# **Environmental** Science & lechnology

### **Environmental Performance of Algal Biofuel Technology Options**

Venkatesh Vasudevan,<sup>\*,†</sup> Russell W. Stratton,<sup>‡</sup> Matthew N. Pearlson,<sup>‡</sup> Gilbert R. Jersey,<sup>†</sup> Abraham G. Beyene,<sup>†</sup> Joseph C. Weissman,<sup>†</sup> Michele Rubino,<sup>§</sup> and James I. Hileman<sup>‡</sup>

<sup>†</sup>ExxonMobil Research and Engineering Company, Annandale, New Jersey 08801, United States

<sup>‡</sup>Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

<sup>§</sup>Synthetic Genomics, La Jolla, California 92037, United States

**S** Supporting Information

ABSTRACT: Considerable research and development is underway to produce fuels from microalgae, one of several options being explored for increasing transportation fuel supplies and mitigating greenhouse gas emissions (GHG). This work models life-cycle GHG and on-site freshwater consumption for algal biofuels over a wide technology space, spanning both near- and long-term options. The environmental performance of algal biofuel production can vary considerably and is influenced by engineering, biological, siting, and land-use considerations. We have examined these considerations for open pond systems, to identify variables that have a strong influence on GHG and freshwater consumption. We conclude that algal biofuels can yield GHG reductions relative to fossil and other biobased fuels with the use of appropriate technology options. Further, freshwater consumption for algal biofuels produced using saline pond systems can be comparable to that of petroleum-derived fuels.

#### INTRODUCTION

Algae have the potential to produce large volumes of fuel per unit area of production on marginal lands using saline water unsuitable for food crops.<sup>1</sup> Thus, algal biofuels could expand transportation energy supplies, without significantly displacing land and water resources that would otherwise have been used for food production. However, algal biofuel production is at an early stage of research and development (R&D) with many possible technology configurations.

Life-cycle assessment (LCA) has emerged as the preferred methodology to model the environmental performance of fuel production systems.<sup>2</sup> Several LCA studies on algae have recently been published in the peer-reviewed literature; see the Supporting Information (SI). The studies differ significantly in their assumptions and scope. These include differences in processing configuration, technologies used in the production facility, key parameters such as algal biomass productivity and oil content, the system boundary definition, the coproducts that are produced, the methodology used to value coproducts, and the end-product (i.e., the functional unit) being assessed. Not surprisingly, a consistent comparison of past work is challenging given the disparity that exists.

Because of the large design and technology space available for algal biofuel production, LCA has the opportunity to serve both as a process design and technology evaluation tool. The goal of this study is to understand how various technology



options affect life-cycle greenhouse gas emissions (GHG) and on-site freshwater consumption and to develop principles that can guide R&D to enable the production of algal biofuels with low GHG and freshwater consumption. Unlike past work, the present study attempts to capture the potential range for these environmental metrics for a wide technology space, spanning a broad range of options. Note that LCA can be used to investigate other environmental impacts not considered in this study, such as eutrophication and acidification.

Algae may be grown in open ponds or in closed reactors.<sup>1</sup> Our analysis framework is based on a small-scale open pond facility (400 ha total pond area) using brackish or saline water as the culture medium. The impact of individual technology options and production parameters has been systematically examined for three distinct oil recovery options: dry extraction, wet extraction, and secretion. These oil recovery options may be grouped into two broad classes: accumulation (or storage) and secretion. In the accumulation cases, oil accumulated and stored in the algal cells is extracted from biomass that is harvested from the growth ponds. The dry and wet extraction options fall in this class. In secretion, the microalgae secrete oils

Received:July 29, 2011Revised:November 16, 2011Accepted:January 10, 2012



**Figure 1.** Resource availability for algae growth in the continental United States. Average annual global horizontal solar insolation; annual average number of frost-free days (90% probability of temperatures >273 K), used as a surrogate for growing season length; location of coal power plants with generation capacity >250 MW. Brackish water availability not included due to limited literature data. A subset of the solar insolation data is shown with cross-hatching to help discern insolation values in regions where there is overlap with growing season data. Inset shows the intersection of growing season >6 months and solar insolation >4 kWh/m<sup>2</sup>/day with operating coal power plants >250 MW capacity. Thresholds represent coarse screening criteria and have been set to identify nominal site locations. Further details and data sources are available as Supporting Information (SI); see Section 2.

that are recovered from the ponds. In this analysis, process configurations and production parameters have been determined based on open literature data (e.g., refs 3 and 4; also see the SI) and the collective engineering judgment of the authors. GHG are considered on a pond-to-wheel basis, where emissions are compiled for each life-cycle stage, including algae growth and harvesting, algal oil recovery, transport, upgrading, finished fuel transport and distribution, and vehicle use. Although the quantitative results apply only to the production system modeled herein, the observed trends should be more broadly applicable.

