

pubs.acs.org/est

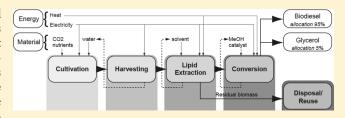
Combinatorial Life Cycle Assessment to Inform Process Design of Industrial Production of Algal Biodiesel

Laura B. Brentner, Matthew J. Eckelman, and Julie B. Zimmerman**, and Julie B. Zimmerman**,

 † Department of Chemical and Environmental Engineering, Yale University, New Haven, CT

Supporting Information

ABSTRACT: The use of algae as a feedstock for biodiesel production is a rapidly growing industry, in the United States and globally. A life cycle assessment (LCA) is presented that compares various methods, either proposed or under development, for algal biodiesel to inform the most promising pathways for sustainable full-scale production. For this analysis, the system is divided into five distinct process steps: (1) microalgae cultivation, (2) harvesting and/or dewatering, (3) lipid extrac-



tion, (4) conversion (transesterification) into biodiesel, and (5) byproduct management. A number of technology options are considered for each process step and various technology combinations are assessed for their life cycle environmental impacts. The optimal option for each process step is selected yielding a best case scenario, comprised of a flat panel enclosed photobioreactor and direct transesterification of algal cells with supercritical methanol. For a functional unit of 10 GJ biodiesel, the best case production system yields a cumulative energy demand savings of more than 65 GJ, reduces water consumption by 585 m³ and decreases greenhouse gas emissions by 86% compared to a base case scenario typical of early industrial practices, highlighting the importance of technological innovation in algae processing and providing guidance on promising production pathways.

■ INTRODUCTION

Using algae as an energy feedstock has recently been revisited with significant interest in response to volatile oil prices, import reliance, depletion of domestic petroleum resources, environmental disasters, and national security concerns. The United States currently uses 58 billion gallons (220 billion liters) of diesel per year, with a mandate to produce at least 21 billion gallons (79 billion liters) of bioderived fuels from sources other than corn by 2022. Biofuel production from conventionally farmed crops, such as corn, has resulted in numerous sustainability challenges, particularly with regard to water consumption, land use, fertilizer and pesticide application, and overall energy balance. 3.4

Compared to conventionally farmed biofuels, producing liquid fuels from algae has the advantages of fast growth, low or marginal land use, higher average oil content per dry weight (20–90% depending on the species and growth conditions) higher yield per acre, $^{\rm 5}$ and exploitation of byproduct resources as feedstocks, such as nutrient-laden wastewater and/or flue gases containing $\rm CO_2$. 6,7 Algae biotechnology is a quickly advancing industry with the potential to provide a renewable and rapidly reproducing feedstock for biodiesel and a variety of value-added chemicals. The developing nature of the algal biotechnology industry provides an opportunity to consider the impacts of material and energy flows enhancing informed decisions before it matures into commercial scale production.

Life cycle assessment (LCA) is a modeling tool to quantify the impacts of products and processes along multiple environmental

categories. Multiple LCA studies of algal production have been conducted recently that highlight environmental challenges for algal biofuels, including large fertilizer and nutrient requirements, 8,9 significant energy required to dewater the algae prior to lipid extraction $^{10-12}$ and for production and delivery of CO_{2} , and high water intensity relative to land-based bioenergy sources. 8,9 Techniques to mitigate this concerns have also been assessed using LCA, including using alternate sources of CO₂ from ammonia production or power plants, ^{13,14} using wastewater for nutrients, 8,14,15 or coupling algae cultivation and biogas production to reduce overall energy demands.¹⁶ Multiple reactor designs for algae cultivation have been evaluated in the literature, in general finding that open raceway ponds (ORPs) have a lower energy use and GHG emissions profile compared to photobioreactors (PBRs), 17,18 although the choice of materials for the PBRs has a significant influence on the results. 14 Compared to petroleum and soy-based biodiesel, algal biodiesel produced using some PBR systems has been found to have a favorable energy and greenhouse gas balance. 19

Detailed comparisons among existing algal LCA studies are hampered by differing assumptions about growth and productivity parameters, allocation among coproducts, treatment of the

Received: March 1, 2011 Accepted: June 9, 2011 Revised: June 1, 2011 Published: June 09, 2011



^{*}School of Forestry and Environmental Studies, Yale University, New Haven, CT

System boundary (excludes labor inputs; transport infrastructure; non-reactor capital equipment)

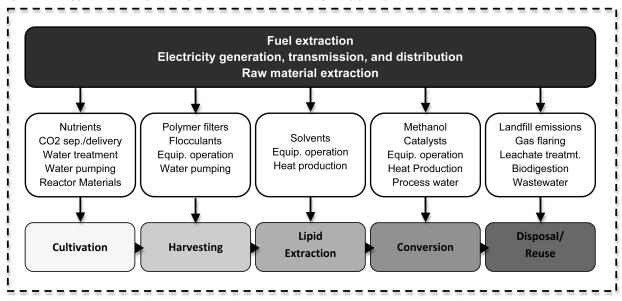


Figure 1. System Boundary of the Present Study.

nonlipid algae fractions, and technology choices used to model algal biodiesel. The other general feature of previous research is that single process routes for algal biodiesel production are evaluated, or if several options are considered, these are usually within one stage of production.²⁰ Descriptive reports exist that cover a wide range of technologies along the entire chain of production,²¹ but these cannot be used for quantitative environmental comparisons. As such, this analysis broadens the scope of analysis by using LCA to consider multiple technologies for each algal biodiesel production step. Rather than evaluating a single process pathway, 160 pathways (combinations of different technologies for each process stage) are modeled and multiple impact categories are considered to identify the most preferable combination of current or proposed technologies. In this way, the most preferable system components for algal biofuel production can be identified to inform further resource investment and development for this maturing industry.

