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Research Article

Techno-economic Analysis and Life Cycle Assessment of an Integrated Wastewater-Derived Duckweed Biorefinery

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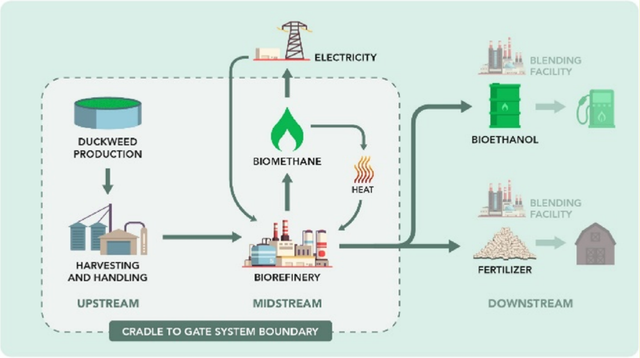
ABSTRACT: Duckweeds are efficient aquatic plants for wastewater treatment due to their high nutrient uptake capabilities, growth rates, and resilience to severe environmental conditions. The high starch and cellulose contents of duckweed species make them an attractive feedstock for biofuels and biochemicals. Experimental studies have shown that sequential anaerobic bioprocessing of duckweed into ethanol, carboxylates, methane, and soil amendment in a biorefinery system is technically feasible. This study aims to identify challenges and opportunities for large-scale wastewater-derived duckweed biorefineries as a way to promote a circular bioeconomy. The most suitable end products from wastewater-derived duckweed biomass, determined in a series of previously reported laboratory batch experiments, were used to estimate the bioproduct yields during the hypothetical operation of a large-scale biorefinery. Techno-economic analysis (TEA) revealed a minimum duckweed selling price of \$7.69 $\mathrm{Mg^{-1}}$ dry matter and a minimum ethanol selling price of \$2.17/L or \$8.23 $\mathrm{gal^{-1}}$. Duckweed pond construction and duckweed harvesting accounted for the largest share of capital (55.6%) and operating expenses (90.4%), respectively. A cradle-to-gate life cycle assessment (LCA) revealed that duckweed pond construction led to increased land use change impacts, but water-quality and eutrophication impacts could be significantly reduced with this integrated system through efficient nutrient upcycling.



KEYWORDS: *duckweed, biorefinery, wastewater upcycling, nutrient recovery, bioethanol*

INTRODUCTION

Lemnaceae (duckweed), a family of simple fast-growing floating aquatic plants, is a promising option for biofuel production and holds several advantages over other bioenergy feedstocks: (1) it can accumulate up to 43% of its biomass as easily degradable starch; (2) it does not require prime agricultural land for production; (3) its cell walls contain very little lignin and so do not require energetically or chemically intensive pretreatment prior to bioconversion into fuels and chemicals; (4) its small size (1 mm to 1 cm) and uniform structure greatly reduce the need for grinding or milling; (5) it can easily be harvested from the water surface (in contrast to microalgae); and (6) it can be grown using nutrients derived from wastewater and therefore can convert a common waste stream directly into a valuable resource.

Recent advancements in utilizing biowaste as feedstock for energy production have gained attention in the context of a circular bioeconomy. Wastewater-derived duckweed is considered an excellent biorefinery feedstock option due to its ability to upcycle nutrients to useful products.[1] The production of biofuels from duckweed has previously been studied for both thermochemical[2] and biochemical platforms[3,4] using a lignocellulosic biorefinery framework. However, Baliban et al. assumed that the duckweed was delivered to the refinery and did not incorporate wastewater treatment.[2] For the biochemical platform, prior studies demonstrated the technical feasibility and optimization of duckweed-based bioethanol production using laboratory- and pilot-scale enzymatic saccharification and fermentation experiments.[1,3−5] Our study compares the conventional ethanol biorefinery approach to a duckweed-based large-scale integrated value cascade biorefinery with multiple synergistic product streams.

Developing a commercial biorefinery of the scale needed to deliver a competitive product to end user markets requires a robust, reliable, and sustainable biofuel supply chain. For this reason, a variety of work has been conducted on biofuel supply chain networks, including the raw material (biomass)

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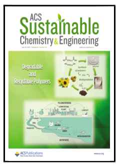

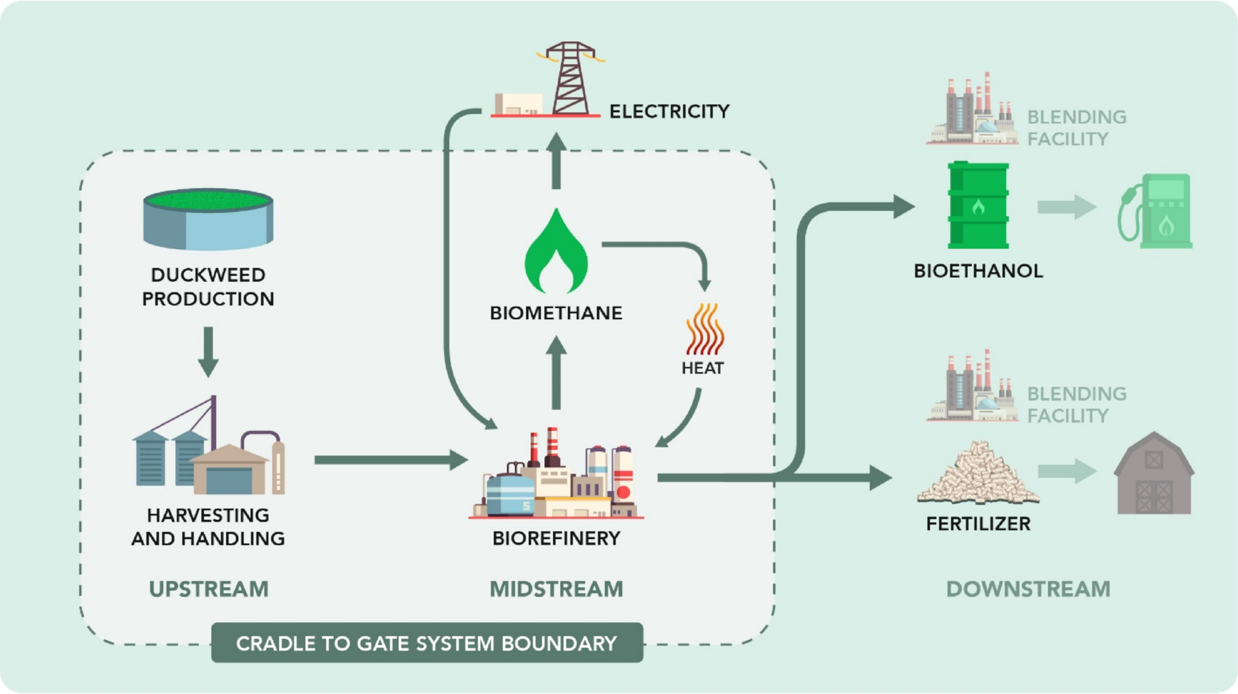

Figure 1. Cradle-to-gate system boundaries of the conceptual supply chain. Downstream processes are excluded.

production processes, storage facilities, biorefineries, blending stations, and end users.[6] In contrast to supply chains of industrial goods, which must adapt to the consumer demand, biorefineries represent a small fraction of very large energy markets and benefit from various regulatory incentives. In 2016, there were over 200 biorefineries in the United States (US) producing around 16 billion gal of ethanol per year, with the majority of them using corn as the primary feedstock.[7−9] Rather than being limited by the market demand, the size and capacity of conventional biorefineries are often restricted by the regional biomass supply and therefore require modeling strategies. Uncertainty in seasonal production of feedstock, extreme weather events, and spatial variability in feedstock availability disrupt the biorefinery supply chain. Therefore, alternative feedstocks like duckweed that can be produced locally with year-round supply are needed. Using such alternative feedstocks would also help meet the targets set by the Energy Independence and Security Act of 2007 (EISA), which states that by 2022, 21 billion gal of biofuel produced in the US must come from cellulosic or advanced biofuels derived from feedstocks other than cornstarch.[9] Feedstock supply constraints are however problematic for duckweed too due to both the cost of transport and the risk of spoilage. These challenges of scale require that the economic feasibility and commercial viability of duckweed-based bioenergy technologies be analyzed by considering the network as a whole. Co-benefits must also be considered to help compensate for the higher costs of smaller biorefineries, and in the case of duckweed, these co-benefits may include savings relative to conventional wastewater treatment. This study uses a holistic approach to evaluate the economic feasibility of the biomass supply when its production is coupled with wastewater treatment.