It is important to note that none of the oil recovery processes described in this paper are currently practiced at the commercial scale with algae feedstock. In fact, some level of R&D is required for all of the oil recovery options to take them from concept development, through scale-up, to commercial production, with some of the options perhaps facing much greater technical challenges than others. As an example, consider the secretion model. While oil secretion has been demonstrated in the lab,<sup>5</sup> there are major hurdles that need to be overcome, and a subset of these are described in the DOE's National Algal Biofuels Technology Roadmap.<sup>6</sup> To quote the DOE roadmap, "pilot-scale experimentation and further metabolic engineering is required to evaluate the advantages and disadvantages of secretion". R&D needs include the development of cost-effective technologies to recover oil that exists in parts-per-million concentration levels in the ponds and approaches to prevent the bacterial degradation of the secreted oil. Like secretion, wet extraction approaches have primarily only been demonstrated at the lab-level and are at a nascent stage of development. Even for an oil recovery option like dry extraction, which incorporates established technologies used in other industries, additional development work is needed to

apply these technologies to algae feedstock and to scale-up the process to commercial-scale fuel production quantities.

For the purposes of the present analysis, we assume that the aforementioned barriers and challenges are overcome. We emphasize that the objective of this article is to evaluate the lifecycle environmental performance of a broad range of technology options being considered for algal biofuels production, and it is <u>not</u> to make judgment on the ultimate commercial viability of these technology options. Viability will clearly be governed by technical progress in the areas discussed above as well as a number of other factors including scale-up, cost, and systems integration.

#### GEOGRAPHICAL AND SITING CONSIDERATIONS

As geographical location can impact resource availability and the environmental performance of the facility, it is qualitatively examined using publicly available data on solar insolation, local climate, and CO<sub>2</sub> point-sources. These metrics are selected as preliminary screening criteria and should not be viewed as engineering decisions. Figure 1 shows that the US Gulf Coast can provide a convergence of conditions suitable for algae growth: modest solar insolation, a moderate growing season, and proximity to CO<sub>2</sub> and saline water from the ocean (see SI, Section 2 for additional details). A more detailed analysis of site selection would also account for temperature, land elevation, topography, existing land use, and water availability.<sup>3,7</sup>

#### ALGAL BIOFUEL PRODUCTION TECHNOLOGIES

This work examines how various technology options affect GHG and freshwater consumption for algal biofuels. Capturing the potential range for these environmental metrics is more appropriate than presenting single point results, given the



Figure 2. Water  $(m^3/day)$  and carbon (tonnes/day) flows in algal oil production for the nominal technology sets. Water consumption in individual process units not included. All flows specific to the 400 ha saline open pond-system modeled; steady state total dissolved solids (TDS) content of 40 parts per thousand (ppt); brackish makeup water with TDS of 20 ppt; evaporation rate of 0.5 cm/day; oil productivity ~2100 gallons/ac/year or 20 m<sup>3</sup>/ha/year.

breadth of available technology options. The understanding gained from exploring the technology space is used to formulate low-impact, nominal, and high-impact cases with optimistic, nominal, and pessimistic assumptions, respectively, regarding the process and system performance. This is done to establish bounds for the environmental impacts associated with the dry extraction, wet extraction, and secretion technology sets. The following discussion outlines the key elements within the algal biofuel life-cycle and the important assumptions made in this work. Additional details on the systems modeled and data sources used are available as SI; see Sections 3 and 4.

We assumed that the land used for the algae facility is degraded, thereby minimizing emissions from land use conversion.<sup>8</sup> Further, we assumed that the pond system is colocated with a coal power plant to provide a relatively high flue gas CO<sub>2</sub> concentration. An alternative would be to use flue gas with lower CO<sub>2</sub> concentration from a natural gas combined cycle power plant. Note that power plant proximity could be a constraining factor for larger-scale production. Both dilute and concentrated CO<sub>2</sub> feed streams are modeled. A monoethanol amine (MEA) scrubber is assumed for the concentrated  $CO_2$ feed stream option. While the coal-fired power plant is outside the boundary of the present analysis, energy and GHG burdens associated with the capture (when used), compression, and supply of  $CO_2$  to the algae facility is within the scope of the assessment. In addition to the CO<sub>2</sub> stream from the power plant (also called 'makeup'), there is a 'recycle' CO<sub>2</sub> feed stream to the ponds - the origin of this recycle stream is described in an ensuing section of the article.

