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Growing Algae for Biodiesel on Direct Sunlight or Sugars: A Comparative Life Cycle Assessment

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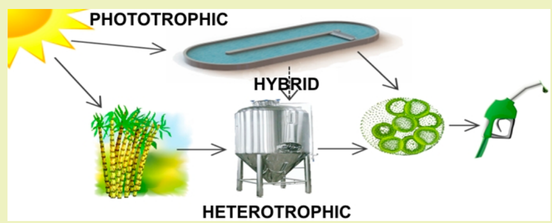
Supporting Information



ABSTRACT: Growing heterotrophic algae in reactors with sugar as the energy and carbon source rather than sunlight and carbon dioxide is an approach being commercialized today. However, the full environmental impacts of this fuel pathway have not been explored. The objective of this analysis was to compare the life cycle impacts of algal biodiesel produced heterotrophically to a phototrophic pathway featuring algae grown in ponds. A third, hybrid approach utilizing algae capable of both phototrophy and heterotrophy was also explored. Sugar beet and sugarcane were examined as feedstocks for the heterotrophic process. The results indicate that a reduction in the global warming potential (GWP) and an improvement in the net energy ratio (NER) for algal biodiesel could be possible for the heterotrophic and hybrid pathways relative to the phototrophic, but only if reactor cultivation can be performed efficiently and with sugarcane as the feedstock. For example, the NER varies from 0.6 to 1.6 for the heterotrophic pathway, depending on reactor performance, compared to 1.3 for the phototrophic pathway. Sugar crops used as feedstocks for heterotrophic cultivation present concerns about land constraints that are less of an issue for the phototrophic pathway. No pathway presented a clear advantage for the water stress impact metric.

KEYWORDS: *Biofuel, LCA, heterotrophic, phototrophic, sugarcane, sugar beet*

INTRODUCTION

The United States intends to increase domestic biofuel production in an effort to reduce dependence on imported petroleum and mitigate the impacts of global warming.[1] Because carbon dioxide is removed from the atmosphere by photosynthesis during feedstock production, biofuels have the potential to reduce the life cycle emissions of greenhouse gases (GHGs) and the overall global warming potential (GWP) relative to conventional fossil fuels. However, life cycle analyses (LCAs) of first-generation biofuels such as corn ethanol and soy biodiesel indicate that these benefits can be greatly reduced by the impacts associated with the production of these energy crops and their conversion into liquid fuels.[2−5] Furthermore, the land required to produce these crops could displace agriculture currently used for food production, presenting the possibility of land use change (LUC) and indirect land use change (iLUC).[6−9]

Phototrophic algae have been proposed as an alternative bioenergy feedstock because of their high growth rate and areal productivity.[10] By growing algae in open ponds, biomass can be produced on marginal, nonarable lands that are not currently used for agriculture.[11] The proposed biofuels target of 36 billion gallons annually by 2022 set by the U.S. Energy Independence and Security Act means that land constraints will become more important as production volumes increase.[1] Furthermore, cultivation in ponds on marginal land means that the potentially deleterious effects of LUC and iLUC can be minimized.

Achieving large-scale production of phototrophic algae has proven difficult, however, primarily due to the capital and operational costs of open ponds.[12,13] Additionally, the relatively low biomass concentration (which typically does not exceed ~0.5 $g \cdot L^{-1}$) requires significant energy inputs to circulate the large volumes of water and to concentrate the harvested biomass.[14] These challenges have prompted exploration of an alternative approach to growing algae: heterotrophic cultivation. Unlike phototrophic algae, the metabolism of heterotrophic algae facilitates fast growth in unlit reactors whereby energy is derived from an organic carbon source rather than sunlight.[15] Mixotrophic species of algae, which can use either sunlight or organic carbon for energy depending on their environment, have also been investigated as part of a hybrid pathway.[16−18]

This study features a comparative life cycle assessment (LCA) evaluating algal biofuel production pathways featuring photo-, mixo-, and heterotrophic metabolisms. To our knowledge, this is the first such analysis of its kind outside of private sector studies that have not been made public. Although

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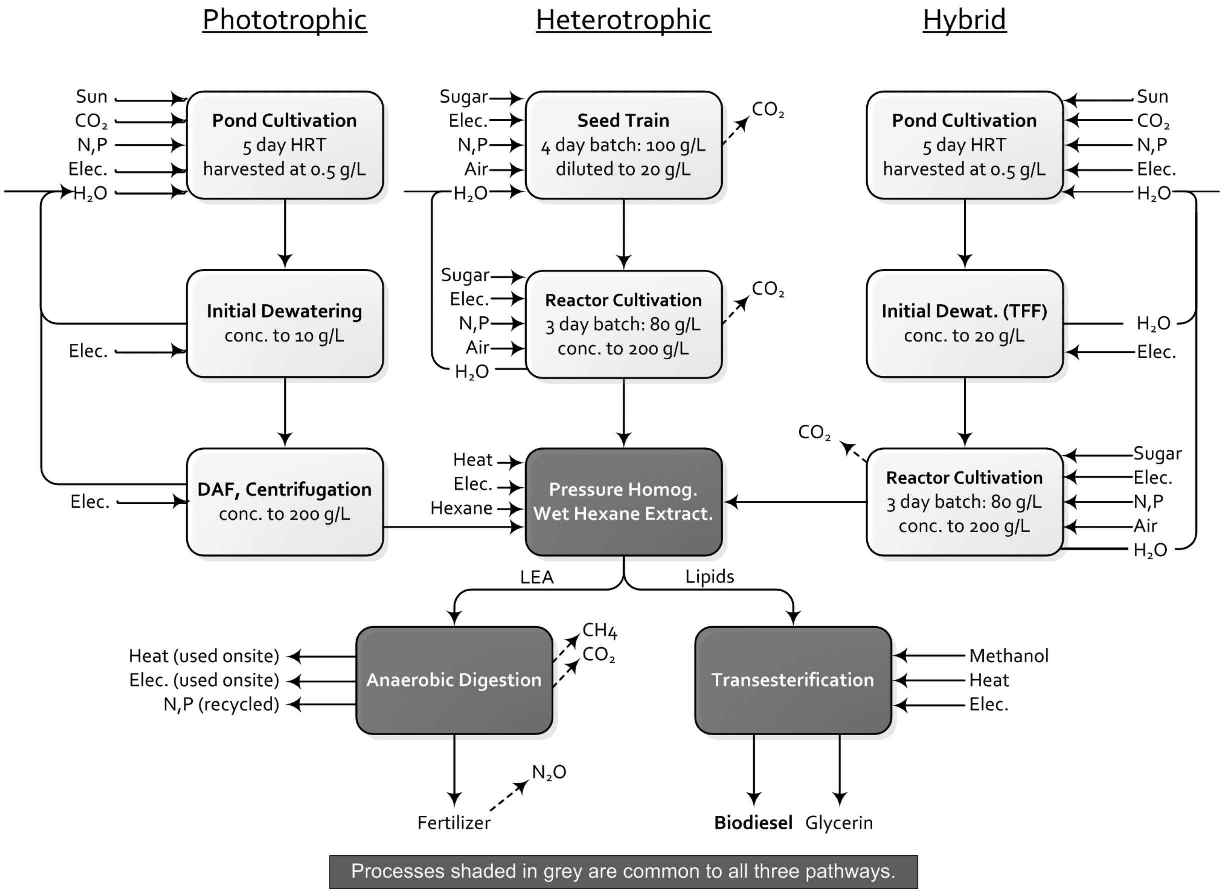