Coupling biofuel production with wastewater treatment may enhance the sustainability of the system as wastewater provides water and nutrient inputs to the process. It can also help reduce greenhouse gas (GHG) emissions and other land use change impacts associated with growing crops that are used as feedstock in conventional biorefineries.[7] Several studies have shown that life cycle impacts of microalgal biofuels are dominated by the cultivation phase if wastewater is not used.[10] Similarly, Murphy and Allen found that an uncoupled microalgal biodiesel system required seven times more energy for wastewater management than is produced from the resulting biodiesel product.[11] While these conclusions are from studies of biofuels derived from microalgae, they also likely apply to duckweed-based biofuels in that a stand-alone system may not be financially or environmentally viable. In this study, we perform both techno-economic analysis (TEA) and life cycle assessment (LCA) of an integrated wastewater treatment, duckweed production, and biorefinery supply chain. A combined TEA-LCA model evaluates the sustainability of the system in comparison to conventional wastewater treatment processes and petroleum refineries.

To inform the modeling framework and parameterize variables, experimental data from previous research and the literature were used to develop a supply chain framework for duckweed biorefineries under a large-scale production scenario. The goal of this TEA was to understand and compare spatial and temporal options for cultivation and harvesting of duckweed, as well as the biorefinery operations required to convert fresh duckweed into a value cascade of end products including ethanol, methane, and soil amendment. This TEA was coupled with LCA as a tool to analyze the environmental impacts and energy consumption of an integrated ecological wastewater treatment and biorefinery system.

■ METHODOLOGY

Model Components. In this study, the following three stages of the supply chain were considered (Figure 1): (1) feedstock production and harvesting, (2) feedstock handling,

Table 1. Expected Water Quality Change in Duckweed Ponds Treating Municipal Wastewater[a]

	influent concentration (mg L^{-1})	k at 20 °C (m day^{-1})	background concentration (mg L^{-1})	effluent concentration (mg L^{-1})	removal efficiency (%)
BOD	140	0.093	10	10	92.9
TSS	70	0.027	5	5	92.9
NH_4^+-N	25	0.049	0.1	0.1	99.6
TP	6	0.033	0.1	0.1	98.3
TN	35	0.06	3	3	91.4
Reference	Metcalf and Eddy[18]	Jørgensen[15]	Jørgensen[15]	Jørgensen[15]	

[a] Influent values listed are typical of effluent from conventional primary treatment, and background concentrations are set to match typical effluent characteristics of free water surface wetlands.

and (3) biorefinery processes. A standard cradle-to-gate system boundary was chosen to avoid the complexities arising from downstream end use processes that are typically affected by current market trends and consumer behavior.[12−14] This additionally helps one to compare duckweed production to commercial alternatives without overcomplicating the model with the logistics of final use. The design period of the integrated wastewater-derived duckweed production and biorefinery system was set at 30 years, and applies to all components of the supply chain. The feedstock production and harvesting component was used to determine the minimum biomass selling price (MBSP), which in turn was used to determine the minimum ethanol selling price (MESP) of the biorefinery component. Cost calculations were performed for a single scenario, with centralized wastewater treatment and biorefinery processes, converting fresh duckweed into ethanol, methane, and soil amendment. The study uses a modular design considering the duckweed pond and biorefinery as independent yet connected systems, with the output of one system (duckweed biomass) as the input to the other. Even though they are assumed to be located adjacent to each other in the present design, the modular framework was adopted such that it offers an option to add a transportation component if needed. Another reason to use this approach was that the pond is a public service, but the biorefinery can be a private entity, and this distinction results in different internal rates of return (IRRs) and interest rates that need to be accounted separately in the discounted cash flow analysis for the pond and the biorefinery. Design assumptions and details for each stage of the supply chain follow.

Feedstock Production and Harvesting. *Pond Design and Wastewater Treatment.* The duckweed production and wastewater treatment design utilized here consists of three 100 acre (47 ha) ponds. This pond design enables "decentralizing" the wastewater treatment system into three production plants and therefore separating the central biorefinery operations as an alternative scenario. For the dual functions of wastewater treatment and duckweed production, each pond was divided into 12 plug flow modules, each with 40,000 m^2 surface area and a length-to-width ratio of 20, as recommended for free water surface wetlands.[15] The depth of water was selected as 0.3 m as previously reported for duckweed ponds,[16] and the hydraulic retention time was set to 18 days to achieve effluent standards.[17] This design required a total flow rate of 23,500 m^3 day^{-1} (6.2 million gal/day, MGD) over the 36 modules. This flow rate is equivalent in scale to a conventional wastewater treatment plant for a population of 62,080, assuming that wastewater generation is the typical 378 L/day (or 100 gal/day (GPD)) per capita from residential communities.[18]

The treatment efficiency of the ponds was estimated using eq 1[15] for free water surface wetland kinetics. The influent wastewater quality was assumed to be equal to typical values[18] for primary effluents and, for the base scenario, to be constant throughout the year (Table 1). The required hydraulic retention time (18 days) was used to calculate the associated effluent concentrations and removal efficiencies of the wastewater components.

$$\ln\left[\left(\frac{C_e - C^*}{C_i - C^*}\right)\right] = \frac{k}{q} \tag{1}$$

In eq 1, C_e is the effluent target concentration (mg L^{-1}), C_i is the influent concentration (mg L^{-1}), C^* is the background concentration (mg L^{-1}), k is the first-order areal rate constant (m day^{-1}), and q is the hydraulic loading rate (m day^{-1}, $q = Q/A$, where Q is the daily flow in m^3 day^{-1} and A is the surface area of the wetland in m^2).

The background pond water quality was set to typical effluent characteristics of free water surface wetlands and the temperature was assumed as 20 °C for the decay coefficient, k (m day^{-1}). The annual treatment efficiency of the system for BOD was used to determine the substitution credits for an equivalent conventional wastewater treatment plant. Only BOD treatment was used to generate a conservative estimate of the substitution credits, thereby avoiding potential overestimation of the pond benefits. Duckweed was assumed to recover 60% of influent ammonium nitrogen (N) and phosphorus (P) and the rest was assumed to be removed by microbial activity.[19−22]

Duckweed Yield Model. Duckweed growth dynamics were simulated using Stella Architect (version 1.1.2), according to the intrinsic growth model developed by Lasfar et al., considering the mat density as a variable for the intrinsic growth rate (Figure S-1 and Box D-1, Supporting Information).[23] The mat density (a key variable that changes with frequent harvesting), N and P concentrations, temperature, and photoperiod were considered as variables in this model. The photoperiod was estimated using an existing model that relies on geographical coordinates and the calendar day to estimate day length (Box D-2, Supporting Information).[24] The city of Fort Myers, Florida, USA, was used as a location in the model because of the potential availability of urban wastewater and optimal weather conditions that promote year-round duckweed growth. Daily temperature data for the location was retrieved from the National Centers for Environmental Information database. The nutrient values used were the average of the influent and effluent of the ponds as N and P.

Harvesting. To achieve the highest biomass yield annually, the optimum harvesting frequency (once every 7 days) and the

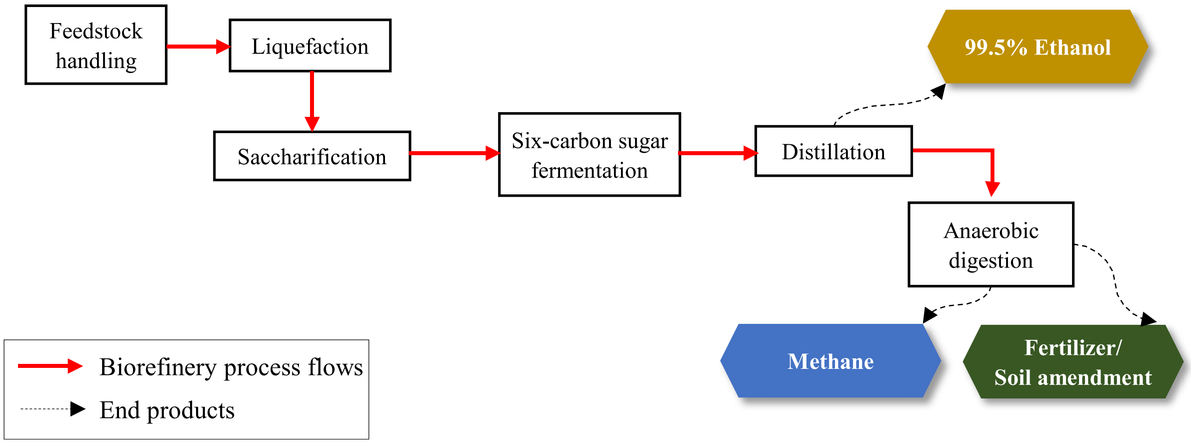

Figure 2. Potential biorefinery process scenario.