This study exclusively considers algae grown in paddlewheelmixed, open raceway ponds. The inoculum required to seed the ponds is produced in closed photobioreactors at a separate facility. The energy and GHG implications of inoculum production are assumed to be sufficiently small to be ignored. The primary inputs needed for algae growth are water, nutrients,  $CO_2$ , and sunlight. Saline growth ponds are used, with brackish makeup water to compensate for evaporation and blowdown (water that is removed to maintain pond salinity). The use of fresh makeup water is also assessed. Nutrients supplied for algae growth include nitrogen, phosphorus, and iron. Energy and GHG burdens associated with the production and supply of nutrients, water, consumables (e.g., flocculants in harvesting), and energy (e.g., natural gas, electricity) are included in the analysis and are within the system boundary.

For the dry and wet extraction technology sets, thickening and dewatering systems are required to increase the biomass concentration in the harvested stream prior to the recovery of algal oil 'accumulated' in the biomass. Emphasis is given to mature technologies that are used commercially in other industries – dissolved air flotation (DAF) or clarifiers for primary harvesting and decanter or disc centrifuges for secondary harvesting. The algal biomass concentration in the growth ponds is assumed to be 0.02-0.05 wt %. The primary harvesting step concentrates the harvested biomass stream to 2-3 wt %, while the secondary harvesting stage produces 12-18 wt % solids. Primary and secondary harvesting, as defined herein, are also referred to as 'thickening' and 'dewatering', respectively, in the literature and are described elsewhere (e.g., ref 9).

In dry extraction, a belt drying system, modeled after commercially available sludge belt dryers, is used to dry the concentrated harvest stream. Algal oil in the form of triacylglycerides (TAGs) is then recovered from dried biomass using hexane. Wet extraction techniques, where the oil is recovered from wet biomass, are assessed using the limited information available in the literature. Many wet extraction methods have been proposed (e.g., ref 10) but, as noted previously, are at a nascent stage of development. Here, we consider a scheme where the culture is first lysed with steam, and oil is recovered from the aqueous biomass-oil broth via a series of centrifugation and wash cycles.  $^{10,11}\,$ 

In secretion, algae secrete oil to the ponds in the form of free fatty acids, which are recovered with a pond skimmer. We assumed that residual biomass is harvested from the ponds to maintain productivity and an optimal biomass concentration. The harvested stream is thickened and dewatered as described above for the two extraction (or 'accumulation') technology sets.

Once the algal oil has been recovered, well-established hydroprocessing techniques are used to upgrade the oil to paraffinic hydrocarbons. In the secretion model, the fuel product slate in the upgrader is modified to account for the processing of free fatty acids instead of triacylglycerides. Residual biomass (post-oil extraction) is sent to a two-stage anaerobic digester to produce biogas used on-site to generate heat and/or electricity (i.e., the biogas-fired electrical generator is within the boundary of the study). Heat, when produced, is completely consumed on-site, while electricity is preferentially utilized internally prior to being exported to displace average US grid power. Any CO2 generated via combustion is recycled for algae growth, reducing the amount of makeup CO<sub>2</sub> from the external power plant. The nutrient-rich digester effluent stream is returned to the ponds for algae growth. We have conservatively assumed that carbon in the digestate streams (effluent and sludge) is not reused and is converted to atmospheric CO<sub>2</sub>.

The water and carbon flows for the nominal technology sets are presented in Figure 2. While water consumed in individual unit processes is within the scope of the analysis, it is not shown in the figure. There is significant water recycle, especially immediately downstream of the pond-system, leading to large volumes of water being handled relative to the volume of algal oil produced. On a volume basis, more than 90% of the water in the harvested stream is recycled. Similarly, a significant fraction of the carbon initized in the algae is recovered from the residual biomass and reused for growth. The dry extraction technology set uses less makeup CO<sub>2</sub> from the power plant because the CO<sub>2</sub> from natural gas-combustion in the biomass drying system is recycled to the ponds. Carbon discharges or outflows from the system include the following: outgassing of  $CO_2$  from the ponds (a measure of how effectively carbon is fixed by the algae), carbon in the digestate (sludge and effluent) from the anaerobic digester, and losses associated with blowdown.