■ GOAL AND SCOPE

The goal of this cradle-to-gate LCA study is (1) to evaluate the options for each process step and (2) to identify design parameters that collectively indicate the most potentially sustainable system for industrial-scale production of algal biodiesel. For this analysis, the system is divided into five distinct process steps: microalgae cultivation, harvesting and dewatering, lipid extraction, conversion (transesterification) into biodiesel, and byproduct management, with each process step having a number of options (Figure 1). The system is modeled using literature-based data supplemented with discussions from industry representatives to direct the study focus, rather than as a primary data source. Robust operational data are not available as there are relatively few facilities worldwide, even at the pilot scale, that are growing algae for biodiesel production, and thus documentation of most of the modeled technologies reflects bench-scale operations.

A life cycle inventory (LCI) was assembled for each process step option. Each design is evaluated for five categories typically associated with biofuels: cumulative energy demand, greenhouse gas (GHG) emissions, water use, eutrophication, and direct land requirements. LCI data were derived from the Ecoinvent 2.2 database using U.S.-specific processes where possible and compiled using a spreadsheet model and SimaPro LCA software. Impact assessment results were calculated using two complementary methods: Cumulative Energy Demand (v1.07) and Building for Environmental and Economic Sustainability (BEES v4.02). Inputs and outputs in the LCI were allocated to coproducts based on economic value. Given current market values of biodiesel and glycerin at \$1.07 kg^{-1} and \$0.51 kg^{-1,24}, respectively, produced at a mass ratio of 9.5:1. The share of environmental burdens associated with production attributed to the biodiesel and glycerin were 95.2% and 4.8%, respectively.

The functional unit used as a basis for comparison is 10 GJ biodiesel (or approximately 294 L assuming an HHV of 34 MJ/L). The location chosen for this analysis is Phoenix, AZ, thought to be an ideal location for algae cultivation in the U.S. due to its ample solar irradiance and available nonarable land area. The annual potential for production of algal oil at this location has been estimated at 53 200 L oil ha⁻¹y⁻¹. 25 Consistent assumptions for external parameters were used for each option as described in Figure 1. The technology options that assemble to form a production system with the lowest energy demand are presented as the best case scenario of an algal biofuel production system. This LCA is cradle-to-gate and does not include labor, transport infrastructure, capital machinery, or combustion of the biodiesel. The LCA incorporates all relevant material and energy inputs into production, including infrastructure needed to produce and deliver these inputs to the model site.

■ PROCESS STEPS

Algal Cultivation: Algae Growth Parameters. Model parameters are based on average freshwater algal productivities, yields and nutrient requirements reported in the literature. Algal biomass composition was used to determine the minimum stoichiometric nutrient requirements for algae of 8.2% and

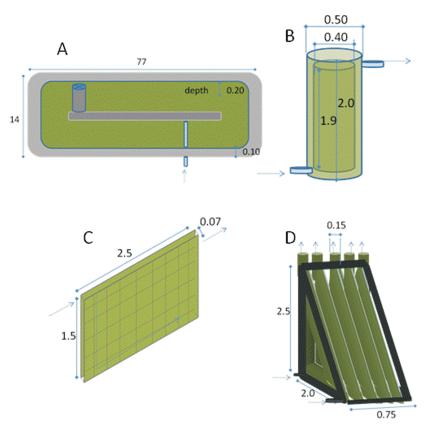


Figure 2. Descriptive diagram of algal cultivation options analyzed. Dimensions are shown but images are not to scale. (A) Open raceway pond, (B) Annular PBR, (C) Flat panel PBR, and (D) Tubular PBR.

1% dwt algae for N and P, respectively; however, algae vary significantly in their preferred source of nitrogen. ²⁶ Ammonium nitrate and calcium phosphate were modeled here as nutrient inputs.

Average algal productivities for enclosed and open systems were modeled based on algal culture densities of 0.47 and 4.0 kg m⁻³ with a dilution rate of 0.25 and 0.384 d⁻¹ for ORPs and PBRs, respectively.⁵ These algal productivity parameters are based on assumptions that represent likely values for future commercial scale-up. 27 The fraction of triglycerides available for conversion is assumed to be 25%, based on the average oil content of the freshwater algae Scenedesmus dimorphus, grown under normal nutrient conditions.²⁸ A CO₂ loading rate of 1.79 kg (kg dwt algae)⁻¹⁵ was assumed with CO₂ sourced as a waste product from either a power or ammonia plant. Thus, none of the upstream environmental burdens of electricity or ammonia production are allocated to the CO₂ inputs. The CO₂ content in the flue gas determines the volume of gas needed for algae growth and the energy required to isolate CO2 in a gas separation plant and to deliver the gas to the cultivation site. Waste gas from a coal-fired power plant was assumed to have 15% CO₂ (requiring 162 MJ (ton algae)⁻¹ for transport to the algal cultivation site) and an ammonia plant was assumed to be nearly 100% CO₂ (requiring 24.5 MJ (ton algae)⁻¹ for delivery to site).¹

