coal.

The significant reduction in the feedstock preparation stage is because of the electricity required for the harvesting/dewatering of the algae and the photobioreactors during algae cultivation, as shown in Table 8 for the base location of Georgia.

Table 8. Contributions to Algae Feedstock Preparation for the Base Location in Georgia

feedstock preparation (g CO_{2eq}/MJ biofuel)	
water	0.01
electricity for algae harvesting/dewatering	22.65
electricity for photobioreactors	115.11
algae nutrient media	16.39
total (g CO_{2eq}/MJ biofuel)	154.16

The most significant change with the different electricity generation mix is observed for the electricity required by the photobioreactors. Modest changes are, however, observed for the harvesting/dewatering of the algae, while the other two contributions remained unchanged.

One topic worthy of mention is the issue of sustainable practices for biomass feedstock procurement of woody biomass and algae. This discussion will focus on issues that may affect the carbon footprint analysis in these forest landscapes and algae. One of the first concepts to acknowledge is that biomass carbon in and on soils is connected to atmospheric carbon (CO_2) through rapid cycles of photosynthesis and mineralization. Therefore, if C in biomass increases on the landscape and in soils, then this increase corresponds to a proportional decrease of C (CO_2) in the atmosphere. Likewise, if landscape biomass C decreases, possibly due to unsustainable biomass collection practices, then C in the atmosphere will increase proportionally. This could lead to an increase in greenhouse gas emissions from biofuel production systems. Most forest-based biofuel systems assume that land-use change impacts on GHG emissions are minimal, but this assumes a sustainable harvest level and a relatively unchanged amount of forested land C as a result of new biofuels use. In forest landscapes where logging residues are collected, if depletion of C from the landscape comes about, this may cause a delay of decades for the benefits of biofuels displacing fossil fuels to be felt.[40] In our LCA, we have assumed that biomass collection for IH^2 biofuel production using forest residue collection would remain within these sustainability constraints. This study looked at woody biomass residue feedstock; it should, however, be noted that the use of cultivated woody biomass crop may lead to a different life cycle result.

Algae has the potential to utilize waste CO_2 from industrial sources and convert this carbon into rapidly growing algae biomass, which makes it a promising feedstock worthy of future study. Previous research has shown that improper siting of algae cultivation facilities may lead to direct land use change impacts from cleared lands, but this is less likely to be an issue with a PBR cultivation system, which should use much less land than an open pond system.[33]

Current LCA cases involving algae assume that all algae that is cultivated in the PBR system is subsequently sent to an IH^2 biofuel production facility, but that may not be the best assumption to use when thinking about how this opportunity may develop in the near term. Companies that are developing algae cultivation systems are often finding markets for algae oil in cosmetics, nutraceuticals, or food applications that are much more lucrative than current opportunities in the renewable fuels sector. It is reasonable to assume that algae cultivation would continue to prioritize those opportunities for algae oil as long as the markets remain favorable. However, the non-lipid biomass that is being cultivated also represents a potential opportunity for fuel production, and thermochemical systems like IH^2 are not dependent on the oil fraction of algae to generate high yields; in fact, comparable yields in the IH^2 process have been achieved using algae with markedly different oil contents. If the lipid-extracted algae (LEA) fraction of algal biomass was sent to a GTI processing system for upgrading to fuels, while the algae oil was sent to traditional market opportunities, it would be worth considering how to allocate the admittedly large environmental impacts associated with algae cultivation between these two products. As an example, if algae is produced at a 25% oil content, 3 kg of non-lipid LEA would be produced for every kilogram of oil. If we assume market values of $5/kg for LEA and $50/kg for algae oil (conservative estimates for current algae oil markets in cosmetics and food sectors[41]), then an economic allocation of impacts for algae cultivation between LEA and oil would result in over 75% of the impacts associated with cultivation being attributed to the oil, while less than 25% would be attributed to the LEA fraction. There are a few more complexities that would result from imagining the algae biomass feedstock opportunity in this fashion, as the co-product of a more lucrative algae industry, but clearly this potential to drastically reduce the impacts associated with algae cultivation would result in biofuels with a more favorable environmental profile. Future scenarios to more thoroughly explore this opportunity will be worth considering.