#### ENERGY BALANCE

In addition to GHG and freshwater consumption, we have calculated the energy inputs and outputs associated with algal biofuel production. Only fossil energy inputs are considered. For nominal dry extraction there is net energy input to the system, (i.e., more energy is consumed in producing algal oil than is available in the oil; see SI, Section 6). Greater than 75% of the total external energy input is from natural gas, associated primarily with the heat required for biomass drying. Conversely, the nominal wet extraction and secretion technology sets have a favorable energy balance. This is because the energy burdens associated with drying are avoided and electricity produced from biogas offsets a portion of the electricity burden associated with algae growth, flue gas distribution, harvesting, and oil recovery (see SI, Section 6). Energy consumption in the wet extraction step is primarily associated with the steam required to lyse the wet biomass; we



Figure 3. Pond-to-wheel GHG estimates for the nominal technology sets (left); parameter/scenario assessment for nominal dry extraction (right). Productivity and process technology assumptions for nominal dry extraction in Table 1. Petroleum diesel value from ref 2. Local sensitivity analysis deemed appropriate because GHG trends largely independent of parameter coupling. Other assumptions and results available as SI; see Sections 4 and 7.

have used estimates for steam consumption from ref 11 which contains a process flowsheet with detailed material and energy flows. In-house calculations using a simple process model suggest a higher steam demand for wet extraction ( $\sim$ 0.7 kg-steam/kg-algae) than reported externally.<sup>11</sup> Our preliminary estimate does not include heat integration and is hence conservative. However, it does provide an upper bound for the steam input for the process.

The energy inputs can be used to determine cumulative energy demand (CED) and net energy ratio (NER) values. CED is defined as the total fossil energy that is required at the source (primary energy) to produce a unit of energy for an enduse, (e.g., heat for drying, power to run paddlewheels, etc.). The CED values, estimated using GREET 1.8b,<sup>12</sup> are  $\sim$ 32 MJ/ kg-algae and ~3.7 MJ/kg-algae (~4.6 MJ/kg-algae with inhouse steam estimate) for the nominal dry and wet extraction technology sets, respectively (as a point of comparison, energy in algal diesel is ~9.2 MJ/kg-algae for these technology sets). The cumulative net energy ratio (NER) is defined as the energy in algal diesel divided by the cumulative energy demand. For nominal dry and wet extraction, the NERs are ~0.3 and ~2.5 ( $\sim$ 2 with in-house steam estimate), respectively. This shows that in the nominal wet extraction technology set, more energy is derived from the fuel product than is used in the production process, on a primary energy basis, whereas the opposite is true in the nominal dry extraction technology set. Note that these estimates do not include the energy expended in the manufacture of construction materials (e.g., pond liners). Also, these estimates are applicable only for the nominal technology cases - higher productivities and the use of more efficient harvesting technologies would lead to improved NER values.

#### POND-TO-WHEEL GREENHOUSE GAS EMISSIONS

The GHG performance of the nominal technology sets is presented in Figure 3. Changes in GHG due to the modification of selected process technologies and parameter values within the nominal <u>dry extraction</u> case are also shown. As discussed below, these sensitivities are used both to identify variables with a strong influence on GHG and to develop bounding low and high-impact cases for each of the three technology sets. The varied parameters and processes may be broadly categorized as productivity, siting and engineering, pond inputs (this term is used broadly and encompasses sensitivities that pertain to the feed streams to the ponds), harvesting process selection, and biomass disposition. The impact of a subset of these parameters and processes is shown in Figure 3.

Productivity related factors include total algae productivity and extractable algal oil fraction. Algal oil fraction has a significant impact on GHG because it linearly scales cultivation and harvesting emissions (Figure 3). Algae productivity, while important, has less influence than oil fraction on pond-to-wheel GHG. Increasing biomass productivity does increase steady state concentration of algae in the ponds (see Table 1). However, since energy debits in the production chain do not change appreciably with this parameter, (e.g., harvesting energy inputs typically scale with total throughput), the impact on GHG is smaller than the impact of oil fraction. Note that the sensitivities shown in Figure 3 for productivity represent distinct scenarios with different photosynthetic efficiencies.

Siting and engineering factors include transportation distances for makeup water and  $CO_2$ , pressure drop in pipelines on-site and to the facility, pond mixing efficiency, and construction materials. The coupling of increased pipeline pressure drop, a surrogate for pipeline diameter, and increased distance for makeup water is multiplicative; hence, as shown in Figure 3, the supply of makeup water can be as important to

## Table 1. Key Assumptions in Low-Impact, Nominal, and High-Impact Cases for Dry Extraction<sup>a</sup>

	low-impact	nominal	high-impact
Scenario Options			
makeup (from power plant) and recycle $\rm CO_2$	flue gas (with limited heat integration)	flue gas	pure
makeup water	municipal wastewater with nutrient value	brackish	brackish
nitrogen nutrient type	ammonia	U.S. average	ammonium nitrate
primary harvesting	clarifiers	dissolved air flotation	dissolved air flotation
secondary harvesting	disc centrifuge	decanter centrifuge	decanter centrifuge
digester sludge disposition	soil conditioner with fertilizer value	waste	waste
Parameter Options			
algae productivity (g/m²/ day)	32	20	15
extractable oil content (wt %)	60	25	15
steady state algae concentration in ponds (ppm)	475	300	225
pond mixing efficiency (%)	60	42	42
nutrient inputs (g/kg- algae)	÷1.5	N: 100, P: 12, Fe: 5	× 1.5