fraction of the duckweed mat (80% of the pond) were determined by incorporating a harvesting module (Figure S-1) into the duckweed growth model.[23] Harvesting was assumed to be performed using conventional machinery for aquatic weed harvesting. The harvester used in this simulation had the capacity to skim 7037 m^2 h^{-1}, which was calculated to require 4.5 h to complete the harvesting of a single pond unit or 1.7 units per 8 h work day. At a total number of 36 modules distributed between three ponds, the current design would require three machines to harvest all the ponds once per week. A quote for this equipment has been provided by Calicioglu.[25]

Duckweed Biorefinery Processes. The process flows for the production of ethanol, methane, and soil amendment from duckweed are shown schematically in Figure 2. Processing consists of feedstock handling, liquefaction, saccharification, fermentation, distillation, anaerobic digestion, and storage. Details for each of these processes follow. Wastewater treatment processes were excluded from the boundary, as the majority of the nutrients are valorized and no harsh chemicals are involved in the biorefining process. For some design specifications, such as energy requirements and residence times, values from the US Department of Energy's National Renewable Energy Laboratory Lignocellulosic Biomass Biorefinery 2011 Report[26] were used.

Plant Size. The overall quantity of duckweed (20.6 dry ton day^{-1}) processed by the biorefinery was determined by assuming that the biorefinery and duckweed production were coupled with the municipal wastewater treatment plant (WWTP). The biorefinery was assumed to be functioning for 350 days a year (97% uptime).

Feedstock Composition and Handling. The feedstock composition was assumed to be equivalent to the duckweed used in a prior experimental study.[1] In this scenario, the moisture content of the duckweed was assumed to be at its natural state of 92%, since the biorefinery was placed next to the WWTP to avoid the need for drying or trucking of biomass. The duckweed feedstock was assumed to be delivered directly after harvesting to a staging area in the biorefinery so that minimal storage and handling would normally be required. From this staging area, the feedstock is further conveyed to the liquefaction unit.

Liquefaction. In the liquefaction unit, the duckweed biomass is autoclaved for sterilization (121 °C, 30 min), then cooled down to 90 °C, and held for 2 h at atmospheric pressure after the addition of alpha amylase (0.3% of total solids) and a negligible amount of water.

Saccharification. In the saccharification unit, duckweed is loaded at 8.0 wt % total solids, and glucoamylase and cellulase are added simultaneously at 0.3% of the total solids at atmospheric temperature. The retention time in this unit was assumed to be 24 h. The temperature is held at 50 °C and pH is held at 5.2.

Fermentation. Fermentation takes place in batch reactors with a solids loading of 7.0 wt % with separate cultivation and addition of the yeast *Saccharomyces cerevisiae* at a loading of 1.6% of feedstock weight on a dry basis. To produce yeast, corn steep liquor and sorbitol were used in a seed reactor. The cellulose and starch components were converted into ethanol by six-carbon sugar utilizing *S. cerevisiae*. The theoretical yields of products observed by Calicioglu et al. were used consistently in this study, which reported the ethanol concentration in the fermentation reactor after 24 h. to be 8.7 ± 0.1 g L^{-1} or 186 ± 1.0 g ethanol per kg of total solids.[1] Fermentation losses due to contamination were neglected. The fermentation residence time in this study was assumed to be 48 h, in alignment with the NREL design. The temperature and pressure are kept at 32 °C and 1.0 atm, respectively. The resulting duckweed beer is then sent through the ethanol recovery train.

Distillation and Rectification. The duckweed beer is separated into ethanol, water, and residual solids by distillation and solid–liquid separation. Ethanol is distilled to a nearly azeotropic mixture with water and then purified to 99.5% using vapor-phase molecular sieve adsorption. Solids and other liquids recovered from the distillation bottoms are sent to the anaerobic digester.

Anaerobic Digestion. The total solids loading of the anaerobic digester is 5.0 wt %, with a retention time of 20 days under atmospheric pressure, 35 °C, and neutral pH. The methane-rich biogas from anaerobic digestion is sent to the combustor.

Soil Amendment Recovery. Since the duckweed moisture content in the base scenario was 92%, it was assumed that the digestate was directly applied to land as soil amendment in the vicinity of the biorefinery, and the costs from the solids recovery were excluded.

Storage. The storage area provides a location for chemicals used and produced in the process, including corn steep liquor (CSL), enzymes, sorbitol, caustic, hydrochloric acid, water, and ethanol.

Combustor, Boiler, and Turbogenerator. The biogas from anaerobic digestion is combusted to produce high-pressure steam for electricity production and process heat. In the original NREL design, 36% of the combustor/boiler and generator system was fed with biomethane, as that system also receives residual process solids and wastewater sludge, which are excluded in our case. This difference has been taken into account while down-sizing the unit.

Techno-economic Analysis (TEA). A spreadsheet-based model was developed to perform the TEA of the duckweed biomass supply chain for a biorefinery targeting ethanol, methane, and soil amendment as end products. The TEA reported here uses "*n*th-plant" economics. The key assumption implied by *n*th-plant economics is that our analysis does not describe a pioneer or "first of a kind" plant; instead, it assumes that several facilities using the same technology have already been built and are operating. Based on that experience, the expectations are that capital and operating costs have decreased and reliability has increased so that the system performs as designed. In contrast, a pioneer plant is likely to have major cost overruns and operational difficulties, which need to be factored into the deployment of new biorefinery technologies.

Duckweed Production and Harvesting. *Duckweed Production Capital Expenses.* In this study, the NREL report on process design and economics for algal biomass production[27] was used as the primary guide and design basis for pond design and techno-economic evaluation. As the design of the pond is similar to the 50 acre design case of the report, the scaling of the cost components was relatively straightforward. One major difference between the designs is that in the NREL model, pond construction included the installation of paddlewheels for mixing the algal ponds. This portion of the design was modified, as duckweed ponds do not require mixing. Instead, the gravitational flow of wastewater throughout the system was assumed. The breakdown of total direct and indirect expenses is given in the Supporting Information (Tables S-1 and S-2) and a summary is provided here in Table 2. Total indirect expenses were calculated as the percentage of total direct costs, with the factors provided in the NREL report. The working capital was assumed as 5% of the fixed operating cost, and the land value was assumed as \$3000 acre^{-1} for the calculation of total investment cost (Table 2).

Duckweed Production Operating Expenses. Since the duckweed production system was assumed to be passive (i.e., gravity-driven), the electricity demand was neglected. For the harvesting operations, the fuel requirements of the aquatic weed harvesters were taken into account. The associated variable operating costs are given in Table 3.

Labor salaries were also taken from the NREL report and the labor burden was applied at 90% as suggested. This labor covers items such as safety, general engineering, general plant maintenance, and payroll overhead (including benefits). The labor demand was down-scaled to meet the requirements of the current design. Property insurance and tax were assumed to be 0.7% of the fixed capital investment. The maintenance of the pond was assumed to require 0.5% of its capital cost annually, and the maintenance requirement of the harvesting machinery was assumed as 4% of its capital cost annually. Total fixed operating costs are presented in Table 3.

For the determination of by-product credit, the amount of BOD treatment achieved in the system was taken as the basis for the comparable cost for the construction and operation of activated sludge unit. The costs of WWTPs were estimated using approximations provided by Fraas and Munley,[29] and the deflator indices were used to estimate the construction and operating costs in 2018 as \$5.92 kg BOD^{-1} year^{-1} and \$0.85 kg BOD^{-1} year^{-1}, respectively. The contribution of activated sludge to WWTP construction (20%) and operation (50%) costs was taken into account, and the resulting construction and operation credits were considered as annual credits in our design. The associated wastewater treatment credits are provided in Table 4.