Figure 1. Simplified process flow diagram summarizing the key inputs and outputs associated with the phototrophic, heterotrophic, and hybrid algal biodiesel production pathways. The processes shaded in gray are those that are the same for each pathway. Dashed lines represent the on-site release of greenhouse gases, though the N_2O emissions do not occur until the digestate residue is land-applied as fertilizer.

several recent LCAs have evaluated algal biofuel,[19−24] compared biofuels from phototrophic algae to other biofuels,[25,26] examined various cultivation strategies for algal biofuels,[27−29] and focused on downstream conversion technologies,[30,31] none have evaluated heterotrophic or hybrid cultivation strategies. This gap in the literature is noteworthy, given that several of the leading private firms in the algae industry, as well as numerous academic groups, are currently pursuing these approaches.

■ METHODOLOGY

Modeling Framework. Modeling was conducted using SimaPro LCA Software, Microsoft Excel spreadsheets, ArcMap spatial analysis software, and MATLAB. Phototrophic pathway process assumptions and operational parameters were based on Argonne National Laboratory's Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model, a well-established analytical tool for fuel LCA modeling.[32] This framework was expanded to model additional pathways and to consider the environmental impact metrics of land use and water stress through a geographic information systems (GIS) approach.

The algal biofuel industry is still nascent, and thus a variety of technologies are under development for nearly all major aspects of the production process (i.e., biomass cultivation, dewatering, biomass conversion, and nutrient recycling). The GREET model was selected for the baseline phototrophic pathway because it makes well-justified process technology selections and provides thorough supplementary resources that make the underlying computations transparent and replicable. The model's process assumptions include use of lipid-extracted algae (LEA, which is the biomass remaining after the lipid has been removed) as a feedstock for anaerobic digestion. An advantage of this approach is that electricity and heat are produced and used onsite to avoid energy imports rather than utilizing the LEA as a coproduct (e.g., animal feed).

Another important assumption of the GREET model is that CO_2 is provided from a power utility's flue gas. The energy required to transport the flue gas is considered, but otherwise the CO_2 is treated as atmospheric because that would have been its fate had it not been pumped to the algae pond. An implication of such an assumption is that a carbon credit cannot be applied for both the power utility and the biofuel. Here, the credit is assigned to the algae. This analysis incorporates the same impact factor and distance assumptions as the GREET model for modeling the transportation of the digestate to the field and handling of the extracted oil through refinement and distribution. This model also adheres to the same coproduct allocation used by GREET for calculating the energy balance and carbon emissions. The impacts associated with lipid production are shared between the algal oil and any energy sent beyond the system boundary, such as surplus electricity generated on site. The distribution was based on energy content of the oil and that of the exported electricity and was only applicable for the highest efficiency scenario explored for the heterotrophic and hybrid pathways. An allocation was also used for the lipid conversion step based on the energy in the fuel and the glycerin coproduct.[32,33]

The phototrophic pathway model used in this analysis deviates from the GREET model in several ways. Most notably, the GIS analysis described later explores the effect of spatially variable climate parameters on the land footprint and evaporative water loss rather than using fixed values. This analysis also incorporates a biomass stoichiometry outlined by Lardon et al.[30] and, when applicable, uses

Table 1. Parameters Used in Biofuel Process Pathway Modeling[a]