<sup>a</sup> In all cases: algae are grown in saline, paddlewheel mixed open raceway ponds; belt drying of biomass; residual biomass digested to biogas for conversion to heat and/or power; nutrient recycle efficiency fixed at 60% and nutrient utilization efficiency of 90% assumed. Brackish makeup water transport over 8 km, pressure drop in pipelines for liquids 0.5 bar/km. Pond operation fixed over productivity range. U.S. average means average nitrogen fertilizer mix used in the U.S. as defined in GREET.<sup>12</sup> Technology choices shown (e.g. disc vs. decanter centrifugation) do not represent engineering selections and are meant only to highlight potential impact on GHG and fossil energy consumption; economic and other factors not considered in this study will play a key role in process technology selection. Highest assumed oil productivity (~8100 gallons/acre/year or 75 m<sup>3</sup>/ha/year) lies within range expected to be practical in the future<sup>14</sup> and is contingent on optimization of cultivation and siting; chosen to be representative of a stretch R&D target. Nominal oil productivity (~2100 gallons/acre/year or 20 m<sup>3</sup>/ha/year) represents a reasonable near-to-mid term technology target,<sup>14</sup> while the lowest assumed oil productivity (~950 gallons/acre/year or 9 m<sup>3</sup>/ha/year) has been demonstrated in past work. The assumed oil productivity levels correspond to approximate photosynthetic efficiencies of ~1.8% (highimpact), ~2.5% (nominal), and ~4.7% (low-impact), for average solar insolation of  $\sim 22 \text{ MJ/m}^2/\text{day}$  (corresponds to the sunniest regions of the U.S. per ref 14). Others have reported theoretical photosynthetic efficiencies of ~10% [e.g. ref 3] though what can actually be realized will depend on the algal strain and the growth system used.

GHG as productivity and oil fraction. The impact can be even higher if makeup water is sourced from an underground aquifer, incurring additional pumping burdens. Pond mixing efficiency has a small effect on GHG for the nominal dry extraction system. The impact is small only because of the large contribution from the belt drying step. In the nominal wet extraction and secretion technology sets where drying is avoided, pond mixing can represent nearly 10% of the GHG because of the reduced nominal GHG values for these technologies. To be consistent with assumptions typically made in the assessment of fuel-vehicle pathways,<sup>2</sup> debits associated with the production of materials used on-site have not been included in our GHG results. However, the manufacture of high-density polyethylene pond liners (assumed life of 10 years) could result in emissions that are  $\sim 2\%$  of the pond-to-wheel GHG impact in the nominal dry extraction technology set and  $\sim 10\%$  in the nominal wet extraction and secretion technology sets (SI, Section 8). Note that the assumed colocation of the facility with a CO<sub>2</sub> source and the use of large ducts to move flue gas to the ponds resulted in small CO<sub>2</sub> transportation emissions in the nominal dry extraction technology set; however, this need not be true for other site selections.

Pond inputs encompass makeup water composition,  $CO_2$  concentration, nutrient requirements, and fertilizer type. Using pure  $CO_2$  as feed to the ponds requires flue gas scrubbing, an energy intensive process resulting in increased GHG; see Figure 3. If municipal wastewater is used as makeup, GHG would decrease due to its lower salinity (reduced pumping associated with blowdown/makeup) as well as reduced fertilizer requirements because of nutrients contained in the wastewater. Changing either nutrient inputs or fertilizer type causes a proportional change in GHG, dictated by GHG from fertilizer production.

For dry extraction, the harvesting configuration is an important technological lever. Primary harvesting is important for its direct energy consumption and secondary harvesting for its indirect impact on drying energy requirements. The use of clarifiers, instead of DAFs, for primary harvesting can yield a reduction in GHG (Figure 3). It is important to note that the reduction appears modest in Figure 3 because of the overwhelming contribution from drving in this technology set. However, when viewed independently as an absolute GHG reduction, the change is in fact quite significant ( $\sim$ 30 g-CO<sub>2</sub>eq/ MJ). Vendor data on centrifuge energy usage (in the secondary harvesting step) indicate a low sensitivity to the biomass content in the concentrated stream from the centrifuge. However, the drying energy requirement is inversely proportional to the biomass content exiting the secondary harvesting unit. Hence, using a disc centrifuge with a higher concentration of solids in the outflow than the nominal decanter centrifuge (18 vs 12 wt %) yields appreciable GHG reductions. Note that these data represent dewatering systems currently available for other applications and are not optimized for algae processing. Because the marginal change in GHG from increasing the extent of dewatering is larger than any other single process within the fuel production chain, dewatering technology is critical to the viability of algal biofuel production using dry extraction.