Table 2. Breakdown of Total Capital Expenses of a Duckweed Production/Wastewater Treatment System (Values Are in US Dollars)

component	value	unit	reference
total installed costs			
pond production			
civil (@ \$910,000/100 acre)	3,200,000	\$	Davis et al.[27]
liner RPP price (@ \$13/m^2)	267,000	\$	Beal et al.[28]
piping (@ \$70,000/100 acre)	244,000	\$	Davis et al.[27]
harvesting	540,000	\$	
total installed costs	4,222,000	\$	
additional direct cost for warehouse	1	% of pond construction	Beal et al.[28]
additional direct costs	48,000	\$	
total direct expenses:	4,270,000	\$	
field expenses	5	% total direct cost	Beal et al.[28]
home office and construction	8	% total direct cost	Beal et al.[28]
project contingency	10	% total direct cost	Beal et al.[28]
other costs	1	% total direct cost	Beal et al.[28]
total indirect expenses	1,170,000	\$	
fixed capital investment	5,340,000	\$	
working capital (@ 5% FCI)	265,000	\$	
land (\$3000/acre)	1,045,000	\$	Davis et al.[27]
total capital investment	6,619,000	\$	

Discounted Cash Flow Analysis. For this analysis, the discount rate, or IRR, was set to 10%, and the plant lifetime was set to 30 years. Consistent with NREL design assumptions, it was assumed that the plant would be 40% equity financed with a 10 year loan at 1% interest. The principal was taken out in stages over the 2 year construction period. Input data for the discounted cash flow rate of return analysis is provided in Table 5. Detailed discounted cash flow analysis is given in the Supporting Information (Table S-5).

Biorefinery Processes. For the biorefinery TEA, prices from the NREL 2011 lignocellulosic ethanol report were taken as a basis,[26] without application of cost year indices. This was done to enable a direct comparison of our results with those of the NREL report and to avoid transient price fluctuations due to the volatility of the ethanol market. The process described in the report uses co-current dilute acid pretreatment of lignocellulosic biomass (corn stover), followed by enzymatic hydrolysis (saccharification) of the remaining cellulose and fermentation of the resulting glucose and xylose to ethanol.

Table 3. Operating Expenses of the Wastewater Treatment/Duckweed Production System (Values Are in US Dollars)

variable operating costs			
pond			
electricity		neglected	
harvesting			
fuel requirement	8.0	h/day	
	2	L/h	
	5568	L/year	
	0.82	$ diesel/L	
	4600	$/year	
fixed operating costs			
pond maintenance	0.5	% of capital cost	Davis et al.[27]
	18,400	$/year	
harvesting			
maintenance	3	% of capital cost	
	16,200	$/year	
labor			Davis et al.[27]
manager	155,400	$/year	
technician	82,000	$/year	
technician	60,000	$/year	
module operator	81,000	$/year	
	378,000	$	
labor burden	90	%	
labor subtotal	719,000	$	
property insurance and tax	0.7	% FCI	
	37,000	$	
total fixed operating costs	795,000	$	

Table 4. Wastewater Treatment Credit Used for the Wastewater Treatment/Duckweed Production System (Values Are in US Dollars)

component	value	unit	reference
BOD removal per year	1,042,000	kg/year	
wastewater treatment construction cost	5.92	$/kg BOD/year	Fraas and Munley[29]
total construction substitution	6,173,000	$/year	
activated sludge portion	0.20	$/$ of WWTP	
construction credit	1,235,000	$/year	
wastewater treatment operation cost	0.85	$/kg BOD/year	Fraas and Munley[29]
total operation substitution	882,000	$/year	
activated sludge portion	0.50	$/$ of WWTP	
operation credit	441,000	$ year	

The process design also includes feedstock handling and storage, product purification, wastewater treatment, lignin combustion, product storage, and required utilities. Since the duckweed design is similar yet also has significant differences, modifications were made where necessary. For example, the duckweed liquefaction stage replaced NREL pretreatment, as our design produces ethanol from both starch and cellulose with the addition of alpha amylase but without pretreatment. The biomass processing capacity for the NREL design is about 100 times larger (2000 dry ton day^{-1}) than our duckweed biorefinery case (20.6 dry ton day^{-1}). The NREL design obtained a detailed quote for the biorefinery, totaling approximately \$20 MM for the whole system.

Table 5. Input Data for the Discounted Cash Flow Rate of Return Analysis of the Wastewater Treatment/Duckweed Production System

component	value	unit	reference
biomass production rate	7200	Mg/year	
BMSP	38.8	$/mg	
equity	40	%	Davis et al.[27]
interest rate	8	%	Davis et al.[27]
loan term	10	years	Davis et al.[27]
inflation rate	0	%	Davis et al.[27]
plant life	30	years	Davis et al.[27]
discount rate (IRR)	10	%	Davis et al.[27]
general plant depreciation	200	%	Davis et al.[27]
general plant recovery period	7	years	Davis et al.[27]
federal tax rate	35	%	Davis et al.[27]
construction period	2	years	modified
first-year expenditure	60	%	modified
second-year expenditure	40	%	modified
working capital	5	% FCI	Davis et al.[27]
start-up time	0.5	years	Davis et al.[27]
variable costs during start-up	75	%	Davis et al.[27]
fixed costs incurred during start-up	100	%	Davis et al.[27]
start-up yield	50	%	modified

Biorefinery Capital Expenses. A factored approach in which multipliers are applied to the purchased equipment cost was considered for the calculation of scaled, purchased, and installed costs, considering the quotes for the NREL biorefinery as a starting point. However, this is very likely an overestimation due to large differences in scale (up to 200 times in some units). Scaling factors were applied using eq 2. The total capital investment for the biorefinery along with a summary of direct and indirect expenses is provided in Table 6 and a detailed breakdown of these expenses is provided in the Supporting Information (Tables S-3 and S-4). A breakdown of the equipment costs is also provided in the Supporting Information (Table S-7).

Table 6. Total Capital Expenses for the Duckweed Biorefinery (Values Are in US Dollars)

component	value	unit	reference
storage and handling	1,964,000	$	
liquefaction totals	78,000	$	
saccharification and fermentation	810,000	$	
distillation and rectification	1,555,000	$	
anaerobic digestion	1,060,000	$	
storage	96,000		
boiler and turbogenerator	5,927,000	$	
total installed costs	11,490,000	$	
additional direct costs (18% of installed cost)	2,011,000	$	NREL[26]
total direct costs	13,501,000	$	
total indirect costs (@ 60% of total direct cost)	8,101,000	$	NREL[26]
fixed capital investment	21,602,000	$	
working capital (@ 5% FCI)	1,080,000	$	NREL[26]
land (@ 25 decreasing factor)	72,000	$	NREL[26]
total capital investment	22,754,000	$	

$$\text{new cost} = (\text{base cost})\left(\frac{\text{new size}}{\text{base size}}\right)^{n} \tag{2}$$

where n is a characteristic scaling exponent (typically in the range of 0.6 to 0.7).

Biorefinery Operating Expenses. The recommended number of employees in the NREL report (60) was scaled down to meet the requirements of the duckweed biorefinery (11). A labor burden of 90% was applied to the total salary. The labor cost breakdown is presented in the Supporting Information (Table S-8). The maintenance was assumed to take 3% of total installed costs, and the property insurance tax would cost 0.7% of the fixed capital investment. A summary breakdown of total fixed and variable operating costs is provided in Table 7.

Table 7. Fixed and Variable Operating Expenses of the Duckweed Biorefinery (Values Are in US Dollars)

component	value	unit	references
fixed operating costs			
labor	1,107,008	$	
maintenance	3	% total installed cost	NREL[26]
	345,000	$	
property insurance and tax	0.7	%	NREL[26]
	151,000	$	
total fixed operating costs	1,603,000	$	
variable operating costs			
feedstock cost	25.2	$/Mg	
excluding enzyme production	23,179	kW requirement	NREL[26]
scale	50		
	464	kW required	
	1.5	MW provided	
	−982	kW extra	
	−8.3	kW/year extra	
	−469,979	$/year credit	
chemicals	4900	$/year	
total variable operating costs	4900	$	
by-product credit	−470,000	$/year credit	

Variable operating costs include the feedstock, chemical, and energy requirements of the biorefinery. In the base scenario, the methane produced by anaerobic digestion was used to supply the energy requirements of the biorefinery processes. This energy requirement was assumed to be 2% of the NREL design case as a conservative estimate. However, the actual energy requirement of this system will likely be less than 2% of the NREL design, if mass and energy balances were to be performed. The by-product credits for additional electricity to the grid assumes 0.07 $/kWh credit, which is consistent with the NREL report. A chemical demand breakdown in biorefinery processes is provided in the Supporting Information (Table S-9).