step	value	units	pathways: photo.	hetero.	hybrid	ref.
open pond cultivation						
paddle-mixing energy inputs	2000	W·ha^{-1}	x		x	12, 32, 34
CO_2 uptake efficiency	0.85	n/a			x	32
evaporative water loss (make-up inputs)	GIS[b]	m^3·kg-algae^{-1}	x		x	35, 36
biomass productivity	25[c], GIS	g·m^{-2}·day^{-1}	x		x	12, 36−38
phototrophic biomass lipid content	25 wt %[d]	n/a	x		x	12, 32, 34
operational period, per year	330	days	x	x	x	34
pumping, to site	$1.23 \cdot 10^{-4}$	kWh·L^{-1}	x		x	34
reactor cultivation						
yield on sugar	0.25[e]	kg-lipid·kg-glucose^{-1}		x	x	39
aeration/mixing energy for 80 g·L^{-1}	3[f], 2, 1	kW·m^{-3}		x	x	18, 40, 41
heterotrophic biomass lipid content	50 wt %			x		42
hybrid pathway heterotrophic biomass lipid content	55 wt %[g]				x	18
harvesting/dewatering						
pumping, on site	$2.5 \cdot 10^{-5}$	kWh·L^{-1}	x	x	x	34
centrifugation energy inputs	$1.93 \cdot 10^{-2}$	kWh·kg-out^{-1}	x			34
cent. mass retention efficiency	0.95		x			32
DAF energy inputs	0.133	kWh·kg-algae^{-1}	x			32, 43
DAF mass retention efficiency	0.9		x		x	32
tangential flow filtration (TFF)	$5 \cdot 10^{-4}$[h]	kWh·L^{-1}			x	
secondary centrifugation energy	$8 \cdot 10^{-3}$	kWh·L^{-1}		x	x	32, 44, 45
cell preparation						
pressure homogenization energy	0.204	kWh·kg-algae^{-1}	x	x	x	32, 13, 27
pressure homogenization mass ret. efficiency	0.9		x	x	x	32
(wet) hexane extraction						
extraction electricity inputs	0.069	kWh·kg-oil^{-1}	x	x	x	34
extraction heat inputs	3.09	kWh·kg-oil^{-1}	x	x	x	34
hexane inputs (amount lost)	5.2	g-hexane·kg-oil^{-1}	x	x	x	32
transesterification						
methanol requirement	0.1001	kg-methanol·kg-biodiesel^{-1}	x	x	x	33, 46, 47
transesterification heat inputs	2.07	MJ·kg-biodiesel^{-1}	x	x	x	33, 46, 47
transesterification electricity inputs	0.107	MJ·kg-biodiesel^{-1}	x	x	x	33, 46, 47
anaerobic digestion						
digestion heat inputs	0.22	kWh·kg-TS^{-1}	x	x	x	34
digestion electrical inputs	0.085	kWh·kg-TS^{-1}	x	x	x	34
CHP electrical efficiency	0.33		x	x	x	32
CHP total efficiency	0.76		x	x	x	32
biogas yield (67% methane)	0.45	L-biogas·g-TS^{-1}	x	x	x	32
biogas cleanup electrical inputs	0.25	kWh·m^{-3} biogas	x	x	x	32, 48
fertilizer coproduct						
fraction of N in digestate	0.20		x	x	x	32
fraction of P in digestate	0.50		x	x	x	32
nitrous oxide emissions	0.01	kg-N_2O−N·kg-N^{1-} in fert.	x	x	x	32, 49
sugar sources						
sugar beet crop yield, sucrose content	GIS	tonnes·ha^{-1}, %		x	x	50
sugarcane crop yield, sucrose content	GIS	tonnes·ha^{-1}, %		x	x	50
sugar beet, sugarcane irrigation requirements	GIS	L-H_2O·tonne^{-1}		x	x	51, 52
surplus bagasse electricity	135[i]	kWh·tonne-cane^{-1}		x	x	53

[a]The "x" marks indicate the pathways in which the parameters were used. All algal mass references indicate ash-free dry weights. [b]The term GIS indicates that a variety of values were incorporated into the model using geographic information systems analyses conducted using the data sources referenced. [c]A value of 25 g·m^{-2}·day^{-1} was used as a baseline, but the GIS analysis was used for determining land occupation and water stress results. [d]For the hybrid pathway, algae are harvested from the pond with a lipid content of 25 wt % prior to being cultivated in the reactor where the lipid content reaches 55 wt %. [e]The reference's authors state that 0.22 kg-lipid·kg-glucose^{-1} is a practical conversion limit with a maximum theoretical conversion limit of 0.33 kg-lipid·kg-glucose^{-1}. The value of 0.25 kg-lipid·kg-glucose^{-1} was selected as an optimiztic approximation. [f]An average value of ∼3 kW·m^{-3} for the entire duration of the cultivation batch was modeled based on derivations from the references listed. More efficient technology scenarios of 2 and 1 kW·m^{-3} were also explored. [g]In the authors' optimized scenario, a maximum lipid content of 58% was achieved for this pathway. In a production setting, the biomass would likely be harvested prior to achieving the maximum lipid content; the value of 55 wt % was chosen as an approximation. [h]This value is for the volume of water processed, based on communications with an industry manufacturer for a 40× concentration factor from 0.5 to 20 g·L^{-1}. [i]The authors cite this value as an achievable surplus of cogenerated electricity (remaining after process requirements at

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Table 1. continued

the sugar plant) for the year 2020. In this model, most or all of this electricity is used on-site for reactor aeration/mixing and processing requirements.

updated values provided in a harmonization study that extends the original GREET LCA[32] and also features a spatial analysis.[34]

A summary of the process flow model is shown in Figure 1, and a list of key parameters used to generate the material and energy inventories for the three pathways is provided in Table 1. The dashed lines represent on-site releases of greenhouse gases into the atmosphere. The N_2O emissions indicated in the diagram occur during land-application of the digestate residue as fertilizer. A fraction of the methane produced during anaerobic digested is expected to leak, contributing to the GWP impact. The impacts associated with producing the flocculants used for the initial dewatering are neglected and therefore excluded from Figure 1 and Table 1. More detailed flow diagrams with notes specifying coproducts and their treatment are provided in the Supporting Information.

Phototrophic Pathway. For the phototrophic pathway, algae biomass is assumed to be produced in open raceway ponds and circulated with a horizontal paddlewheel with operational assumptions conforming to those outlined by GREET.[32] Although it is possible to cultivate algae in photobioreactors, recent analyses suggest that with current technologies this is impractical from both an environmental impact and economic perspective.[28] An average biomass yield of 25 g·m^{-2}·day^{-1} for the baseline scenario allows for one-fifth of the pond's volume to be withdrawn daily at a concentration of 0.5 g·L^{-1}. Regional variations of this average yield are also explored in the assessment of the land use and water stress impacts. The dilute biomass is pumped to a settling pond where the addition of flocculants allows a concentration of the biomass to 10 g·L^{-1}; removed water is recycled back to the pond. Subsequent dewatering using dissolved air flotation (DAF) and centrifugation further concentrates the biomass to 200 g·L^{-1}.