The systems analyzed herein intentionally minimize coproduct formation through internal recycle loops. The nominal configuration anaerobically digests the residual biomass, producing biogas that is entirely consumed on-site for heat. Using biogas for both heat and electricity via a combined heat and power (CHP) system would reduce GHG (Figure 3). All heat and electricity is internally consumed in the nominal dry extraction case, so there are no coproducts. To assess the impact of coproduct formation and valuation, we consider the sale of residual biomass as animal feed in just the sensitivity analysis. Here, we assumed system expansion to displace soybeans, based on protein equivalency.<sup>13</sup> Figure 3 shows that using the residual biomass as animal feed could result in reduced GHG. This is because the algal biofuel does not incur a debit for the biomass carbon leaving the system, and a credit is derived from avoided soybean cultivation. Therefore,



**Figure 4.** Pond-to-wheel GHG estimates for the low-impact, nominal, and high-impact algal diesel fuel technology sets. Well-to-wheel GHG estimates for palm hydrotreated renewable diesel (HRD) fuel, with and without direct LUC, and diesel fuel<sup>2</sup> included to enable comparisons. Contribution by stage shown in the inset charts. Asymmetry in GHG ranges due to underlying technology and parameter assumptions; see Table 1 and SI Section 7. Direct LUC for algal diesel is small (as degraded lands are assumed) and not shown; see SI Section 10. Wet extraction calculations assume steam requirements from ref 11. With higher steam requirements (see text and SI), pond-to-wheel GHG for wet extraction are higher: ~5, ~72, and ~416 g-CO<sub>2</sub> eq/MJ for the low-impact, nominal, and high-impact technology sets, respectively.

carbon accounting becomes particularly important when coproducts are not internally consumed.

The sensitivity assessments are used to develop bounding low and high-impact (GHG) cases for each of the technology sets considered. The important differences between the nominal technology sets and the bounding cases for  $\frac{dry}{extraction}$  are summarized in Table 1. A more detailed description of the underlying assumptions is available as SI; see Sections 4 and 7.

The previous discussion focused on dry extraction. The observations for the nominal wet extraction and secretion technology sets are similar with the notable exception that drying is eliminated. Therefore, the indirect influence of harvesting is limited to dry extraction.

Figure 4 presents GHG ranges for the nominal and bounding technology cases. The life-cycle stage-specific GHG contribution, presented in the insets, shows that for the nominal and high-impact cases, a significant fraction of GHG results from growth and harvesting (includes drying, and CO<sub>2</sub> and nutrient delivery), while oil extraction and upgrading are less significant. Makeup CO<sub>2</sub> that is fixed in the algae during growth, marked by the light green bars in the insets, is attributed as a credit to the algal biofuel. The other credit corresponds to on-site electricity generation from biogas. This electricity is fully consumed on-site in all cases except for the low-impact secretion and wet extraction technology sets where surplus power is exported to the grid. All carbon fixed in the algae is eventually released, either through discharges from the production system (carbon discharges in Figure 4) or as emissions to the atmosphere when the fuel product is combusted in a vehicle - fuel combustion emissions are the same for all technology cases. To be consistent with the conventional and palm diesel fuel estimates shown in Figure 4,<sup>2</sup>

vehicle efficiency has not been considered, and all fuel carbon is assumed to be converted to  $CO_2$  on a lower heating value basis.

Carbon discharges can represent a moderate fraction of pond-to-wheel GHG (light gray bars in Figure 4 insets). As mentioned previously, these are carbon outflows from the system  $-CO_2$  outgassing from the ponds, and carbon in the digestate (effluent and sludge) and blowdown streams. We conservatively assume that the carbon in the digestate and blowdown streams is converted to CO<sub>2</sub> and released to the atmosphere. These flows must be managed effectively and value derived from them where possible. For instance, in the nominal and high-impact cases, we conservatively treat the sludge from the anaerobic digester as waste, i.e. the sludge is disposed and no value or use is derived from it. However, as assumed in the low-impact cases (Table 1), the sludge could potentially be used as a soil conditioner (fertilizer) for its residual nutrient content, and a GHG credit (or offset) attributed to the algal biofuel for the incremental value that is then derived.