■ CONCLUSION

The main purpose of this study is to evaluate the effect of increasing biofuel yield from the IH^2 process on life cycle greenhouse gas emissions and fossil energy demand. Our results show that for forest feedstocks increasing biofuel yield using the IH^2 Plus cool GTL processes increases emissions per MJ of biofuel produced, but a greater than 60% savings compared to fossil fuels is achievable. For algae feedstock, increasing biofuel yield decreases life cycle GHG emissions; this is the opposite to forest feedstocks. This study showed the importance of the interplay between biofuel yield, feedstock production emissions, and emissions for H_2 production. IH^2 renewable fuels produced from woody biomass show considerable GHG savings compared to their fossil fuel counterparts. Depending on the H_2 sources and other processing assumptions, IH^2 fuel blends from woody biomass processed through the unoptimized IH^2 and IH^2 Plus cool GTL processes would achieve 55−87% reductions in life cycle GHG emissions compared to fossil fuels. IH^2 renewable fuels produced from algae have a GHG emissions profile that is highly sensitive to the electricity generation mix of the plant location. Depending on the H_2 sources and other processing assumptions, IH^2 fuel blends from algae biomass processed through the IH^2 Plus cool GTL process would achieve 13−42% reductions in some locations with a low GHG intensity grid and 112−140% additions in some locations with a high GHG intensity grid in life cycle GHG emissions compared to fossil fuels.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.8b02091.

> Input and output data for the scenario analysis for cases 2 and 4; inventory inputs for the electricity mix of selected states in the U.S.; ultimate analysis of wood, algae, gasoline, and diesel; recipe for the algae nutrient; and sample calculation for fuel counterpart comparison (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: owinjobi@mtu.edu. Tel.: 906-487-3468.

ORCID

Olumide Winjobi: 0000-0001-6251-0450

Bethany Klemetsrud: 0000-0001-8348-2903

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This material is based upon work supported by the Department of Energy and Gas Technology Institute (DE-EE007009). The authors also acknowledge the contributions of James Winfield of Algae Energy to this study.

■ REFERENCES

(1) Tollefson, J. Not your father's biofuels: if biofuels are to help the fight against climate change, they have to be made from more appropriate materials and in better ways. Jeff Tollefson asks what innovation can do to improve the outlook. *Nature* **2008**, *451* (7181), 880−884.

(2) U.S. Department of Energy, et al. U.S. Billion-Ton Update: Biomass Supply for a Bioenergy and Bioproducts Industry, ORNL/TM-2011/224. *Agricultural and Biosystems Engineering Technical*

reports and White Papers; Oak Ridge National Laboratory, Oak Ridge, TN, 2011; pp 227, https://lib.dr.iastate.edu/abe_eng_reports/16/.

(3) Shonnard, D. R.; Brodeur-Campbell, M. J.; Martin-Garcia, A. R.; Kalnes, T. N. In *Handbook of Bioenergy Crop Plants*; Kole, C., Joshi, C. P., Shonnard, D. R., Eds.; CRC Press: Boca Raton, FL, 2012.

(4) Ginzburg, B.-Z. Liquid fuel (oil) from halophilic algae: a renewable source of non-polluting energy. *Renewable Energy* **1993**, *3* (2−3), 249−252.

(5) Dote, Y.; Sawayama, S.; Inoue, S.; Minowa, T.; Yokoyama, S.-y. Recovery of liquid fuel from hydrocarbon-rich microalgae by thermochemical liquefaction. *Fuel* **1994**, *73* (12), 1855−1857.

(6) Minowa, T.; Yokoyama, S.-y.; Kishimoto, M.; Okakura, T. Oil production from algal cells of Dunaliella tertiolecta by direct thermochemical liquefaction. *Fuel* **1995**, *74* (12), 1735−1738.

(7) Marker, T. L.; Felix, L. G.; Linck, M. B.; Roberts, M. J. Integrated hydropyrolysis and hydroconversion (IH2) for the direct production of gasoline and diesel fuels or blending components from biomass, part 1: Proof of principle testing. *Environ. Prog. Sustainable Energy* **2012**, *31* (2), 191−199.

(8) Lane, J. $2.25 per Gallon Biohydrocarbon Fuels, Unsubsidized? Biozin Licenses IH2 Technology — Heads for Commercial-scale in Norway. In *BiofuelsDigest*; Biofuels Digest: November 15, 2017; http://www.biofuelsdigest.com/bdigest/2017/11/15/2-25-per-gallon-biohydrocarbon-fuels-unsubsidized-biozin-licenses-ih2-technology-heads-for-commercial-scale-in-norway/ (accessed March 22, 2018).