This slurry is processed wet to extract to the oil because thermal drying would offset much of the energy content of the biodiesel product.[30] Algae cells are first lysed by pumping the slurry through a small orifice in a process called high-pressure homogenization and then contacted with hexane to extract the lipids. Following removal of the solids (i.e., LEA), the hexane is evaporated and recovered, resulting in crude algae oil. Removing the residual solvent from the solids yields the LEA. The crude oil is upgraded via transesterification with methanol to produce biodiesel while the LEA is sent to an anaerobic digester. The biogas produced from the digester is scrubbed to remove H_2S and then utilized in a combined heat and power (CHP) system to produce heat and electricity to be used on site. The amount of energy recovered from the LEA is sufficient to meet all of the thermal energy demands for the phototrophic pathway and the majority of the electricity requirements. For the other pathways the higher lipid biomass means less LEA is available for digestion and therefore natural gas imports are required. We assume here that 76% of the nitrogen and 50% of the phosphorus are recovered from the digester supernatant and recycled to the cultivation pond to reduce fertilizer inputs as outlined by the GREET process model.[32]

Heterotrophic Pathway. Heterotrophic biomass is cultivated in a cylindrical reactor modeled with a height to width ratio of 2:1. The algal biomass is grown from an initial concentration of 20 to 80 g·L^{-1} over a 3 day batch, approximations based on results from Xiong et al.[18] The sensitivity of the results to this batch length is explored in the Supporting Information. The two most significant inputs for this stage are the aeration and mixing electrical energy inputs required for operating the reactor and the upstream impacts associated with producing the sugar that is fed to the algae. Modeling the reactor energy requirements for aeration and mixing proved to be a challenge; there are limited examples in literature and within this small sample there are significant discrepancies in the maximum biomass concentrations observed and the time required to achieve these concentrations. Uncertainty is exacerbated by the fact that the private sector does not publicize details about its technology's performance. The 80 g·L^{-1} concentration achieved by Xiong et al. is relatively high compared to results reported in other academic papers,[15,17,54−56] but is likely still lower than concentrations achieved by private sector firms with the financial resources to pursue optimized operations and to employ genetic engineering.

Centrifugation is used to further concentrate the biomass to 200 g·L^{-1} prior to cell rupture and lipid extraction, which is modeled using the same process assumptions described above for the phototrophic pathway. The heterotrophic algal biomass is assumed to have 50 wt % lipid content rather than the 25 wt % lipids modeled for the phototrophic pathway. Studies have shown lipid content ranging from 15 wt % to 55 wt %,[17,55−57] but 50 wt % is typical. The high lipid content of heterotrophic algae means less total biomass must be processed to produce the same amount of fuel and less nitrogen and phosphorus inputs are required, but also less energy can be recovered via anaerobic digestion due to reduced LEA yields.

Reactor aeration and mixing energy was calculated based on the oxygen uptake rate reported by Bottomley and Baalen (1978) for a heterotrophic alga *Nostoc*, and energy calculations were conducted as prescribed by the Environmental Protection Agency (EPA) Design Manual for Fine Pore Aeration Systems.[40,41] These energy inputs could most likely be reduced below our estimates by optimizing reactor design and operation (e.g., impeller speed and blower size) as well as through the use of genetically engineered species with higher lipid content, increased glucose conversion efficiency, and lower oxygen requirements. Therefore, the baseline reactor aeration and mixing energy, determined to be ∼3 kw·m^{-3} based on the outlined operating assumptions, was explored alongside two improved technology scenarios of 2 and 1 kW·m^{-3}. Approximately 40% of this power is mechanical aeration/mixing and the remaining is for diffused air injection. A seed train has been modeled to provide the initial biomass for the production reactor. This seed train is a reactor vessel that is one-fifth the volume of the production reactor, and it is assumed that a concentration of 100 g·L^{-1} is achieved after 4 days of cultivation. The biomass slurry is then transferred to the production reactor along with additional sterile media to provide the diluted initial concentration of 20 g·L^{-1}. The impacts associated with providing the inoculum for the seed train are neglected, as is the case with the phototrophic and hybrid pathways.

Sugarcane and sugar beet were considered in this analysis, as these are the two primary sources of sugar produced within the United States.[50] An inventory for the agricultural operations and sugar processing was adapted from work by Macedo et al., which analyzed sugarcane production in Brazil and projected a scenario for the future that is feasible with existing technologies.[53] Crop yields, sucrose content fractions, and irrigation requirements are of course different in the United States than in Brazil (and in fact have significant variations within the United States), so domestic data were used for these aspects as will be explained in the Spatial Analysis subsection later in this study. A significant amount of energy from the sugarcane crop resides in the bagasse, the fibrous material remaining after the juice has been extracted.[58] This analysis incorporates the assumption that the bagasse and a portion of the sugarcane trash is combusted and used in a high-pressure cogeneration steam cycle system to produce electricity onsite, similar to how sugarcane is used at ethanol refineries in Brazil. The model assumes that a surplus electricity export of 135 kW·h per tonne of sugarcane is produced (after on-site energy is utilized at the sugar plant), corresponding to the technology forecast for Brazil in the year 2020.[53] This electricity export would be equivalent to a cogeneration system with 23% electrical efficiency if 28% of the sugarcane crop is bagasse with an energy content of 7.62 MJ·kg^{-1} (LHV, at 50% moisture), which are similar to values reported for a sugar plant in Florida.[59] This extent of bagasse energy recovery is assumed for a condensing extraction steam turbine operating at a pressure of 6.5 MPa and 480 °C temperature.[53] The cogenerated electricity reduces