Discounted Cash Flow Analysis. For this analysis, the IRR and loan interest were set to 2% and 1%, respectively, and the plant lifetime was set to 30 years. Other assumptions used for this analysis pertaining to equity and loan term were similar to that taken for the discounted cash flow analysis for feedstock production and harvesting. Details of the analysis are provided in the Supporting Information (Table S-6) and the input data used for the analysis is given in Table 8.

Table 8. Input Data for the Discounted Cash Flow Rate of Return Analysis of the Wastewater Treatment/Duckweed Production System

component	value	unit
feedstock cost	176,000	$/year
ethanol production rate	1662	L/year
equity	40	% interest
interest rate	8	%
loan term	10	years
inflation rate	0	%
plant life	30	years
discount rate (internal rate of return)	2	%
general plant depreciation	150	%
general plant recovery period	7	years
federal tax rate	35	%
construction period	2	years
first-year expenditure	60	%
second-year expenditure	40	%
working capital	5	% FCI
start-up time	0.5	years
variable costs during start-up	75	%
fixed costs incurred during start-up	100	%
start-up yield	50	%
by-product credit	577,000	$

Life Cycle Assessment (LCA). The LCA of the integrated duckweed production, wastewater treatment, and biorefinery system was conducted according to the standards set forth by the International Organization for Standardization (ISO) ISO 14040:2006 and ISO 14044:2006. Brightway2, an open source LCA framework, was used for LCA inventory modeling and calculations.[30]

Goal and Scope Definition. The goal of this LCA was to assess the environmental impacts associated with the life cycle of municipal wastewater-derived duckweed biorefineries, producing bioethanol, biomethane, and soil amendment over a 30 year design period. The system boundary was defined as cradle-to-gate, including the construction and operation of wetlands for duckweed production and excluding the biorefinery end product distribution.

Functional Unit. The functional unit was selected as one square meter (m^2) for duckweed production/wastewater treatment, in order to facilitate a comparison of the effects with agricultural feedstocks. All calculations were made for both wastewater treatment and biorefinery processes, taking the functional unit into account.

Life Cycle Inventory (LCI). The life cycle inventory (LCI) was performed for the following phases of the biorefinery supply chain: pond construction and operation; duckweed cultivation; biorefinery construction; fermentation; distillation; anaerobic digestion; and solids recovery for soil amendment. The end products (i.e., bioethanol, biomethane, and soil amendment) were assumed to substitute for gasoline, natural gas, and synthetic N fertilizer (liquid ammonia with a 1:1 substitution on a N basis), and the associated impacts with the production of commercial fuels and chemicals were credited to our system. The energy requirements for the biorefinery were calculated based on the NREL biorefinery model[26] using appropriate scaling factors for each process. Life cycle inventory materials for the biorefinery were taken from the ecoinvent database (v3.3 cutoff), with details provided in the Supporting Information (Table S-10).

Life Cycle Impact Assessment (LCIA). *Impact Categories.* The impact categories used in this study were as follows:

global warming potential (IPCC 2013, climate change, GWP 100a, in units of kg CO_2 equiv); eutrophication potential (ReCiPe Endpoint, freshwater eutrophication, in units of kg P); water depletion potential (ReCiPe Midpoint, water depletion, in units of m^3); human health impact (ReCiPe Endpoint, human health, total, in units of disability-adjusted life years (DALY)); and land use impact (ReCiPe Endpoint, natural land transformation, in units of m^2).

RESULTS AND DISCUSSION

Techno-economic Analysis (TEA) Results. *Duckweed Production and Harvesting.* The duckweed growth modeled using the three 100 ha ponds yielded a total biomass of 7200 Mg. A similar size agricultural land of 300 acres cultivated with *Miscanthus* grass would yield 3000 Mg biomass, assuming an average yield of 10 dry tons/acre.[31] Figure 3 shows the breakdown of the capital and operating expenses of the wastewater treatment/duckweed production system. It was found that the largest contributor of the duckweed cultivation capital expenses is the pond construction (55.6%), followed by the land cost (15.8%). Within the total lifetime of 30 years, the operational expenses are more significant compared to capital expenses (Tables 2 and 3).

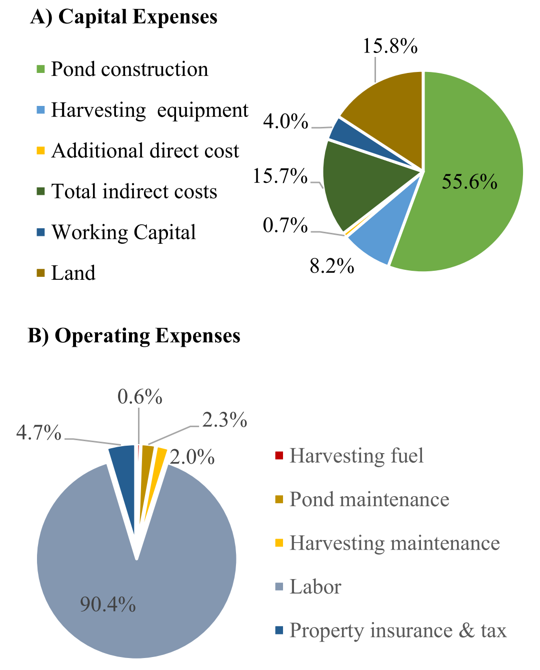

Figure 3. Breakdown summary of (the capital (A) and operating (B) expenses of a wastewater treatment/duckweed production system.

The duckweed pond functions to replace the conventional activated sludge-based secondary wastewater treatment. Discounted cash flow rate of return results for duckweed production alone revealed that a minimum duckweed biomass selling price of \$7.69 per dry Mg with a 10% IRR could be achieved if the activated sludge construction and operation are credited to the system (Figure 4). This assumption caused a major drop in the prices (Figure 5). The credits used here are in alignment with the assumed construction and operating costs of WWTPs provided in Table 4. Depending on the country or region considered and the corresponding variation in the assumed WWTP costs, these credits can vary. The minimum duckweed biomass selling price obtained in this study is lower than those of agricultural residues such as corn stover (\$40/Mg), wheat straw (\$55/Mg to \$75/Mg), and rice straw (\$15/Mg to \$35/Mg) and slightly higher than that of rice husk (\$6/Mg).[32−35] A sensitivity analysis carried out within a range of ±10% of parameter values revealed that the by-product credit is the most sensitive toward mean duckweed selling price, showing ±382% change in price relative to the base price of \$7.69/Mg, followed by IRR and labor cost (Figure 6).

Biorefinery Processes. Using the yields provided in the experimental studies of Calicioglu et al.,[1] a TEA of a hypothetical large-scale duckweed production/wastewater treatment and biorefinery system was performed. Over 30 years, the total expenses for the wastewater-derived duckweed biorefinery amounted to \$70,587,000 (Figure 7) present value, of which \$35,891,000 resulted from fixed operating costs and \$21,861,000 from fixed capital investment. With 2% IRR, \$1,412,000 was earned as profit, of which \$1,203,000 (85.2%) can be attributed to ethanol and the rest to the by-product (biogas converted to electricity) in proportion to the revenues they generated. Ethanol sales dominate the revenues for the biorefinery, and similar to the duckweed pond model, operating expenses are more significant as compared to the capital expenses for the biorefinery.

Modification and downscaling of National Renewable Energy Laboratory 2011 Report[26] on the lignocellulosic biorefinery to a daily processing capacity of 20.1 Mg dry weight of duckweed biomass revealed a minimum ethanol selling price (MESP) of \$2.17/L (\$8.23/U.S. gal) with a 2% IRR, which is a four times higher price than NREL findings for the ethanol biorefinery (Figure 8), and more than five times 2020 ethanol market prices. The MESP already accounts for the wastewater treatment credits from the duckweed pond

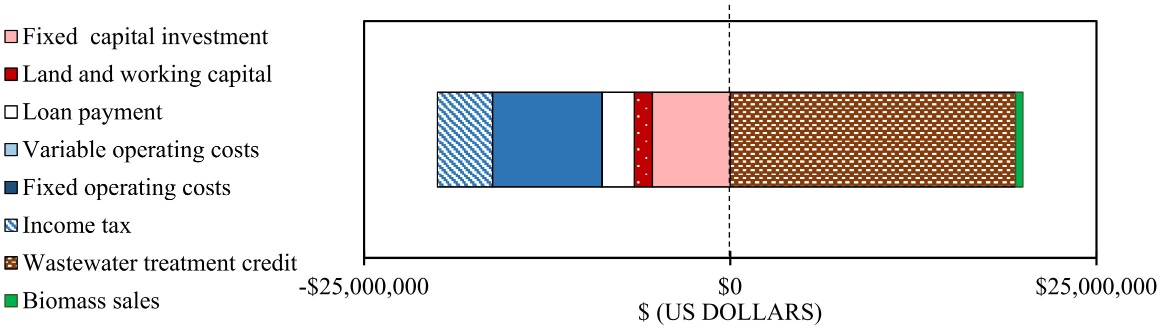

Figure 4. Breakdown of costs and revenues for the discounted cash flow analysis for a minimum biomass selling price of \$7.69/Mg.