Algal Cultivation: Bioreactor Design. There is considerable debate among which reactor type, a simple open raceway pond or an enclosed photobioreactor, will be advantageous for algal cultivation for industrial-scale biodiesel production.²⁷ ORPs are simplistic in their design and operation, requiring only slow mixing by paddle wheel. ORPs are also typically much less material and capital intensive than PBRs due to their much larger unit capacity

and open design. However, they suffer from a host of disadvantages including risk of culture contamination, low light utilization rates, low aerial productivity, low volumetric productivity, and poor mixing and temperature control. Because they can achieve shallower cultures that allow light to penetrate more fully, reaching more algal cells, PBRs can achieve high volumetric concentrations with the ability to control mixing while preventing contamination and evaporation. PBRs are generally made from plastics or glass and tend to have a much shorter lifetime than ORPs, which increases the overall material demands for these systems.

Several review papers on reactor design have helped to identify feasible options for industrial scale cultivation of algae in various reactor types. 29-34 Figure 2 presents the design of the different reactors used in this analysis and Table 1 summarizes their inputs and environmental impacts. The four designs evaluated include an ORP³⁵ and three enclosed PBRs: annular,³⁶ inclined tubular,^{37,38} and flat panel.³⁹ Each of the reactors considered has published data available related to design parameters for fieldscale operation. Hybrid reactor approaches are also possible, where a PBR is used for growing inoculate that is then fed into an ORP for production, ⁴⁰ but these are not considered here. For the ORP system, CO₂ is assumed to be introduced by a gas sparger and circulated by a paddle wheel whereas the PBRs are assumed to rely on aeration. Pumping of the culture medium to the harvesting operation is also considered. Other operation-related energy use includes requirements to pump, treat, and deliver water to the site, to manufacture and to deliver nutrients, and to deliver the CO₂ gas stream. The energy required to manufacture the reactor materials is also included, scaled to the functional unit according to the expected lifetime of each reactor component.

Table 1. Algal Cultivation Design and Operational Parameters to Produce One Functional Unit (f.u.) of 10⁴ MJ of Algal Biodiesel under Economic Allocation

reactor type		photobioreactors		
parameter	raceway	annular	tubular	flat-panel
volumetric productivity (kg/m³)	0.5	4.0	4.0	4.0
total volume required (m ³)	2495	312	312	312
reactor unit volume (m ³)	200	0.12	0.16	0.26
reactor units required	12.5	2599	2943	1188
residence time (d)	4.0	2.6	2.1	2.6
nutrients required (kg)	1248	1248	1248	1248
water use				
recycled (m ³)	1996	250	250	250
lost to evaporation (m ³)	78	0	0	0
input required per f.u. (m ³)	577	62	62	62
electricity use				
hours of operation (hr/d)	10	10	10	10
paddle wheel (W/m^3)	3.75	-	-	-
aeration (W/m³)	0.25	1680	6760	53
outflow pumping (Wh/m^3)	88	88	88	88
input required per f.u. (kWh)	616	13700	43900	544
land use				
aerial productivity $(kg/m^2 \cdot d)$	0.048	0.096	0.646	0.068
reactor unit area (m²)	1000	0.4	0.6	11.3
area of reactor array (m ²)	13100	9982	1177	14075
input required per f.u. (m ²)	4.1	1.4	0.7	1.9
reactor material use				
lifetime of installation (yr)	50	35	15	50
concrete (kg)	967	19.5	-	-
polymethyl methacrylate (kg)	-	38.4	-	-
polycarbonate (kg)	-	-	0.7	-
LDPE sheet (kg)	-	-	-	7.6
steel (kg)	-	-	1.5	0.6

Harvesting. Due to the small diameter and surface charge of algae, harvesting can be among the most energy intensive processes in algal biofuel production. Table 2 presents a comparison of harvesting options: centrifugation, filtration, and flocculation/settling. Currently, the only full-scale algae production facilities are designed for the extraction of nutriceuticals, or nutrient supplements. In these facilities, centrifugation, which is reliable but energy intensive and subsequently costly, is often used for harvesting the cells, a reasonable strategy given that the desired products are much more valuable than biofuels. ⁴¹ Filtration is another option for harvesting cells. Sometimes used for processing in wastewater treatment plants, a recessed chamber press filter was also included for comparison.

Flocculation and settling are another option for harvesting that only requires energy for a short period to mix the cells with a coagulant. Algae vary significantly in their response to certain flocculants. Some algae will aggregate and settle with an increase in pH, which can be controlled through changes in aeration with CO₂ or through the addition of lime. Aluminum sulfate and chitosan have also been shown to be effective flocculants. Previous LCA studies have assumed aluminum sulfate as the flocculant shift but other potential flocculants have not been evaluated. For example, chitosan is a promising emerging coagulant

that is manufactured from crustacean fishery waste, making it a renewable resource. 44,46 The effectiveness of a particular flocculant and its dosage will vary tremendously from one algal species to another. Modeled doses for each flocculant are included in Table 2, 11,43,44 and the sensitivity of the results to flocculant dose is evaluated (see Supporting Information (SI)).