Solar drying has been proposed as a possible alternative to conventional drying systems to mitigate the drying burden in dry extraction. If we assume technical feasibility and favorable climate, solar drying could yield large GHG reductions. For example, in the nominal dry extraction technology set, our modeling indicates that if solar drying is used instead of belt drying, pond-to-wheel GHG are lower by ~77%. However, land requirements could increase, with an additional area of 5–10% of the pond area.<sup>15</sup>

As is evident from Figure 4, the carbon footprint of algal diesel fuel can vary considerably and is influenced by many factors. While algal biofuels can yield GHG reductions relative to the fossil baseline, this is only possible with appropriate process technology options. More importantly, a number of different biomass processing and oil recovery routes can



**Figure 5.** On-site freshwater consumption for algal diesel fuel using dry extraction versus other fuels.<sup>16–18</sup> Low, nominal, and high cases as defined in Table 1. Algae are grown in saline water with TDS of 40 ppt; brackish makeup water with TDS of 20 ppt. To enable comparisons, scenarios where culture is brackish (~20 ppt), with freshwater makeup ( $\leq 1$  ppt) to the ponds, are shown. Pond evaporation rate of 0.5 cm/day assumed. Pie charts show major on-site freshwater consumers. Other data assumptions available as SI; see Section 9.

provide GHG mitigation benefits. For instance, the low-impact dry extraction technology set has a carbon footprint that is almost 50% lower than the fossil baseline, despite requiring a significant amount of fossil energy to dry the biomass. Likewise, the nominal secretion and wet extraction technology sets have large GHG mitigation benefits versus conventional diesel fuel. On the other hand, GHG in the high-impact cases can be more than four times the fossil baseline, with the worst case being comparable to palm diesel fuel with direct land use change (LUC) from peatland rainforest conversion.<sup>2</sup> The large values in the high-impact cases are a consequence of several assumptions, including low algal oil yields, the need to capture CO<sub>2</sub> from a flue gas stream before being fed to the ponds, and high pressure drop in pipes used to move liquids to and in the facility. This emphasizes the importance of not only achieving productivity targets but also addressing other aspects of the system, such as process layout, process selection, engineering considerations, and siting.

#### ON-SITE FRESHWATER CONSUMPTION

In addition to GHG, we have estimated on-site (direct) freshwater consumption for the production of algal diesel fuel for a number of different configurations. Our analysis defines consumption as water removed from a source (e.g., aquifer) and not returned directly to that source. The results presented here-in are site and system specific and depend on the assumed pond salinity, evaporation rate, and processing configuration (see SI, Section 9).

Direct freshwater consumption for algal biofuel produced via dry extraction is compared with fossil fuels and other biofuel pathways<sup>16–18</sup> in Figure 5. Results are shown for the nominal and two bounding technology cases described previously. We anticipate similar ranges for secretion. There is greater uncertainty associated with freshwater use in wet extraction, and the results will depend on the extraction method used.

Direct freshwater consumption per unit volume of algal biofuel production is strongly affected by the oil yield. Higher oil yield is primarily responsible for lower consumptive freshwater use in the low-impact technology cases in Figure 5. The nature of the makeup water to the ponds has the largest impact on freshwater consumption. Freshwater makeup can increase consumption by over an order of magnitude versus brackish makeup and should be avoided. When makeup is brackish, algal biofuel freshwater consumption can be comparable to petroleum-derived fuels (e.g., nominal or low-impact cases with brackish makeup in Figure 5). As shown by the inset pie charts in Figure 5, for the brackish makeup cases,  $CO_2$  capture is an important contributor to freshwater consumption when included in the technology set. Using brackish water for all of the cooling loops could reduce freshwater consumption; however, cost trade-offs need to be assessed to check viability.

#### DISCUSSION

We have explored the impact of a wide parameter and technology space on GHG and on-site freshwater consumption for algal biofuel production by modeling various representative cases. Our analysis indicates that GHG for the nominal dry extraction technology set is significantly higher than the fossil baseline (Figure 4). This is a consequence of the large amount of primary fossil energy required to produce algal oil in this technology set; see SI Section 6. However, if stretch productivity targets are met and more effective and efficient dewatering technologies are used (or if a large fraction of the thermal energy input in drying is 'renewable' or ' waste' heat), this technology set can have a favorable energy balance and provide GHG mitigation benefits relative to petroleum-derived fuels.

If R&D hurdles for wet extraction are overcome, there exists potential for large reductions (>50%) in GHG with this technology option, see Figure 4. The energy balance can also be favorable, with more energy available in the algal oil than the primary fossil energy required to produce the oil (SI, Section 6). As is evident from Figure 4, GHG mitigation benefits could potentially be realized at lower oil productivity levels than in dry extraction. Similar GHG reductions can be enabled with secretion; however, as stated previously, the R&D challenges that need to be overcome may be significant. Our water

assessment indicates that algal biofuels produced in saline systems that use brackish makeup water to compensate for losses from the ponds can have freshwater consumption comparable to that of petroleum-derived fuels.