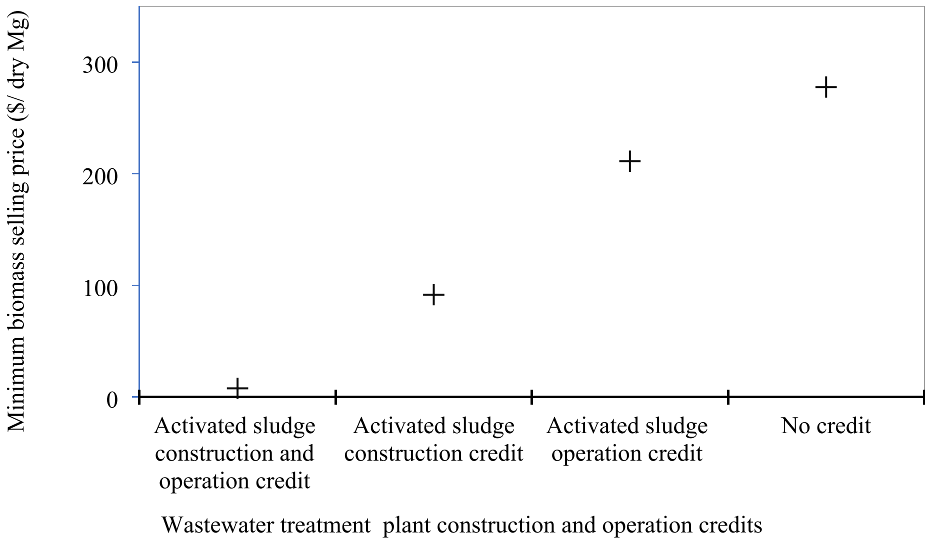

Figure 5. Minimum biomass selling price (MBSP) for different considerations of wastewater treatment credits. An MBSP of $7.69/Mg was obtained, considering the activated sludge construction and operation credit.

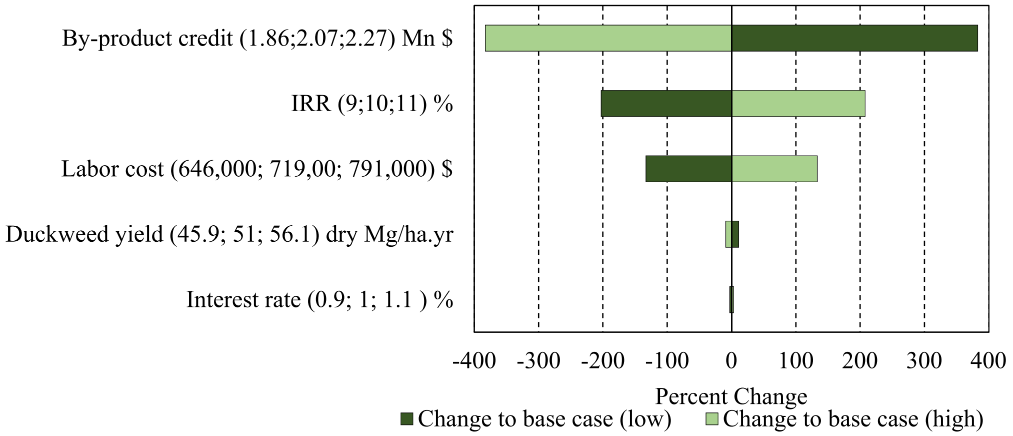

Figure 6. Sensitivity analysis of parameters (by-product credit, IRR, labor cost, duckweed yield, and interest rate) within a range of ±10%. The *x*-axis shows the percent change in MBSP of duckweed relative to the base case ($7.69/Mg). The *y*-axis values in parentheses show parameter values for low, base, and high cases.

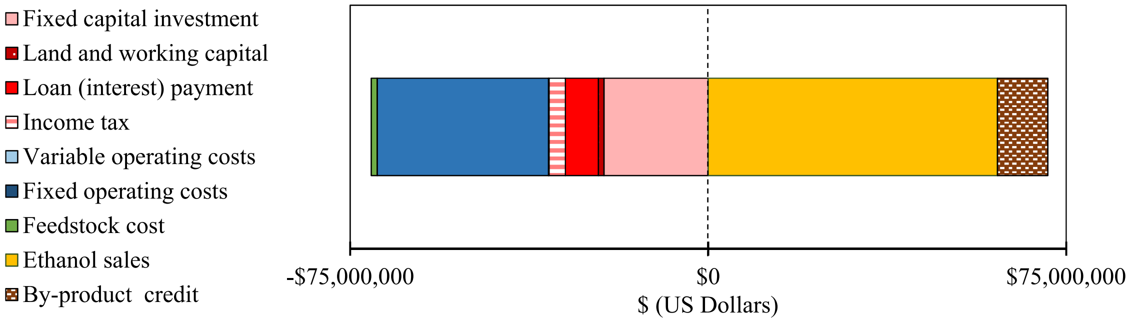

Figure 7. Breakdown of costs and revenues for the discounted cash flow analysis for a minimum duckweed ethanol selling price of $2.17/L.

analysis by using biomass selling price as an input to this biorefinery analysis. Figure 8 illustrates the minimum ethanol selling price versus plant capacity curve. This curve would have a higher slope if capital costs were the primary driver; however, for a duckweed production system and integrated biorefinery, labor is the primary cost, so fewer economies of scale are expected. The most sensitive parameter in the biorefinery TEA was ethanol yield, which resulted in up to 11% decrease in MESP for a 10% increase in the yield value (Figure 9). Total fixed operating costs and total direct costs follow ethanol yield in terms of sensitivity toward MESP.

This high price for duckweed ethanol may be due to an overestimation of costs associated with capital expenses and energy requirements during scale-down but may also indicate that much larger facilities are needed to achieve economies of scale with this configuration of technologies or even that

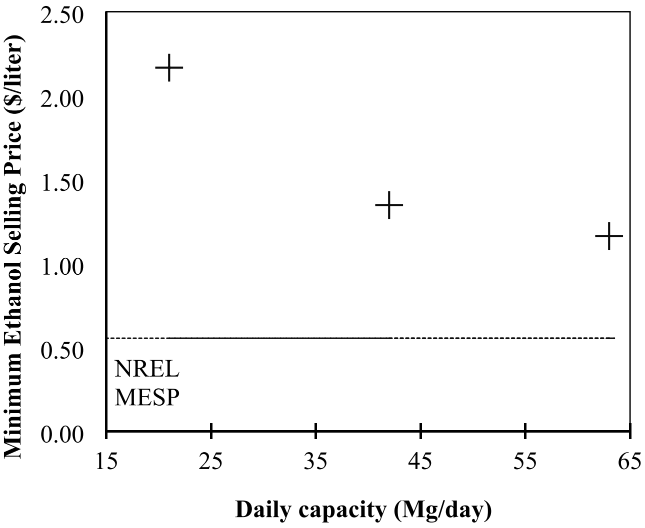

Figure 8. Minimum duckweed ethanol selling price at different daily processing capacities compared to NREL's minimum ethanol selling price.

marginal operating costs alone are too great to justify this approach. For the calculation of a more realistic minimum ethanol selling price, rigorous mass and energy balances and detailed labor and management analysis must be performed by designing the units independently, instead of scaling down an already existing NREL and ecoinvent dataset.