Lipid Extraction and Transesterification. Lipid extraction from microalgae may be one of the least developed areas in the algal biodiesel industry. Several options are considered for these process steps ranging from conventional processes for soybean oil to newly developed lab-scale approaches using supercritical fluids (Table 3). Approaches that obviate the need for extraction through genetic engineering or selection of algae to excrete lipids would likely have significant environmental benefits, ⁴⁷ but the material and energy implications of these approaches have not been characterized fully enough to include in the present analysis.

Soybean oil processing (with minor modifications) has been used by previous LCA studies as a proxy for conventional algal oil processing. 10,111 This technique uses a drill press to break open the plant cells followed by solvent extraction, most often with recovered and recycled hexane, followed by transesterification. The conventional transesterification process for soybean oil conversion is more readily applicable to oil from microalgae than the conventional extraction process, which is presented as the first technological option, from the Ecoinvent database ("soybean methyl ester, at esterification plant US/U")²² adapted for use with microalgae by substituting soy oil inputs with algal oil. Supercritical CO₂ extraction (option 2) has the potential for enhanced specificity in selectively extracting lipids more relevant to biodiesel or to nutriceuticals and avoids the use of organic solvents. 48,49 Optimal extraction conditions were assumed to be 30 MPa and $100\,^{\circ}$ C, while assuming minimal energy losses for a commercial scale version of the process. S0,51 Another recent study has demonstrated the potential for direct transesterification of microalgae (option 3), with methanol added directly to dried, disrupted cells using sulfuric acid as a catalyst. 52 Supercritical methanol (option 4) also shows promise for combined lipid extraction and transesterification of oils from wet algae. 53,54 Supercritical methanol extraction has been shown to be a cleaner and more selective process as compared to conventional methods requiring no catalyst and producing less waste. 55 However, there is a relatively high energy burden associated with a high reaction temperature (\sim 250 °C), pumping required to supercritical pressures, and methanol recovery. While this process is energy intensive, avoiding drying and combining lipid extraction and conversion processes may present a significant advantage.

Disposal and Recycling of Residual Algal Biomass. The use of the algal biomass remaining after lipid extraction greatly affects the balance of energy and material inputs and environmental impacts associated with biodiesel production. Recycling some portion of the algal biomass residue for its nutrient content is considered a best practice that reduces the need for fertilizer inputs, but developing a biorefinery approach to algal biofuels by producing additional chemicals and feedstocks from the residue is seen as essential for the long-term economic viability of the fuel. This is in addition to creating new value for the glycerol that results from transesterification. These value-added coproducts and applications are largely still under development and it is difficult to predict if and when they will be viable at significant volumes.

Table 2. Algae Harvesting Design and Operational Parameters to Produce One Functional Unit (f.u.) of 10⁴ MJ of Algal Biodiesel under Economic Allocation

			${\it flocculation}^b$		
parameter	centrifugation	chamber press filtration ^a	pH-lime	aluminum	chitosan
cell recovery efficiency	95%	95%	95%	95%	95%
electricity use (kWh/m³)	1	0.88	0.1	0.1	0.1
electricity use (kWh)	2500	2200	250	250	250
material use					
polypropylene filters (kg)	-	0.15	-	-	-
flocculant (kg)	-	-	750	175	75

^a Ertel Alsop (Kingston, NY) 1500 mm EA-series chamber press with polypropylene filters. ^b EMI/Cleveland Eastern (Clinton, CT) HGD 20 hp mixer.

Table 3. Lipid Extraction and Conversion Design and Operational Parameters to Produce One Functional Unit (f.u.) of 10^4 MJ of Algal Biodiesel under Economic Allocation

parameter	option 1: press + cosolvent + esterification	option 2: scCO ₂ extraction+ esterification	option 3: ultrasonication + direct esterification	option 4:supercritical methanol
references	23	49-51	52	53
extraction efficiency	91%	95%	-	-
extraction conditions	STP	100 °C, 30 MPa	STP	-
conversion efficiency	98%	98%	98%	98%
conversion conditions	50 °C	50 °C	70 °C	250 °C, 8.3 MPa
electricity use				
extraction (kWh)	59	1830	3190	-
conversion (kWh)	10	10	-	141
heat use				
drying (MJ)	16,360	-	14,885	-
extraction (MJ)	1000	-	-	-
conversion (MJ)	225	225	400	7388
reagents use				
HCl (30% vol) (kg)	1.1	1.1	403	-
H_3PO_4 (85% vol) (kg)	2.8	2.8	537	-