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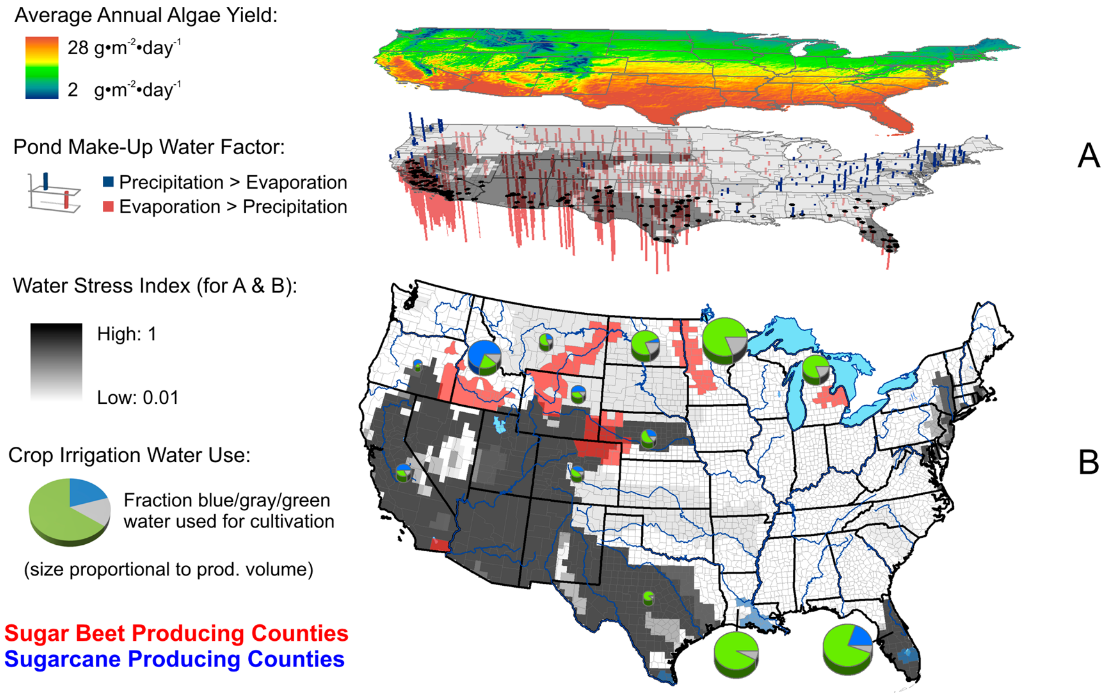

Figure 2. Summary of the GIS analysis used to determine the water stress impact of the phototrophic pathway (A) and heterotrophic pathway (B). Water stress for the hybrid pathway is derived from colocated results of the other two pathways. The bars in panel A indicate the difference between evaporation and precipitation rates at that site with blue bars indicating locations where the precipitation exceeds evaporation. The grayscale shading in both figures represents the Water Stress Index (WSI) value at that location. The counties of panel B shaded in red indicate locations where sugar beet is produced and the counties shaded in blue indicate where sugarcane is produced. The pie charts show the distribution of water sources used for irrigation and the size of the pie is proportional to the volume produced in that state.

the amount of electricity required to be imported from the grid. In the case of the 1 kW·m^{-3} aeration/mixing energy scenario, there is a surplus of electricity that is exported and treated as a coproduct.

Hybrid Pathway. The hybrid pathway is similar to the heterotrophic pathway but that an open pond system is used in place of the seed train to provide the initial biomass. Biomass is grown to 0.5 g·L^{-1} in the pond and 20% of the pond volume is harvested each day, as in the phototrophic case. The harvested culture is concentrated by tangential flow filtration (TFF) to 20 g·L^{-1} and then pumped into a production reactor. The two main rationales for exploring this pathway are that producing a fraction of the biomass photosynthetically reduces sugar demands and there is evidence to suggest the efficiency of heterotrophic growth can be improved by using a light-grown seed culture.[18] Xiong et al. showed that *Chlorella protothecoides* grown phototrophically and then heterotrophically exhibited a higher sugar conversion efficiency and a higher lipid content than cells grown only heterotrophically (cf. 58[18] vs 50 wt %[42]). They hypothesized that phototrophically grown cells retain the capacity to uptake CO_2 released by heterotrophic metabolism after incubation with glucose, thereby more efficiently converting feedstock carbon into biomass. In a related work, Heredia-Arroyo et al. also demonstrated higher lipid content for mixotrophic biomass compared to heterotrophic biomass.[17]

Therefore, a lipid content of 55 wt % is assumed rather than the value of 50 wt % assumed for the heterotrophic system. Each pathway features the same processes mentioned previously for cell rupture, lipid extraction, oil upgrading, and energy recovery via anaerobic digestion. The composition of the biomass is different for each of the pathways, however, based on assumptions of the macromolecule composition (i.e., lipid, carbohydrate, and protein fraction) provided by Lardon et al.[30] and consequently the elemental mass flows (i.e., carbon, nitrogen, phosphorus) are unique to each process. The Supporting Information provides further detail about these assumptions.

Spatial Analysis. As with any bioenergy system, the environmental impacts vary greatly depending on the region. The locations where phototrophic algae grow most quickly, for example, also typically experience more evaporation than rainfall. If the makeup water is removed from a depleted resource, the stress to the aquifer can be substantial.[32,60] Similarly, the amount of occupied land and water use associated with cultivating algae on sugars depends largely on the type of crop used (sugarcane or sugar beet) to produce the sugar. The water stress depends on the crop's yield, the amount of irrigation water required, and, as with the phototrophic pathway, the condition of the aquifer from which the water is withdrawn.[60,61] Therefore, a GIS approach was used to evaluate the effect of these regional considerations toward the variability of the results.

Annual pan evaporation data from the National Oceanic and Atmospheric Administration (NOAA) for several hundred specific sites[35] was used in conjunction with a dataset of national average annual precipitation[62] and overlaid with a GIS layer summarizing the average growth rate for algae grown in phototrophic ponds across the nation.[63] The average phototrophic growth rate data layer was built upon national historical solar insolation and temperature profiles and a growth model that predicts algae yield based on these criteria. The evaporation data was published by NOAA in 1982; it is possible that national climate trends have shifted slightly in the last 3 decades, but the dataset was chosen due to a lack of an alternate national data source. Statewide average crop-specific irrigation water use data[51] was used with county-level crop yield estimates from the National Agricultural Statistics Service (NASS)[50] and previous research results outlining water stress indices for specific aquifers[60] to derive the occupied land and water stress of the mixotrophic and heterotrophic pathways.

