

Life Cycle Impacts and Techno-economic Implications of Flash Hydrolysis in Algae Processing

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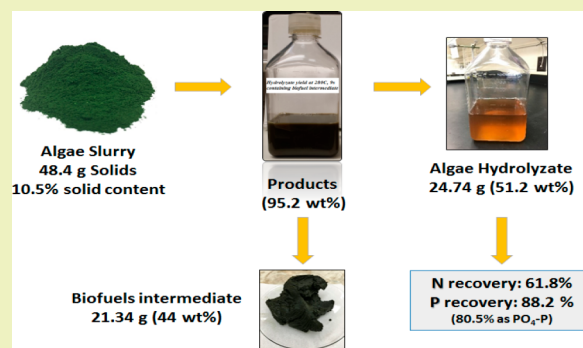
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Supporting Information

ABSTRACT: Generation of coproducts from nutrients is purported to improve the sustainability of algae-derived transportation fuels by minimizing life cycle impacts and improving economic sustainability. Although algae cultivation produces lipids that is upgraded to drop-in transportation fuel products, life cycle assessment and techno-economic analysis have shown that without coproducts, energy/economic returns are diminishing regardless of processing methods. This study utilizes a combined flash hydrolysis (FH), hydrothermal liquefaction (HTL), and coproduct conversion technology (atmospheric precipitation/AP; hydrothermal mineralization/HTM) to conserve the most recyclable nutrients for coproduct marketability. Six biofuel pathways were developed and compared in terms of “well-to-pump” energy, life cycle greenhouse gas (LC-GHG) emissions, and economic profitability: renewable diesel II (RDII), renewable gasoline (RG), and hydroprocessed renewable jet (HRJ) fuel, each were modeled for AP and HTM coproduct conversion. A functional unit of 1 MJ usable energy was employed. RG showed a promising energy-return-on-investment (EROI) due to multiple coproducts. All models demonstrated favorable EROI (EROI > 1). LC-GHG emissions tie in with EROI such that RG produced the least emissions. HRJ-HTM was determined to be the most profitable model with a profitability index (PI) of 0.75. Sensitivity analyses revealed that dewatering affects EROI and PI significantly. To achieve break-even, gasoline must sell at \$4.10/gal, diesel at \$5.64/gal, and jet fuel at \$3.43/gal.

KEYWORDS: Microalgae, Flash hydrolysis, Life cycle assessment, Techno-economic analysis, Hydrothermal liquefaction, Hydrothermal mineralization, Atmospheric precipitation



INTRODUCTION

There has been an abundance of research published over the past few years that show that microalgae have the potential to be a feedstock contender in biofuels technology. Microalgae has several properties that are purported by researchers to produce advanced biofuels with low overall production cost and better environmental performance.^{1,2} In the past, most biofuel production in the United States has been associated with corn ethanol and over time, other biofuel feedstocks such as microalgae have been studied. EISA requires that by the year 2022, 36 BGY of renewable fuels (20% of the U.S. consumption) must be produced annually.³ Feedstock for the renewable fuel must come from lignocellulosic biomass (oxygenated hydrocarbons), energy crops, and other biomass sources. Researchers and industry professionals are developing ways to increase the conversion efficiency of nonfood feedstocks such as forest residues, agricultural residues, and energy crops that are not used for food production.^{4,5} Currently, thermochemical conversion processes of nonfood biomass are still inefficient. Algae has the potential to fill the

gap that exists in our renewable fuels technology and to address critical LC-GHG requirements set forth by EISA. Water-based microalgae has several advantages over other lignocellulosic biomass. It has a rapid growth rate, grows well in wastewater effluent and saltwater streams,^{6,7} does not require arable land making it noncompetitive with food crops,⁸ and can utilize CO₂-rich flue gas emissions.⁹ Microalgae also contains a high proportion of lipids. This is important because lipid is the main component that will yield the bio-oil which is subsequently upgraded to liquid fuels suitable for use in ground and air transportation. Microalgae is typically between 20 and 50% lipid content.⁸

Recycling and recovery of nutrients during microalgae cultivation and processing is the motivation for numerous life cycle assessments (LCA) and techno-economic analyses (TEA) performed on microalgae.^{2,10–16} These studies seek to evaluate

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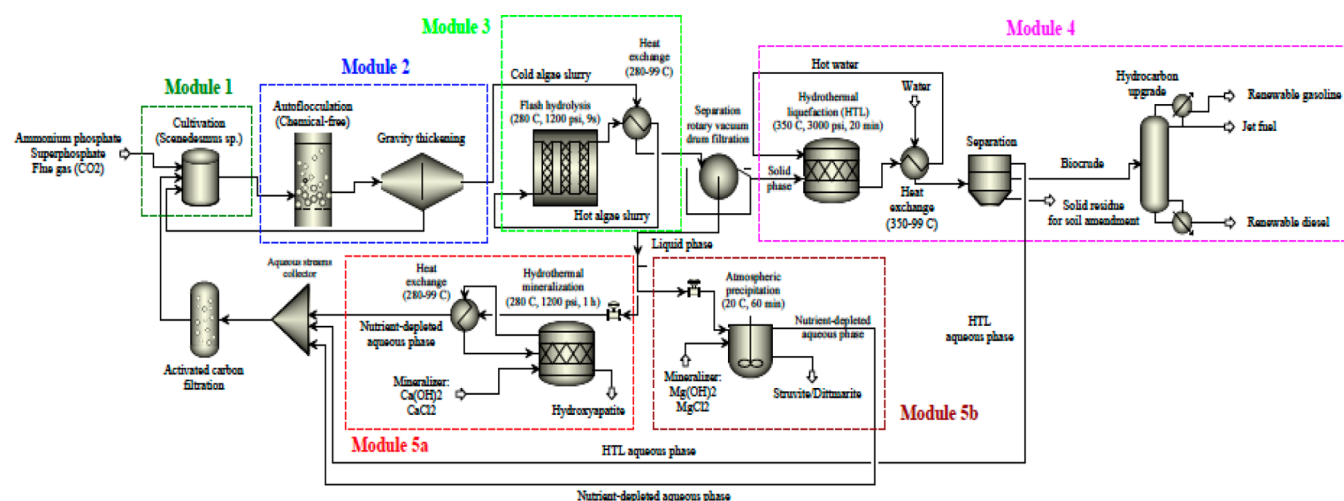