In this study, only landfilling and anaerobic digestion of residual algal biomass are considered in the quantitative model, although other options are discussed qualitatively in the SI. Microbial digestion has been well explored as a necessary step toward sustainable algal biofuel due to the energy (methane gas) and nutrients (nitrogen and phosphorus) that can be recycled within the system. 56,57 Methane recovery estimates are based on estimates of protein, carbohydrate and recalcitrant contents of residual biomass (52%, 25%, and 23%, respectively) and methane yield estimates for those contents based on Angelidaki and Sanders.⁵⁸ It is assumed that digestion occurs at 40 °C with a hydraulic retention time of 10 days. The nitrogen associated with the high protein content of the starting material can be problematic as it may lead to ammonia build-up in the digester, which can inhibit the anaerobic bacteria. This may be corrected for by using ammonia-tolerant bacteria,⁵⁶ as is assumed here. Digester outputs are 0.1 kg (0.08 m³) methane per kg algal biomass residue.⁵⁶ Methane is assumed to generate electricity through combustion in a gas turbine. 22 A 70% recovery rate for residual nutrients that are recycled back into the system is also assumed. The electricity generated from recovered methane is assumed to be used for internal system processes with no excess available to sell to the

grid. Since no additional valuable products are leaving the system in this scenario, the allocation procedure does not change.

■ RESULTS AND DISCUSSION

Assembling the Best Case Scenario. The overall best case scenario was assembled with the process options contributing the least energy demand at each step (Figure 3). For the cultivation step, based on the bioreactor comparison, the best reactor for algal cultivation among current technologies is the flat panel PBR, which was found to have the lowest impacts for all environmental impact categories except for land use. The cumulative energy demand for the flat panel PBR is more than 30 times lower than the tubular PBR, 10 times lower than the annular PBR, and about 20% lower than the ORP. Table 4 summarizes the inputs and LCA results for the different algal cultivation processes. Direct water use is the same for all of the PBRs, which were assumed to have the same algal productivities. With water recycling, PBRs use about 10 times less water than ORPs

For harvesting algae, flocculation is clearly the lowest impact process but most of the environmental burden comes from the flocculant choice. Lime addition carries a heavy burden, but chitosan and aluminum sulfate are close in their overall impacts.

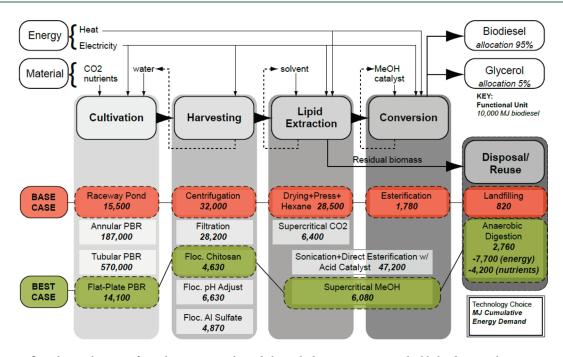


Figure 3. System flow-chart with options for each process step shown below. The base case options are highlighted among the process options above in red and the best case options are highlighted below in green. All reactors are evaluated for cultivation in Phoenix, AZ, where the average solar irradiance is $5500 \text{ W/m}^2/\text{day}$. Harvesting steps show cumulative energy values based on base case (raceway pond) cultivation, which requires a higher volume of water than the best case scenario, and therefore greater levels of processing.

Chitosan has the lowest energy demand with aluminum sulfate and lime requiring 240 and 1900 more MJ than chitosan, respectively. Centrifugation and filtration are an order magnitude greater for every impact considered. Chitosan has the lowest impact of the harvesting methods considered here, but self-floculating algae that would avoid a floculant input could significantly improve the environmental impacts of this process.

The need for a wet process following harvesting is highlighted by the large energy demand associated with the heat required to dry algae to an appropriate solids content. Direct transesterification by supercritical methanol is an energy intensive process, but its application to wet algae saves a substantial amount of heat energy. The high efficiency (~98%) of the supercritical methanol combined extraction and transesterification method⁵³ also saves on the quantity of algal biomass that must be cultivated, leading to decreases in energy, water, and nutrient consumption throughout the system. Because the supercritical methanol method does not rely on the use of a catalyst or a pretreatment of the alga cells (drying, ultrasonication, or additional lipid extraction steps), it is able to save significant inputs overall.

Finally, the use of residual algal biomass for nutrient recycling and energy production provides a useful reduction in primary energy inputs. This option reduces the energy demand by reducing dependence on synthetic fertilizers and recycles energy back into the system through the recovery of biogas. Based on the burning of biogas in a gas turbine the energy recovered is 2.6 GJ, about 20% of the cumulative energy demand and about 60% of the direct energy use. The energy savings to be realized by reducing the nutrient input by 70% is 1.1 GJ.

Base Case versus Best Case Scenario. The combination of technologies that make up the best case scenario shows significant reductions in energy demand and eutrophication with moderate reductions in water and land use compared with the base case, which consists of ORP cultivation, centrifugation,

drying and hexane extraction of the oil, standard transesterification with methanol, and landfilling of residual biomass (Figure 3). The cumulative energy demand in the best case scenario represents an 85% savings relative to the base case. The energy recovered from biogas from anaerobic digestion is equivalent to 10% of the energy deficit of the base case and supplies about 65% of the energy demand of the best case scenario. The GHG emissions of the best case scenario comprise only 14% of the base case emissions. The best case uses up only 42% of the direct land use required by the base case scenario and 52% of the direct water consumption. It is worth noting that for the best case scenario, the net energy balance is only slightly negative, and future process improvements, particularly as harvesting and processing technologies are brought to scale, will likely result in a positive energy balance for the best case scenario, and probably for other process combinations as well.