Figure 2 illustrates the approach used to determine the water stress. On the lower tier of graphic A, each point represents a location where evaporation rates have been measured; the difference between evaporation and precipitation at that location is indicated by the height of the bar extending from that point. Net losses (more evaporation than precipitation) are shown in red and net gains are in blue with the losses protruding downward and the gains upward. The top tier of graphic A indicates the average annual phototrophic algae yield, with red being the greatest yield and blue the least.[63] The growth

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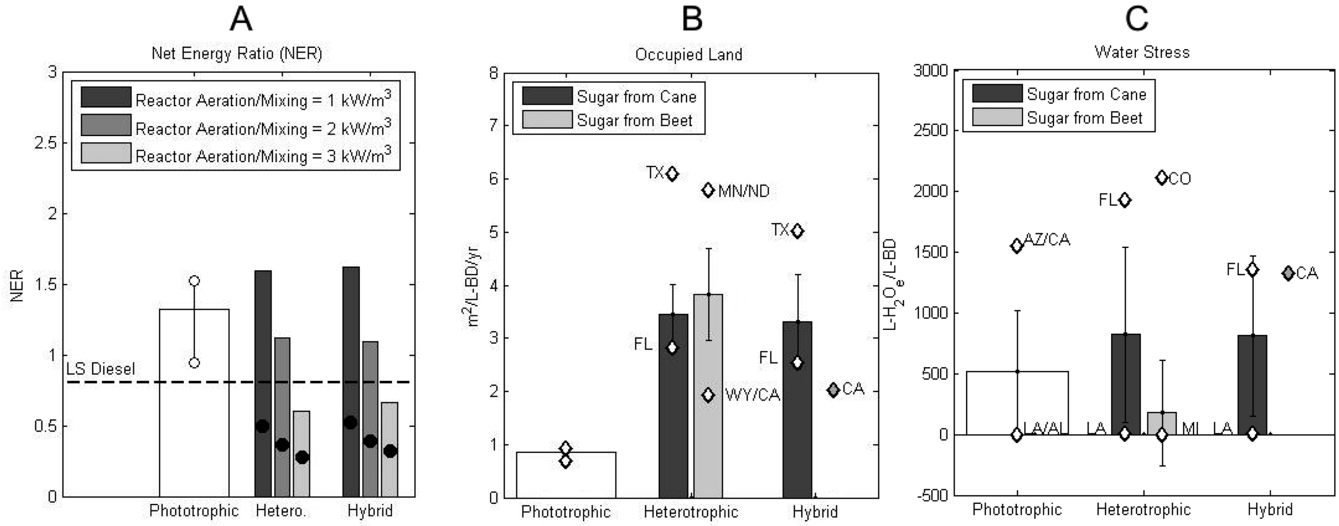

Figure 3. Results of the life cycle assessment for the net energy ratio (NER), occupied land, and water stress impact metrics. The dashed line on chart A indicates the baseline for conventional diesel fuel. The bars in panel A indicate the results if sugarcane is used as the carbon feedstock; the black circles represent the results if sugar beet is used. The error bar with white circles included in panel A indicates the range of results obtained by adjusting the baseline growth rate to the low or high scenarios. The diamonds on panels B and C indicate high/low values based on the range of locations considered in the GIS analysis. The error bars on panels B and C indicate the weighted standard deviation of the results.

rate affects the water use because locations with high yields require smaller ponds and hence less area exposed to evaporative losses. The points that are emphasized with a black circle have average annual phototrophic biomass yields exceeding 20 $g \cdot m^{-2} \cdot day^{-1}$ and are therefore considered realistic sites for open pond cultivation; the other, less productive, sites are excluded from the analysis. In both graphics, the grayscale shading indicates the water stress index (WSI) of the groundwater source at that location, with darker shades indicating the most stressed aquifers. The WSI values, which are derived from the ratio of water withdrawn from the aquifer to the total amount of water available, were obtained from Pfister et al.[60] To simplify the analysis, it is assumed that the water withdrawn for power generation comes from the same aquifer used for algae and/or sugar cultivation for all three pathways. In graphic B, the counties shaded with red produce sugar from sugar beet and counties shaded with blue from sugarcane. The pie charts indicate the fraction of blue, green, and grey water required to produce the crop. Blue water refers to water that is withdrawn from a surface or groundwater source, as opposed to green water which is received from precipitation. The grey water footprint, unused in this analysis, is a theoretical figure that refers to the volume of freshwater that would be required to dilute pollutant loads from irrigation back to natural conditions.[51] The size of the pie indicates the volume of sugar produced in that state as reported by the NASS.[50] The scale of production in each of the regions is significant because the results are reported by the volume-weighted average.

Recall that a benefit of phototrophic algae is that it can be grown with higher areal productivity than terrestrial crops and on marginal lands that could not be used for agriculture. The arable land used to grow sugar for cultivation of algae in reactors, conversely, is not exempt from the land constraint concerns that surround other biofuels. The effects of land use change must therefore also be discussed in the analysis. The premise of including effects of LUC and iLUC is that as food crops are diverted for use in biofuels, the global food market will respond by adding new agricultural capacity elsewhere to satisfy global demand.[64] As land is cleared to serve its new purpose, substantial amounts of carbon emissions released as organic carbon stocks, both above ground and below, are converted to GHGs by microbial decay and burning.[65,66] The amount of carbon emitted depends heavily on the type of land converted and the long-term accumulation or continued release of soil organic carbon depends on the vegetation type that is planted.[67] Plevin et al. evaluated the effects of iLUC with special attention to uncertainty.[68] Their model was only applied to US corn ethanol, however, and therefore cannot be directly incorporated into this study.