According to a prior experimental work conducted by Calicioglu et al.,[1] the bioprocessing sequence of ethanol fermentation followed by anaerobic digestion would have a low duckweed biomass to product yield. The total yield from ethanol and methane would account for 41% total carbon recovery. The biogas produced using this technique is utilized for generating part of the electricity required by the biorefinery and hence is not considered as a final product. As an alternative to having ethanol as the first stage of this value cascade, two-stage anaerobic digestion (i.e., where acidogenic digestion effluents are subjected to methanogenic digestion) could provide high biomethane conversion yields and the produced biogas could be converted to renewable natural gas.[1]

The left-over duckweed residue after anaerobic digestion can be dried and utilized as soil amendment to be applied in fields adjacent to the biorefinery. This practice is however assumed to be done free of cost and is not accounted for in the TEA presented here. Considering that the current cost of N fertilizers range from $200 to $500 per ton,[36] including the cost of soil amendment substitution would further strengthen the cost benefits of a duckweed-based wastewater treatment/biorefinery system. Nevertheless, to improve the overall economic feasibility of the system, higher value products such as proteins could be targeted upstream of ethanol production. For example, one more end product, mixed carboxylic acids, could be added to the value cascade grid of the biorefinery and should be included in the assessment as another scenario.

Life Cycle Assessment (LCA) Results. Figure 10 shows the contribution of life cycle phases of wastewater-derived duckweed biorefinery supply chain to environmental impact categories when duckweed is grown in land-based ponds in Fort Myers, FL, USA. The net impact on global warming potential, freshwater eutrophication potential, water depletion potential, human health, and land use were estimated as 49 kg CO_2 equiv, −0.11 kg P, 0.13 m^3, 0.67 DALY, and 1.59 m^2, respectively. These correspond to impacts from treating 180 m^3 of wastewater per m^2 and producing approximately 0.15 ton of duckweed over the span of 30 years, assuming a duckweed production rate of 51 Mg ha^{-1} $year^{-1}$. This converts to 0.27 kg CO_2 equiv GHG emissions per m^3 (or 271 kg CO_2 equiv per million liters (ML)) of wastewater treated. In comparison, GHG emissions per m^3 of wastewater treated in a microalgae-based biorefinery and in a conventional wastewater treatment plant were found to be 0.28 kg CO_2 equiv and 0.30−0.47 kg CO_2 equiv, respectively.[37−39] A breakdown of each life cycle phase's contribution to different impact categories in absolute

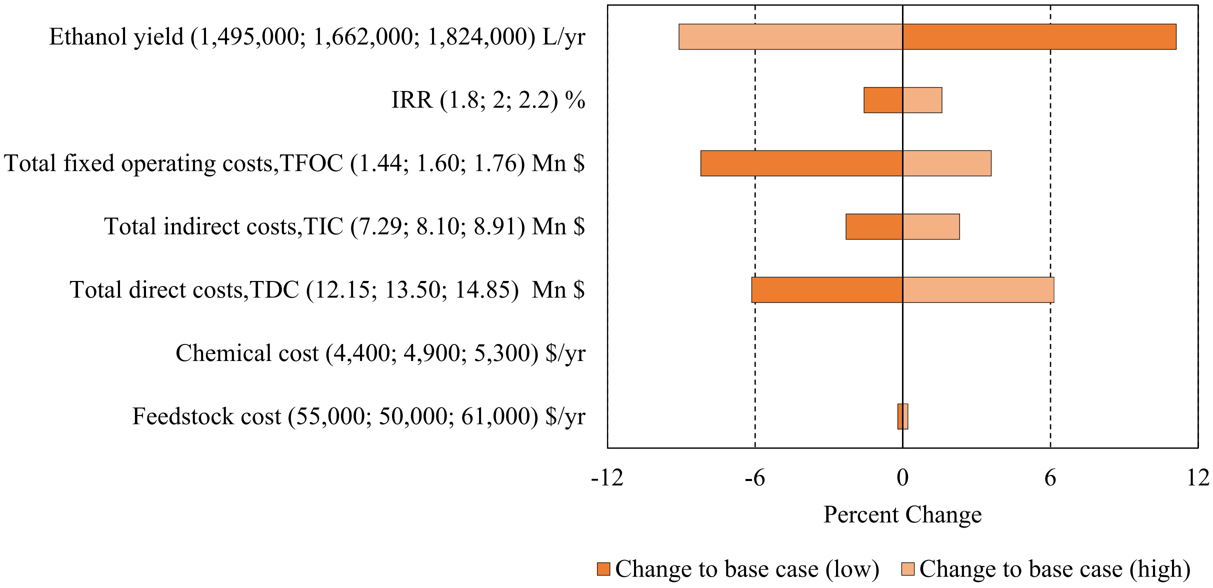

Figure 9. Sensitivity analysis of parameters (ethanol yield, IRR, TFOC, TIC, TDC, and chemical and feedstock costs) within a range of ±10%. The *x*-axis shows the percent change in MESP relative to the base case ($2.17/L). The *y*-axis values in parentheses show parameter values for low, base, and high cases. All values in US dollars.

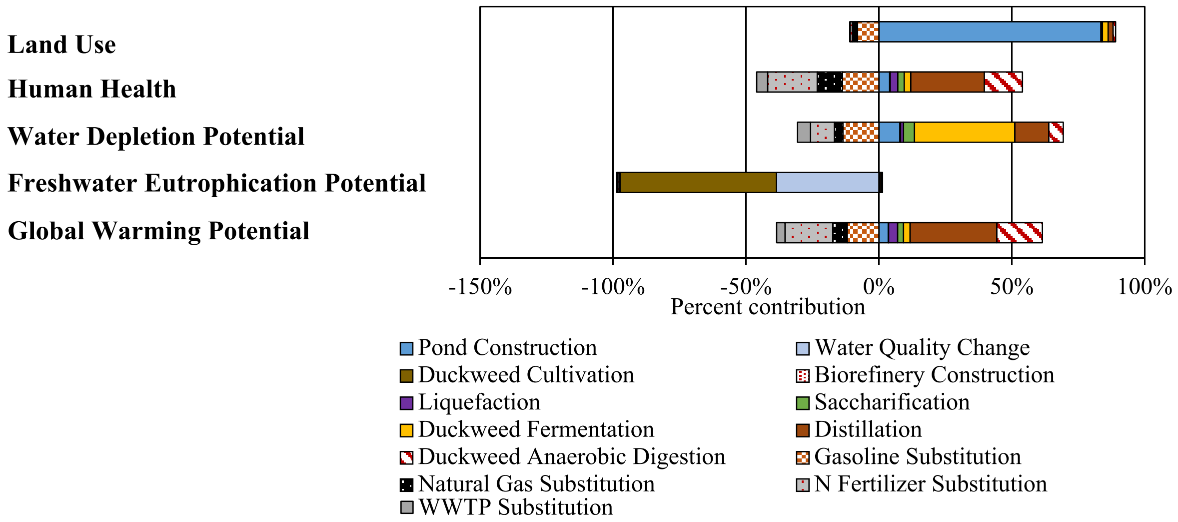

Figure 10. Contribution of life cycle phases of the wastewater-derived duckweed biorefinery supply chain to environmental impact categories when duckweed is grown in land-based ponds in Florida, USA.

Table 9. Impact Reduction from Substituting Gasoline, Natural Gas, N Fertilizer, and WWTP with Duckweed Biorefinery Products

	impact category				
substituted product	global warming potential (kg CO_2 equiv)	freshwater eutrophication potential (g P)	water depletion potential (m^3)	human health (DALY)	land use (m^2)
gasoline	−25.27	−0.32	−0.05	−1.14	−0.16
natural gas	−11.45	−0.18	−0.01	−0.79	−0.04
N fertilizer	−37.97	−0.69	−0.03	−1.56	−0.02
WWTP	−6.70	−0.28	−0.02	−0.34	0.00

values is provided in the Supporting Information (Table S-11). A strong net benefit was observed on freshwater eutrophication potential due to the recovery of nutrients from wastewater into duckweed biomass. N and P are typically not removed by the conventional activated sludge process, but by substituting it with duckweed-based treatment, nutrient uptake in the pond provides extra benefit in the form of reduced eutrophication compared to conventional systems. The net high reduction in eutrophication potential (95%) is achieved by considering the impact of water quality change but without accounting for nutrient removal benefits of conventional tertiary treatment processes. When the impact of water quality change (a decrease of 0.044 kg P) is ignored and only the benefits of N and P uptake through duckweed cultivation are considered, a 56% reduction in eutrophication potential would still be achieved.