Model Sensitivity, Uncertainty, And Alternate Assumptions. The performance and economic viability of an algal biorefinery will vary greatly with location, depending on the physical and technological environment in which it is sited. Parameters such as solar irradiance and ambient temperature clearly affect the potential growth rate of algae. See the SI for further sensitivity and uncertainty analyses, as well as additional considerations for process options, including use of artificial light inputs in cultivation, nutrient recycling options, temperature regulation, and other end-of-life options for the algae cake. The most sensitive impact factor to algal culture density is land use, with an 11% increase or 9% decrease in land use with a 10% decrease or increase in algal culture density respectively. Nearly the same result was obtained by a 10% change in algal oil content (Figure S1 in the SI).

Technological advances are happening quickly in the algae industry, such that the inherent delays associated with publishing data can result in obsolete factors being assumed in economic and environmental models. The work reported here relies largely

Table 4. Summary of Base Case V. Best Case Scenario Comparison (Cumulative Energy Demand, Global Warming Potential, Water Use, Eutrophication, and Land Use)^a

,	,	,
parameter	base case	best case
Cumulative Energy Der	mand (Mleg)	
cultivation processes	nuna (mjeq)	
water delivery and storage	690	350
gas delivery	720	6620
paddle wheel operation	4770	0020
water pumping to harvesting	2810	350
construction materials	760	
		990
nutrient production	5770	5770
harvesting processes	22 000	2/0
operation	32 000	360
flocculant production	-	170
lipid extraction processes		
electricity	760	1800
heat production	27 590	2070
solvent production	190	-
conversion processes		
esterification	1060	1060
equipment materials	220	-
waste mgmt. processes		
landfilling/spreading	820	190
anaerobic biodigestion	-	2280
water treatment	-	780
credit (nutrients)	0	-4200
credit (energy)	0	-7770
total CED	78 200	10 800
GHG emissions (kg CO ₂ eq)	5340	805
eutrophication (g Neq)	2820	615
direct water use (m ³)	1210	625
cultivation land use (m ²)	4.1	1.9
a TAT . 1 . 1 1	. 1. 1 1	1 1

^a Water use does not include water used to produce hydroelectricity.

on secondary data reported in the literature taken over the past several years, which prolongs this delay, and any interpretation of the results should be made with this in mind. Cooperation and participation of the nascent algae industry by sharing relevant, unclassified operational data will be crucial in accurately tracking the life cycle performance of algal biodiesel and associated bioproducts in the future. This will allow for better application of LCA research and transparent analysis to support sustainable growth of the industry.

■ ASSOCIATED CONTENT

Supporting Information. Additional information including equations, Figure S1 and Table S1. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: julie.zimmerman@yale.edu.

■ REFERENCES

(1) U.S. Energy Information Administration; Washington, D.C., 2011 www.eia.gov (accessed).