Two agencies within the United States have published land use carbon emission factor values for sugarcane ethanol. The Environmental Protection Agency (EPA) implemented the model developed by the Food and Agricultural Policy and Research Institute in the Center for Agricultural and Rural Development (FAPRI-CARD) at Iowa State University.[69] The California Air Resource Board (CARB) implemented the Global Trade Analysis Project (GTAP) model developed by the Center for Global Trade Analysis at Purdue University.[70] The results obtained by these two models highlight the uncertainty associated with such calculations, as the emissions reported by the CARB are nearly 1 order of magnitude greater than those reported by the EPA.[71−73] The discrepancy between the models is primarily due to differences in assumptions on volume of increased ethanol production, elasticity of input parameters, and the land conversion emission values.[71] Results from these models were adapted for this analysis to demonstrate the range of possible emissions from LUC and iLUC. The energy content of algal biodiesel is higher than that of ethanol while the yield of fuel per unit of sugar is lower, so adjustments to the emissions factors were required. Comparable studies for production of ethanol from sugar beets have not been conducted, so this analysis assumes that the carbon emissions from LUC and iLUC will be the same regardless of whether the sugar is sourced from sugarcane or sugar beet. This is a simplification, but regardless of the sugar crop used to source the sugar the effect on global demand is similar and therefore the implications on indirect land use are likely also similar.

■ RESULTS AND DISCUSSION

Net Energy Ratio. The net energy ratio (NER, or the energy in the fuel divided by the total life cycle nonrenewable energy inputs) was calculated for biodiesel produced from each pathway, and the results are shown in Figure 3a. It is apparent that biodiesel from each pathway, with the exception of the heterotrophic and hybrid pathways with the highest reactor operational energy expenditure (3 $kW \cdot m^{-3}$), achieves a NER greater than unity and represents an improvement relative to fossil diesel. For example, the baseline phototrophic case produces fuel with a NER that is 65% higher than fossil diesel. Recall that the baseline results for the phototrophic pathway

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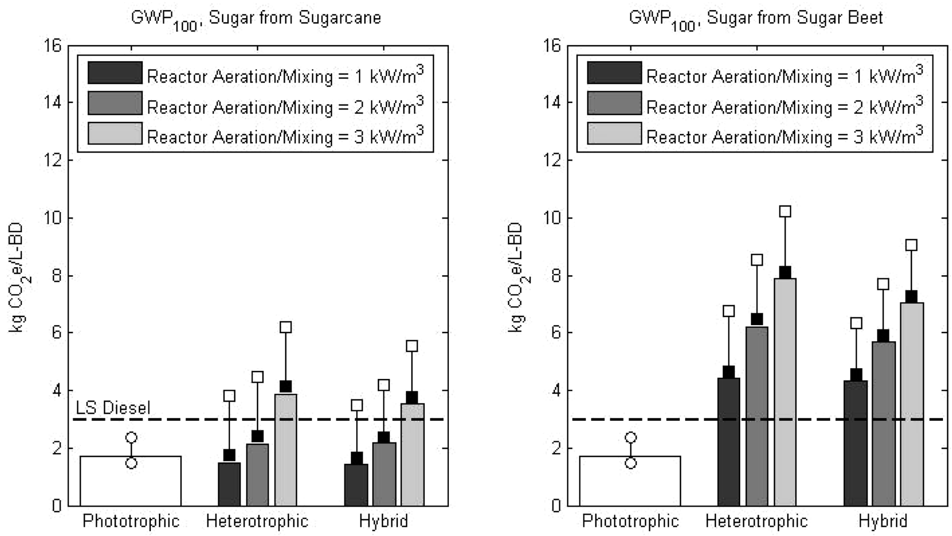

Figure 4. Global warming potential (GWP) metric considering both sugar from sugarcane (A) and sugar from sugar beet (B). The error bars with white circles indicate the range of results obtained by adjusting the baseline growth rate to the low or high scenarios. The black squares show the results with iLUC included if the EPA value is used and the white squares include iLUC impacts if the CARB value is used. Phototrophic cultivation does not utilize sugar and is assumed to not compete with agriculture and therefore there are no iLUC impacts.

assume an average growth rate of 25 $g \cdot m^{-2} \cdot day^{-1}$. The error bar with white circles in Figure 3a represents the range of results if the baseline were reduced to a low growth scenario of 12.5 $g \cdot m^{-2} \cdot day^{-1}$ or a high growth scenario of 37.5 $g \cdot m^{-2} \cdot day^{-1}$. A more thorough sensitivity analysis is included in the Supporting Information. The sharp decline in NER with an increase in reactor operational energy input suggest this is one of the key determinants of the impact of biodiesel arising from the heterotrophic and hybrid pathways. The bars presented in Figure 3a represent the results if sugarcane is the carbon feedstock. The results if sugar beet is the used are indicated by the black circles. These results show that when using sugar beet a NER greater than one is not achieved in any of the technology scenarios, primarily due to the lack of energy production from crop byproducts such as is possible with sugarcane bagasse.

For comparison, a recent analysis by Sills et al. (2013) examined 15 LCAs and found NER results ranging from as low as 0.09 to as high as 4.3.[74] The authors dissected the various models reported in literature and compiled uncertainty analyses using Monte Carlo simulations to isolate the most likely range of results for specific scenarios. They found that for the base productivity case (which matches the growth rate assumption used in this study) and a wet extraction process (which was also modeled in this study) the NER falls between 0.6 and 1.9 for 95% of the simulation results. All of the baseline scenarios explored in this analysis, assuming sugarcane as the sugar case for the heterotrophic and hybrid pathways, fall within this range.

Occupied Land. The phototrophic pathway requires less land than the other pathways, as shown in Figure 3b. This result is not surprising because one of the appealing features of phototrophic algae is its fast growth rate relative to terrestrial bioenergy crops like sugar beet and sugarcane. In the United States, sugar beet and sugarcane have comparable sugar production per hectare, so the land footprint is similar. The diamond points indicate the full range of values observed in the GIS analysis, with the labels indicating the state where the maximum or minimum value was observed. The lack of a bar in Figures 3b,c for the hybrid pathway is because there was only one existing beet cultivation location that was deemed to have a viable climate for also cultivating algae phototrophically; the results for this site are marked with a diamond. The occupied land associated with upstream fertilizer and electricity production accounted for less than 3% of the land footprint for the phototrophic pathway, with the rest of the impacts coming from the cultivation ponds. Land for growing the sugar crop dominated the footprint for the heterotrophic pathway, with the upstream impacts of the rest of the inputs contributing less than a percent of the total result. The land occupied by the hybrid pathway was slightly less than that of the heterotrophic pathway, primarily because its sugar input requirements were 13% less due to the fact that some of the biomass was produced in ponds.