(9) Tan, E. C.; Marker, T. L.; Roberts, M. J. Direct production of gasoline and diesel fuels from biomass via integrated hydropyrolysis and hydroconversion process—A techno-economic analysis. *Environ. Prog. Sustainable Energy* **2014**, *33* (2), 609−617.

(10) Fan, J.; Gephart, J.; Marker, T.; Stover, D.; Updike, B.; Shonnard, D. R. Carbon footprint analysis of gasoline and diesel from forest residues and corn stover using integrated hydropyrolysis and hydroconversion. *ACS Sustainable Chem. Eng.* **2016**, *4* (1), 284−290.

(11) Bailey, A.; Leong, G. J.; Fitzgerald, N. *Bioproducts to Enable Biofuels Workshop Summary Report*; U.S. Department of Energy: Westminster, Colorado, 2015.

(12) Kulas, D.; Winjobi, O.; Zhou, W.; Shonnard, D. Effects of Coproduct Uses on Environmental and Economic Sustainability of Hydrocarbon Biofuel from One- and Two-Step Pyrolysis of Poplar. *ACS Sustainable Chem. Eng.* **2018**, *6* (5), 5969−5980.

(13) Arbogast, S.; Bellman, D.; Paynter, J.; Wykowski, J. Advanced biofuels from pyrolysis oil··· Opportunities for cost reduction. *Fuel Process. Technol.* **2013**, *106*, 518−525.

(14) Fahmi, R.; Bridgwater, A. V.; Donnison, I.; Yates, N.; Jones, J. The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability. *Fuel* **2008**, *87* (7), 1230−1240.

(15) Di Blasi, C.; Galgano, A.; Branca, C. Influences of the chemical state of alkaline compounds and the nature of alkali metal on wood pyrolysis. *Ind. Eng. Chem. Res.* **2009**, *48* (7), 3359−3369.

(16) Scott, D. S.; Paterson, L.; Piskorz, J.; Radlein, D. Pretreatment of poplar wood for fast pyrolysis: rate of cation removal. *J. Anal. Appl. Pyrolysis* **2001**, *57* (2), 169−176.

(17) Shafizadeh, F. Introduction to pyrolysis of biomass. *J. Anal. Appl. Pyrolysis* **1982**, *3* (4), 283−305.

(18) Pandey, A.; Bhaskar, T.; Stöcker, M.; Sukumaran, R. *Recent Advances in Thermochemical Conversion of Biomass* **2015**, 11.

(19) Karnjanakom, S.; Guan, G.; Asep, B.; Du, X.; Hao, X.; Yang, J.; Samart, C.; Abudula, A. A green method to increase yield and quality of bio-oil: ultrasonic pretreatment of biomass and catalytic upgrading of bio-oil over metal (Cu, Fe and/or Zn)/γ-Al 2 O 3. *RSC Adv.* **2015**, *5* (101), 83494−83503.

(20) Shi, W.; Jia, J.; Gao, Y.; Zhao, Y. Influence of ultrasonic pretreatment on the yield of bio-oil prepared by thermo-chemical conversion of rice husk in hot-compressed water. *Bioresour. Technol.* **2013**, *146*, 355−362.

(21) Finnveden, G.; Hauschild, M. Z.; Ekvall, T.; Guinée, J.; Heijungs, R.; Hellweg, S.; Koehler, A.; Pennington, D.; Suh, S. Recent developments in life cycle assessment. *J. Environ. Manage.* **2009**, *91* (1), 1−21.

(22) Handler, R. M.; Shonnard, D. R.; Kalnes, T. N.; Lupton, F. S. Life cycle assessment of algal biofuels: Influence of feedstock cultivation systems and conversion platforms. *Algal Res.* **2014**, *4*, 105−115.

(23) Chan, Y. H.; Yusup, S.; Quitain, A. T.; Tan, R. R.; Sasaki, M.; Lam, H. L.; Uemura, Y. Effect of process parameters on hydrothermal liquefaction of oil palm biomass for bio-oil production and its life cycle assessment. *Energy Convers. Manage.* **2015**, *104*, 180−188.