- (2) The Energy Independence and Security Act of 2007, PL110-140; U.S. Government Printing Office: Washington, DC.
- (3) Chisti, Y. Biodiesel from microalgae beats bioethanol. *Trends Biotechnol.* **2008**, 26 (3), 126–131.
- (4) Dominguez-Faus, R.; Powers, S. E.; Burken, J. G.; Alvarez, P. J. The water footprint of biofuels: A drink or drive issue? *Environ. Sci. Technol.* **2009**, 43, 3005–3010.
- (5) Chisti, Y. Biodiesel from microalgae. *Biotechnol. Adv.* 2007, 25, 294–306.
- (6) Kosaric, N.; Nguyen, H. T.; Bergougnou, M. A. Growth of *Spirulina maxima* algae in effluents from secondary waste-water treatment plants. *Biotechnol. Bioeng.* 1974, 16, 881–896.
- (7) Pittman, J. K.; Dean, A. P.; Osundeko, O. The potential of sustainable algal biofuel production using wastewater resources. *Bioresour. Technol.* **2011**, *102* (1), 17–25.
- (8) Clarens, A. F.; Resurreccion, E. P.; White, M. A.; Colosi, L. M. Environmental life cycle comparison of algae to other bioenergy feedstocks. *Environ. Sci. Technol.* **2010**, *44* (5), 1813–1819.
- (9) Yang, J.; Xu, M.; Zhang, X.; Hu, Q.; Sommerfeld, M.; Chen, Y. Life cycle analysis on biodiesel production from microalgae: Water footprint and nutrients balance. *Bioresour. Technol.* **2011**, *102* (1), 159–165.
- (10) Sander, K.; Murthy, G. S. Life cycle analysis of algae biodiesel. *Int. J. Life Cycle Assess.* **2010**, *15*, 704–714.
- (11) Lardon, L.; Helias, A.; Sialve, B.; Steyer, J.-P.; Bernard, O. Lifecycle assessment of biodiesel production from microalgae. *Environ. Sci. Technol.* **2009**, *43* (17), 6475–6481.
- (12) Xu, L.; Wim Brilman, D. W. F.; Withag, J. A. M.; Brem, G.; Kersten, S. Assessment of a dry and a wet route for the production of biofuels from microalgae: Energy balance analysis. *Bioresour. Technol.* **2011**, *102* (8), 5113–5122.
- (13) Campbell, P.; Beer, T.; Batten, D. Life cycle assessment of biodiesel production from microalgae in ponds. *Bioresour. Technol.* **2010**, 102 (1), 50–56.
- (14) Soratana, K.; Landis, A. E., Evaluating industrial symbiosis and algae cultivation from a life cycle perspective. *Bioresour. Technol.* **2011**; DOI: 10.1016/j.biortech.2011.04.018.
- (15) Sturm, B. S. M.; Lamer, S. L., An energy evaluation of coupling nutrient removal from wastewater with algal biomass production. *Appl. Energy* **2011**; DOI: 10.1016/j.apenergy.2010.12.056.
- (16) Collet, P.; Hélias Arnaud, A.; Lardon, L.; Ras, M.; Goy, R. A.; Steyer, J. P. Life-cycle assessment of microalgae culture coupled to biogas production. *Bioresour. Technol.* **2011**, *102* (1), 207–214.
- (17) Stephenson, A. L.; Kazamia, E.; Dennis, J. S.; Howe, C. J.; Scott, S. A.; Smith, A. G. Life-cycle assessment of potential algae biodiesel production in the United Kingdom: a comparison of raceways and air-lift tubular bioreactors. *Energy Fuels* **2010**, *24*, 4062–4077.
- (18) Jorquera, O.; Kiperstok, A.; Sales, E.; Embiruçu, M.; Ghirardi, M. Comparative energy life-cycle analyses of microalgal biomass production in open ponds and photobioreactors. *Bioresour. Technol.* **2010**, *101* (4), 1406–1413.
- (19) Batan, L.; Quinn, J.; Willson, B.; Bradley, T. Net energy and greenhouse gas emission evaluation of biodiesel derived from microalgae. *Environ. Sci. Technol.* **2010**, 44 (20), 7975–7980.
- (20) Lee, J. Y.; Yoo, C.; Jun, S. Y.; Ahn, C. Y.; Oh, H.-M. Comparison of several methods for effective lipid extraction from microalgae. *Bioresour. Technol.* **2010**, *101*, 575–577.
- (21) Brennan, L.; Owende, P. Biofuels from microalgae--A review of technologies for production, processing, and extractions of biofuels and co-products. *Renewable Sustainable Energy Rev.* **2010**, *14* (2), 557–577.
- (22) Ecoinvent Centre. Ecoinvent data v2.2. http://www.ecoinvent.org (accessed).
- (23) Frischknecht, R.; Jungbluth, N. Implementation of Life Cycle Impact Assessment Methods. Final Report; Swiss Centre for LCI: Duebendorf, Switzerland, 2003.
- (24) Clean Cities Alternative Fuel Price Report; U.S. Department of Energy, Energy Efficiency and Renewable Energy: Washington, DC, 2010.