Water Stress. Water stress results were highly geographically dependent, as shown in Figure 3c, with no clear difference among the three pathways. Sites with high precipitation relative to evaporation and access to aquifers that are not stressed will have a low water stress impact regardless of which pathway or sugar crop is used. Heterotrophic algae cultivated on sugar from sugar beet had the lowest average water stress, but, as with each of the scenarios, a range of results was observed depending primarily on the regional stress indices. Recall that blue water refers to withdrawn water whereas green water is that which is received from precipitation. Sugar beet or sugarcane cultivation sites that have sufficient precipitation require little or no blue water extraction for irrigation and hence inflict less water stress. This correlation is not always true, however. For example, sugar beet farms in Idaho require more blue water than farms in Colorado, but the aquifers in Idaho are under less stress and therefore the water stress impact of sugar from Colorado sugar beet is greater. For phototrophic cultivation, focus has typically been on the southwestern portion of the United States such as Arizona and New Mexico, but these arid locations have high evaporative losses and the water resources are often stressed. For reduced water stress, open pond cultivation should shift toward southeastern locations like Louisiana and Alabama

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where the water stress is much lower despite the slightly lower average algal biomass yields.

Global Warming Potential. This analysis indicates that biodiesel produced from phototrophic algae can reduce GHGs by 43% compared to conventional diesel. But with more optimistic growth rate assumptions (explored in the Supporting Information), it would be possible to meet the 50% reduction required to qualify as an advanced biofuel as defined by the National Renewable Fuels Standard program. The utility of a heterotrophic algal production platform, either in isolation or as a hybrid system utilizing ponds to generate seed material, was analyzed to determine whether further reductions in life cycle impacts could be achieved relative to the phototrophic scenario. Figure 4 illustrates the results for the GWP metric. Reductions in GWP were predicated on reactor efficiency and the sugar source; under the most optimistic case for the heterotrophic and hybrid pathways (i.e., high efficiency reactor cultivation, sugarcane as the sugar source, and ILUC ignored), GWP was reduced 51% and 15% relative to conventional diesel or the phototrophic pathway, respectively. The error bar with white circles in Figure 4 represents the range of results if the baseline were reduced to a low growth scenario of 12.5 $g{\cdot}m^{-2}{\cdot}day^{-1}$ or a high growth scenario of 37.5 $g{\cdot}m^{-2}{\cdot}day^{-1}$.

The ability to recover energy from bagasse makes sugarcane a more attractive option from the perspective of GWP and NER. In the most efficient reactor cultivation scenario (1 $kW{\cdot}m^{-3}$), there is a surplus of electricity from bagasse combustion, so all of the electricity input for the reactor is offset and a portion of the electricity produced is returned to the grid. For the other scenarios, however, the electricity input requirements are reduced but not fully met. Sugar beets, conversely, do not have energy-rich residuals that can be utilized for energy production on site and consequently have a higher GWP. The GWP results featuring sugar from sugar beet are shown in Figure 4b, illustrating that in no scenario can GWP improve beyond that of fossil diesel. The Supporting Information contains a more detailed plot showing the impacts and credits toward the GWP results, highlighting the significance of energy recovery from both anaerobic digestion of the LEA and cogenerated electricity from sugarcane bagasse.

Indirect Land Use Change. The potential of the most efficient heterotrophic or hybrid scenario to reduce GWP relative to the phototrophic model must be considered in light of the effects of LUC and iLUC. For example, if the values reported by CARB are used all GWP improvements are negated and the resulting release of GHGs is comparable to that of fossil petroleum-derived diesel. The black squares in Figure 4 show the results with LUC and iLUC included if the adapted values from the EPA are used and the white squares include adapted values from CARB.

The effects of LUC and iLUC are complex and therefore difficult to quantify. The concerns regarding land use as well as the uncertainties associated with the methodologies for quantifying its impact are pursued in greater depth in academic literature elsewhere[64−66,68] and are beyond the scope of this work. The purpose of including the potential impacts from LUC and iLUC in this analysis is not to state the impacts definitively but rather to bring the topic into the discussion and provide an approximate scale of these impacts in terms of GWP. Notably, the hybrid pathway has slightly less of a contribution to GWP from LUC and iLUC than the heterotrophic pathway because less sugar is required to produce the same functional unit of fuel due to the cultivation of a portion of the biomass in open ponds.

Outlook. The heterotrophic and hybrid pathways have the potential to produce an algal biodiesel with reduced GWP and an improved NER relative to the phototrophic pathway and conventional diesel, but if these technologies are to be scaled to large production volumes the consumption of sugar could result in land use changes that cannot be overlooked. The use of waste feedstocks or cellulosic bioenergy crops as the carbon source for heterotrophic cultivation could reduce these concerns, but the availability of these feedstocks is limited today (e.g., glycerol) and the technologies required to process them (e.g., cellulosic sugars) have yet to be reliably demonstrated at scale. This is an area of research that deserves further exploration. Domestically produced sweet sorghum is another option that could be investigated as a source of sugars for heterotrophic cultivation.

The high consumption rate of petroleum for transportation fuels suggests that purpose-grown bioenergy sources will be required if noticeable reductions in petroleum use are to be achieved. Although the heterotrophic pathway is attractive because it utilizes well-established reactor cultivation technologies, the land and resource constraints associated with producing the carbon source must be critically evaluated. The relatively small land footprint of the phototrophic pathway, conversely, facilitates scaling to large production volumes without being constrained by the availability of sugars.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

More detailed carbon accounting, an outline of the biomass composition assumptions, details about the GIS methodology employed in the analysis, an environmental impact factor table, inventory tables, a more detailed sensitivity analysis, and flow diagrams for each of the individual pathways. This material is available free of charge via the Internet at http://pubs.acs.org/.

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Notes

The authors declare no competing financial interest.

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