Issues pertaining to scale-up, systems integration, and economic cost, not considered in this study, need to be addressed, as the ultimate viability and sustainability of algal biofuels will also be governed by these factors.

#### ASSOCIATED CONTENT

#### Supporting Information

Figures S1-S6, Tables S1-S13, and text. This material is available free of charge via the Internet at http://pubs.acs.org.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: venkatesh.vasudevan@exxonmobil.com.

#### ACKNOWLEDGMENTS

The authors would like to thank John Farrell, Gary Casty, John Robbins, David Marler, Ari Patrinos, David Long, Ryan Couture, James Bielenberg, William Novak, Mike Raterman, Paul Roessler, and Malcolm Weiss for generously contributing their time and expertise to discuss, provide inputs to and review this work. This work was supported by internal Exxon Mobil research funds.

#### REFERENCES

(1) Wijffels, R. H.; Barbosa, M. J. An outlook on algal biofuels. Science 2010, 329, 796-799.

(2) Stratton, R. W.; Wong, H. M.; Hileman, J. I. Quantifying variability in life cycle greenhouse gas inventories of alternative middle distillate transportation fuels. Environ. Sci. Technol. 2011, 45, 4637-4644.

(3) Lundquist, T. J.; Woertz, I. C.; Quinn, N. W. T.; Benemann, J. R. A Realistic Technology and Engineering Assessment of Algae Biofuel Production; Energy Biosciences Institute, University of California: Berkeley, CA, 2010. http://www.ascension-publishing.com/BIZ/ Algae-EBI.pdf (accessed Dec 2010).

(4) Weissman, J. C.; Goebel, R. P. Design and Analysis of Microalgal Open Pond Systems for the Purpose of Producing Fuels; Tech. Rep. SERI/ STR-231-2840; Solar Energy Research Institute: Golden, CO, 1987.

(5) Roessler, P.; Chen, Y.; Liu, B.; Dodge, C. N. Secretion of fatty acids by photosynthetic microorganisms. WO 2009/076559 A1, 2009.

(6) National Algal Biofuels Technology Roadmap; U.S. Department of Energy: Washington, DC, 2010.

(7) Wigmosta, M. S.; Coleman, A. M.; Skaggs, R. J.; Huesemann, M. H.; Lane, L. J. National microalgae biofuel production potential and resource demand. Water Resour. Res. 2011, 47, W00H04 DOI: 10.1029/2010WR009966.

(8) Fargione, J.; Hill, J.; Tilman, D.; Polasky, S.; Hawthorne, P. Land clearing and the biofuel carbon debt. Science 2008, 319, 1235-1237. (9) Vesilind, P. A. Wastewater Treatment Plant Design; IWA Publishing: VA, 2003.

(10) Ruecker, C. M.; Adu-peasah, A. P.; Engelhardt, B. S.; Veeder, G. T. Solventless extraction process. U.S. Patent 7,351,558 B2, 2008.

(11) Vaswani, S. Biodiesel from Algae; Process Economics Program Review 2009-9; SRI Consulting: Menlo Park, CA, 2009.

(12) GREET Ver. 1.8b. http://www.transportation.anl.gov/ modeling simulation/GREET/ (accessed Sep 2008).

(13) Brune, D. E.; Lundquist, T. J.; Benemann, J. R. Microalgal biomass for greenhouse gas reductions: potential for replacement of fossil-fuels and animal feeds. J. Environ. Eng. 2009, 135, 1136-1144.

(14) Stephens, E.; et al. An economic and technical evaluation of microalgal biofuels. Nat. Biotechnol. 2010, 28, 126-128.

(15) Benemann, J. R.; Pedroni, P. M. Biofixation of fossil CO<sub>2</sub> by microalgae for greenhouse gas abatement. In Encyclopedia of Hydrocarbons Volume III; Amadei, C. et al., Eds.; ENI: 2008; pp 837-861.

(16) Energy Demands on Water Resources; Report to Congress; Department of Energy: Washington, DC, 2006.

(17) Wu, M.; Mintz, M.; Arora, S.; Wang, M. Consumptive Water Use in the Production of Ethanol and Petroleum Gasoline; Tech. Rep. ANL/ ESD-09-1; Argonne National Laboratory: Argonne, IL, 2009.

(18) Water Implications of Biofuels Production in the United States; National Research Council; National Academies Press: Washington, DC, 2008.

Article