- (25) Weyer, K. M.; Bush, D. R.; Darzins, A.; Willson, B. D. Theoretical maximum algal oil production. *Bioenergy Res.* **2010**, *3*, 204–213.
- (26) Grobbelaar, J. U., Algal nutrition. In *Handbook of Microalgal Culture: Biotechnology and Applied Phycology*; Richmond, A., Ed.; Blackwell Science Ltd: Oxford, UK, 2004; pp 97—115.
- (27) Wijffels, R. H.; Barbosa, M. J. An outlook on microalgal biofuels. *Science* **2010**, *379*, 796–799.
- (28) Griffiths, M. J.; Harrison, S. T. L. Lipid productivity as a key characteristic for choosing algal species for biodiesel production. *J. Appl. Phycol.* **2009**, *21*, 493–507.
- (29) Borowitzka, M. A. Commercial production of microalgae: Ponds, tanks, tubes and fermenters. *J. Biotechnol.* **1999**, *70*, 313–321.
- (30) Carvalho, A. P.; Meireles, L. A.; Malcata, F. X. Microalgal reactors: A review of enclosed system designs and performances. *Biotechnol. Prog.* **2006**, 22, 1490–1506.
- (31) Morweiser, M.; Kruse, O.; Hankamer, B.; Posten, C. Developments and perspectives of photobioreactors for biofuel production. *Appl. Microbiol. Biotechnol.* **2010**, *87*, 1291–1301.
- (32) Posten, C. Design principles of photo-bioreactors for cultivation of microalgae. Eng. Life Sci. 2009, 9 (3), 165–177.
- (33) Pulz, O. Photobioreactors: production systems for phototrophic microorganisms. *Appl. Microbiol. Biotechnol.* **2001**, *57*, 287–293.
- (34) Ugwu, C. U.; Aoyagi, H.; Uchiyama, H. Photobioreactors for mass cultivation of algae. *Bioresour. Technol.* **2008**, *99*, 4021–4028.
- (35) Benemann, J. R.; Oswald, W. J. Systems and Economic Analysis of Microalgae Ponds for Conversion of CO₂ to Biomass; Pittsburgh Energy Technology Center: Pittsburgh, PA, 1996.
- (36) Chini Zittelli, G.; Rodolfi, L.; Biondi, N.; Tredici, M. R. Productivity and photosynthetic efficiency of outdoor cultures of *Tetraselmis suecica* in annular columns. *Aquaculture* **2006**, *261*, 932–943.
- (37) Merchuk, J. C.; Rosenblat, Y.; Berzin, I. Fluid flow and mass transfer in a counter-current gas-liquid inclined tubes photo-bioreactor. *Chem. Eng. Sci.* **2007**, *62*, 7414–7425.
- (38) Vunjak-Novakovic, G.; Kim, Y.; Wu, X.; Berzin, I.; Merchuk, J. C. Air-lift bioreactors for algal growth on flue gas: mathematical modeling and pilot plant studies. *Ind. Eng. Chem. Res.* **2005**, *44*, 6154–6163.
- (39) Sierra, E.; Acien Fernandez, F. G.; Garcia, J. L.; Gonzalez, C.; Molina Grima, E. Characterization of a flat plate photobioreactor for the production of microalgae. *Chem. Eng. J.* **2008**, *138*, 136–147.
- (40) Schenk, P. M.; Thomas-Hall, S. R.; Stephens, E.; Marx, U. C.; Mussnug, J. H.; Posten, C.; Kruse, O.; Hankamer, B. Second generation biofuels: high-efficiency microalgae for biodiesel production. *Bioenergy Research* 2008, 1, 20–43.
- (41) Foley, P. M.; Beach, E. S.; Zimmerman, J. B., Algae as a source of renewable chemicals: Opportunities and challenges. *Green Chem.* **2011**; DOI: 10.1039/C1GC00015B.
- (42) Lee, S. J.; Kim, S.-B.; Kim, J.; Kwon, G.; Yoon, B.; Oh, H. Effects of harvesting method and growth stage on the flocculation of the green alga *Botryococcus braunii*. *Lett. Appl. Microbiol.* **1998**, *27*, 14–18.
- (43) Grima, E. M.; Belarbi, E.-H.; Acien Fernandez, F. G.; Robles Medina, A.; Chisti, Y. Recovery of microalgal biomass and metabolites: process options and economics. *Biotechnol. Adv.* **2003**, *20*, 491–515.
- (44) Divakaran, R.; Pillai, V. N. S. Flocculation of algae using chitosan. *J. Appl. Phycol.* **2002**, *14*, 419–422.
- (45) Lubian, L. M. Concentrating culture marine microalgae with chitosan. *Aquacult. Eng.* **1989**, *8*, 257–265.
- (46) Peter, M. G. Applications and environmental aspects of chitin and chitosan. *J. Macromol. Sci., Part A: Pure Appl. Chem.* 1995, 32 (4), 629–640.
- (47) Radakovits, R.; Jinkerson, R. E.; Darzins, A.; Posewitz, M. C. Genetic engineering of algae for enhanced biofuel production. *Eukaryotic Cell* **2010**, 9 (4), 486–501.
- (48) Cooney, M.; Young, G.; Nagle, N. Extraction of bio-oils from microalgae. Sep. Purif. Rev. 2009, 38, 291–325.
- (49) Mendes, R. L.; Fernandes, H. L.; Coelho, J. P.; Reis, E. C.; Cabral, J. M. S.; Novais, J. M.; Palavra, A. F. Supercritical CO₂ extraction of carotenoids and other lipids from *Chlorella vulgaris*. Food Chem. **1995**, 53, 99–103.

- (50) Smith, R.; Inomata, H.; Kanno, M.; Arai, K. Energy analysis of supercritical carbon dioxide extraction processes. *J. Supercrit. Fluids* **1999**, *15* (2), 145–156.
- (51) Del Valle, J. M.; Aguilera, J. M. An improved equation for predicting the solubility of vegetable oils in supercritical carbon dioxide. *Ind. Eng. Chem. Res.* **1988**, 27 (8), 1551–1553.
- (52) Liu, B.; Zhao, Z. K. Biodiesel production by direct methanolysis of oleaginous microbial biomass. *J. Chem. Technol. Biotechnol.* **2007**, 82, 775–780.
- (53) Patil, P. D.; Gude, V. G.; Mannarswamy, A.; Deng, S.; Cooke, P.; Munson-Mcgee, S.; Rhodes, I.; Lammers, P.; Nirmalakhandan, N. Optimization of direct conversion of wet algae to biodiesel under supercritical methanol conditions. *Bioresour. Technol.* **2011**, *102* (1), 118–122.
- (54) Soh, L.; Zimmerman, J. B., Biodiesel production: the potential of algal lipids extracted with supercritical carbon dioxide. *Green Chem.* **2011**; DOI: 10.1039/C1GC15068E.
- (55) Kiwjaroun, C.; Tubtimdee, C.; Piumsomboon, P. LCA studies comparing biodiesel synthesized by conventional and supercritical methanol methods. *J. Clean. Prod.* **2009**, *17*, 143–153.
- (56) Sialve, B.; Bernet, N.; Bernard, A. Anaerobic digestion of microalgae as a necessary step to make microalgal diesel sustainable. *Biotechnol. Adv.* **2009**, *27*, 409–416.
- (57) De Schamphelaire, L.; Verstraete, W. Revival of the biological sunlight-to-biogas energy conversion system. *Biotechnol. Bioeng.* **2009**, 103 (2), 296–304.
- (58) Angelidaki, I.; Sanders, W. Assessment of the anaerobic biodegradability of macropollutants. *Rev. Environ. Sci. Biotechnol.* **2004**, 3, 117–129.