(24) Wang, H.; Wang, L.; Shahbazi, A. Life cycle assessment of fast pyrolysis of municipal solid waste in North Carolina of USA. *J. Cleaner Prod.* **2015**, *87*, 511−519.

(25) Weidema, B.; Bauer, C.; Hischier, R.; Mutel, C.; Nemecek, T.; Reinhard, J.; Vadenbo, C.; Wernet, G. Overview and methodology: Data quality guideline for the ecoinvent database, version 2013. *Ecoinvent Report 1(v3)*; Swiss Centre for Life Cycle Inventories: St. Gallen, 2013.

(26) ISO. *Environmental management--Life cycle assessment--Goal and scope definition and inventory analysis*; International Organization for Standardization: 1998.

(27) U.S. Environmental Protection Agency. Chapter 6, Life cycle Impacts on Fossil Energy and Greenhouse Gases, EPA420-R-07−004. In *Regulatory Impact Analysis: Renewable Fuel Standard Program*; Assessment and Standards Division, Office of Transportation and Air Quality: 2007.

(28) Guillard, R. R. *Culture of marine invertebrate animals*; Springer: 1975.

(29) Guillard, R. R.; Ryther, J. H. Studies of marine planktonic diatoms: I. Cyclotella Nana Hustedt, and Detonula Confervacea (CLEVE) Gran. *Can. J. Microbiol.* **1962**, *8* (2), 229−239.

(30) Price, N. M.; Harrison, G. I.; Hering, J. G.; Hudson, R. J.; Nirel, P. M.; Palenik, B.; Morel, F. M. Preparation and chemistry of the artificial algal culture medium Aquil. *Biological oceanography* **1989**, *6* (5−6), 443−461.

(31) Argonne National Laboratory. *GREET 2017 Life-cycle Model*; Center for Transportation Research, Energy System Division: 2017; https://greet.es.anl.gov.

(32) Brack, D. *Woody Biomass for Power and Heat: Impacts on the Global Climate*; Environment, Energy, and Resources Department, Chatham House: 2017.

(33) Handler, R. M.; Shi, R.; Shonnard, D. R. Land use change implications for large-scale cultivation of algae feedstocks in the United States Gulf Coast. *J. Cleaner Prod.* **2017**, *153*, 15−25.

(34) Cooney, G.; Jamieson, M.; Marriott, J.; Bergerson, J.; Brandt, A.; Skone, T. J. Updating the US Life Cycle GHG Petroleum Baseline to 2014 with Projections to 2040 Using Open-Source Engineering-Based Models. *Environ. Sci. Technol.* **2017**, *51* (2), 977−987.

(35) U.S. Environmental Protection Agency eGRID Year 2014 Summary Tables. https://www.epa.gov/energy/egrid-2014-summary-tables.

(36) U.S. Environmental Protection Agency. *Renewable fuel standard program (RFS2) regulatory impact analysis*; Assessment and Standards Division, Office of Transportation and Air Quality: Ann Arbor, MI, 2010.

(37) Zaimes, G. G.; Beck, A. W.; Janupala, R. R.; Resasco, D. E.; Crossley, S. P.; Lobban, L. L.; Khanna, V. Multistage torrefaction and in situ catalytic upgrading to hydrocarbon biofuels: analysis of life cycle energy use and greenhouse gas emissions. *Energy Environ. Sci.* **2017**, *10* (5), 1034−1050.

(38) Winjobi, O.; Zhou, W.; Kulas, D.; Nowicki, J.; Shonnard, D. R. Production of Hydrocarbon Fuel Using Two-Step Torrefaction and Fast Pyrolysis of Pine. Part 2: Life-Cycle Carbon Footprint. *ACS Sustainable Chem. Eng.* **2017**, *5* (6), 4541−4551.

(39) Iribarren, D.; Peters, J. F.; Dufour, J. Life cycle assessment of transportation fuels from biomass pyrolysis. *Fuel* **2012**, *97*, 812−821.

(40) McKechnie, J.; Colombo, S.; Chen, J.; Mabee, W.; MacLean, H. L. Forest bioenergy or forest carbon? Assessing trade-offs in

greenhouse gas mitigation with wood-based fuels. *Environ. Sci. Technol.* **2011**, *45* (2), 789−795.

(41) *Algae Energy*. Personal communication, 2017.

DOI: 10.1021/acssuschemeng.8b02091
ACS Sustainable Chem. Eng. 2018, 6, 10766−10777