The impact of substituting WWTP, natural gas, gasoline, and synthetic N fertilizer with the products generated from the proposed duckweed biorefinery is accounted in the LCA. The highest benefits are achieved by gasoline and N fertilizer substitution, which helps reduce global warming potential by 25 kg CO_2 equiv and 38 kg CO_2 equiv, respectively, and human health damage by 1.1 DALY and 1.5 DALY, respectively (Table 9). Gasoline substitution further decreases water depletion potential by 0.05 m^3. Per ton of duckweed produced, this LCA estimated a reduction of 165 kg CO_2 equiv and 248 kg CO_2 equiv with gasoline and N fertilizer substitution, respectively. In a different study conducted in Thailand using rice straw, substituting gasoline with rice straw bioethanol and chemical fertilizer with rice straw fertilizer yielded reduction values of 474 kg CO_2 equiv and 72 kg CO_2 equiv per ton of dry rice straw, respectively.[40] The same study reported a total reduction in eutrophication potential of 0.4 kg PO_4^{3-} equiv per ton of dry rice straw used as fertilizer, while our study yielded a reduction of 0.72 kg P in eutrophication potential (Figure 10). Overall, the environmental impacts of a duckweed biorefinery appear to be more harmful than those of the substituted products. The environmental impacts of duckweed biorefinery products relative to substituted products (i.e., gasoline, natural gas, and chemical fertilizers) could depend on the biorefinery size: the larger the biorefinery, the smaller the detrimental environmental impacts.

At the scale analyzed, the highest contribution to harmful environmental impacts in the land use category was associated with the construction of the duckweed growth ponds. However, since duckweed ponds can be constructed on lands otherwise unsuitable for farming, it avoids significant competition for arable land unlike traditional land-grown crops. Additionally, the ponds could have useful ecological functions and positive impacts on biodiversity, but this was not included in the LCA. Since the pond construction impacts were estimated using a dataset for aerated lagoons, the wastewater treatment phase requires further analysis for a more realistic result. In addition, vertical farming of duckweed could be used to minimize land use. The largest detrimental human health impact originated from the distillation unit due to the volatile organic compound losses during the process. The duckweed fermentation unit revealed the highest impacts on water depletion potential due to the water demand associated with the production of yeast.

Limitations. Dynamic modeling was used to determine potential duckweed yields when the system is coupled with wastewater treatment. This study assumed constant N uptake as a percent of N available in the ponds, rather than considering the actual kinetics of N uptake. The implications of harvesting (i.e., the absence of coverage on the surface of the ponds) on N availability and treatment efficiency were beyond the scope of this study. Therefore, a better N balance can be performed in parallel with further experimental work to validate the assumptions of the model. Similarly, a more comprehensive mass balance for BOD removal would be useful in determining wastewater treatment efficiencies and, in turn, wastewater treatment credits associated with the integrated wastewater treatment-duckweed production design. In addition, a detailed analysis of the BOD removal mechanisms would provide insight into the potential for methane emissions from the ponds caused by lowered rates of oxygen penetration in the presence of duckweed (due to lowered diffusion potential and the absence of light for algal growth). Determination of methane loss potential is particularly important for a comprehensive evaluation of the system's impact on climate change.

Designing shallow ponds would enable better diffusion efficiency and may avoid anaerobic conditions resulting in methane release. In addition, shallow ponds in a vertical farming setting could increase the area available for duckweed production and could reduce the need for the utilization of primary wastewater effluents, as growing on secondary treatment effluents could be a viable option in that case even with slower yields. In pilot-scale studies, duckweed growth was similar on different strength wastewaters,[41] so the true biomass yields may actually be similar in primary or secondary effluents at the full scale. Growing duckweed on secondary treatment effluents would decrease the uncertainty about BOD treatment efficiency, and avoid the risks of methane emissions. However, eliminating the process of treating primary effluents using duckweed would decrease the wastewater treatment credits as estimated in this study, since only a smaller portion of BOD removal will be achieved in the secondary effluent. Yet, if duckweed efficiently removes nutrients below strict nutrient limits (e.g., <3 mg/L TN and <0.1 mg/L TP in the Chesapeake Bay area), the credits can be still significant since such low nutrient limits require costly treatment technologies. However, such a design receiving secondary effluents in shallow trays needs additional experimental evidence for validation.

When the biorefinery capacity for ethanol production is coupled with wastewater treatment, the scale was found to be too small compared to estimates of the economies of scale needed for commercial lignocellulosic biorefineries. Such a large scale-down from the base NREL design scale (about 1:100) is likely to introduce errors; mass and energy balances at the original scale of the design could reveal more realistic economic performance of the system. While designing the duckweed system, the process configurations could be selected differently for the specific units, compared to conventional methods. For example, the VFA production results by Calicioglu et al. suggest that a batch fermentation system may have advantages over a continuous system, unlike the conventional acidogenic digestion processes.[42] In the near future, carbon dioxide credits for capture and utilization, or geological storage of that CO_2, could improve the economics of this particular scenario.

This study was the first to evaluate the environmental performance of duckweed production on wastewater and its conversion into valuable fuels and chemicals in a biorefinery concept. This analysis revealed beneficial impacts on eutrophication mitigation; however, its high detrimental impact on land use when grown in ponds suggests that vertical farming options should be investigated, especially for urban areas. Depending on whether the duckweed pond is constructed in a rural or urban area, the capital and operating expenses of the biorefinery would also change, taking into account constraints on land price and availability and differences in incoming wastewater concentrations. The water quality change coming from the duckweed-based wastewater treatment and resulting reduction in eutrophication should be interpreted with caution since the system boundaries used in this study do not consider conventional tertiary treatment processes. It was assumed that the duckweed ponds would be lined with a reinforced polypropylene (RPP) membrane, which brought additional detrimental environmental impacts. Depending on the underlying geology and distance to groundwater, these plastic liners might not be necessary and could be excluded from the design, which would partially improve the environmental impacts of pond construction. In the biorefinery, the distillation process was found to have high environmental "costs". High-solids fermentation might improve the outcomes but might require dewatering and drying of duckweed to obtain higher solids content, which could bring additional environmental burdens in terms of energy consumption. Duckweed dewatering with equipment such as belt filter press could however pose a less energy-intensive scenario compared to ethanol dewatering, but additional LCA studies are needed to corroborate this hypothesis. A sensitivity analysis on duckweed moisture reduction and high solids fermentation would be necessary to understand the relationship between solids content and associated environmental impacts.

Apart from the proposed options to improve the economics and environmental performance of the current design as mentioned above, other scenarios should be evaluated for integrated wastewater treatment/duckweed production pathways. For example, similar to the approach of the experimental work as detailed by Calicioglu et al., individual and sequential processes targeting one or more end products must be simulated for a more comprehensive TEA and LCA.[1] Such an approach could reveal interesting outcomes if the fuel and chemical production trains are excluded, and the duckweed is instead utilized as a high protein feedstock only. In that case however, the system might not be suitable for coupling with municipal wastewater treatment due to social acceptance. In such a scenario, the wastewater might need substitution (with fertilizers or at least a more homogeneous waste stream as opposed to municipal wastewater) for the growth of duckweed, and its impacts on the system economics might be significant. Utilizing multiple feedstocks in biorefineries can lower the risks associated with supply fluctuations and make the system more profitable.[7,43] Therefore, scenarios assessing the potential of combining other feedstocks such as agricultural residues from surrounding areas should further be studied as an option to mitigate the high marginal costs associated with duckweed-based biorefineries. Additional sensitivity analyses for different duckweed production scenarios (pond vs vertical growth and wastewater vs fertilizer), conversion processes (producing one or more end products), and market prices (for the product portfolio under the different scenarios) are required.

■ CONCLUSIONS

Previous laboratory studies demonstrated that duckweed is a technically feasible alternative feedstock for the production of fuels and chemicals but did not address environmental impacts. Integrating duckweed production with wastewater treatment has positive impacts on eutrophication mitigation. However, pond construction brings significant burden in terms of land use, and this issue must be addressed by investigating vertical farming options as another production scenario. Offsets for gasoline, natural gas, and fertilizer substitution by biorefinery products, as well as wastewater treatment credits, can reduce the global warming potential of the system but not to zero. Downscaling an already existing biorefinery model for the estimation of the life cycle burden associated with the system at hand may not have been sufficient to properly assess these impacts at a much smaller scale. Therefore, an LCA inventory and analysis at a higher resolution are needed to develop a more realistic impact assessment of potential duckweed biorefinery processes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.1c02539.

> Stella model schematic diagram; duckweed growth model equation; day length model equation; expense breakdown of duckweed production/wastewater treatment system and biorefinery; aquatic weed harvester specifications; discounted cash flow analysis details; biorefinery equipment, labor, and chemical cost breakdown (PDF)

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Notes

The authors declare no competing financial interest.

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