Figure 1. Overall schematic for the life cycle assessment (LCA) and techno-economic analysis (TEA) of renewable diesel II (RDII), renewable gasoline (RG), or hydroprocessed renewable jet (HRJ) fuel as modeled in Aspen Plus chemical process software.

algal biofuels sustainability. Most of these modeling efforts utilize some form of dewatering process to concentrate microalgae slurry and hydrothermal liquefaction (HTL) to convert wet microalgae slurry into biocrude. This work offers an alternative conversion pathway via flash hydrolysis (FH). It differs from traditional HTL in that it requires very short residence time (9 s) at 280 °C in a continuous flow reactor.^{20,21,23,24} FH partitions microalgae in an aqueous protein-rich peptides and arginine (low-value bioproducts) and a solid lipid-rich “biofuels” intermediates phase.¹⁷ The aqueous phase undergoes hydrothermal mineralization (HTM) or atmospheric precipitation (AP) because these processes recover/store the maximum macronutrients as valuable coproducts. The struvite and hydroxyapatite obtained from HTM and AP, respectively, offer more economic value as opposed to peptides and arginine, with an estimated market value of \$200/Mg for struvite and \$500/Mg for hydroxyapatite and because they are in a stable form with market demand. The solid phase is transferred to HTL via a rotary vacuum drum filter to produce biocrude. The nutrient demands for industrial-scale algae production are extremely large therefore it is critical that nutrients are incorporated into coproducts and/or recycled back into cultivation to minimize impacts on terrestrial food production.¹⁸ In addition, studies have shown that phosphorus, which is in limited supply, could be depleted in the 21st century.¹⁹ Biomass-based sources of renewable fuels such as microalgae are expected to exacerbate this situation.²⁰ Research conducted at Old Dominion University over the past several years^{17,21–27} has shown that the FH process has the potential to produce biocrude while preserving macronutrients as valuable coproducts. However, a comprehensive LCA or TEA has not been conducted to quantify environmental impacts and assess economic profitability.

It is imperative that assessments are made on the combined FH-HTL-HTM/FH-HTL-AP systems to determine if the energy-return-on-investment (EROI) and profitability are measurably beneficial. Though it is apparent that the HTM process requires more energy compared to AP because of the required hydrothermal conditions, it is still unknown by how much this increase in energy is if the overall “well-to-pump” production of drop-in transportation (ground and air) fuel is evaluated. We know that the production of hydroxyapatite via

HTM creates a more valuable coproduct when compared to the production of struvite/dittmarite via AP, but we do not know by how much this affects the overall TEA when assessed in combination with the drop-in fuel production and varying yields of coproduct generation.

The main objective of this study is to provide an overall LCA and TEA for the FH process in conjunction with HTM/AP using a “well-to-pump” system boundary. This study is the first of its kind to compare the production of three fuel products (renewable diesel II (RDII), renewable gasoline (RG), and hydroprocessed renewable jet fuel (HRJ)) using FH as the central thermochemical process in the production of intermediates, HTM/AP as coproduct generation processes in the recovery of macronutrients, and HTL as a method of producing biocrude, the raw material for drop-in transportation fuel. The results determined the environmental performance of FH/coproduct generation for drop-in renewable transportation fuels. Finally, this study evaluated how the combined FH-HTL-HTM/FH-HTL-AP processes compare to a standalone HTL.

METHODS

The LCA and TEA of FH with HTM/AP as coproduct generation pathway and HTL as biofuel production method was accomplished through the creation of six models which were subsequently compared with each other: (1) RDII-AP, (2) RDII-HTM, (3) RG-AP, (4) RG-HTM, (5) HRJ-AP, and (6) HRJ-HTM. The models were developed using Microsoft Excel and the Crystal Ball add-in suite. Impact factors for the LCA were obtained from either EcoInvent or Tool for the Reduction and Assessment of Chemical and other Environmental Impacts (TRACI) databases contained in SimaPro v8, a LCA modeling software; Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) database developed by Argonne National Laboratory;²⁸ and other open source LCA databases. The overall model scheme can be seen in Figure 1.

Cultivation/Biomass Preprocessing (Module 1/Module 2).

Algal biomass cultivation in Module 1 was modeled utilizing an open pond system and high-protein content *Scenedesmus* sp.,²⁹ which is important for macronutrient preservation and coproduct generation.²¹ The open pond system utilized ten paddle wheels per hectare at 10 rotations per minute (rpm),¹⁴ assuming an electrical demand of 0.0037 kW/paddle wheel.³⁰ The carbon dioxide requirement for the microalgae cultivation was supplied via flue gas at a 12.5% CO₂ concentration.³¹ Nitrogen and phosphorus nutrient requirements were assumed to be supplied by ammonium phosphate [(NH₄)₃PO₄] and by superphosphate [(CaPO₄)]. Preliminary dewatering of the algae

biomass in Module 2 is a two-step process that generates 20% algae biomass slurry for the FH continuous flow reactor. The first step is an autoflocculation (AF) process that increases the pH of the slurry to approximately 10.5 via the addition of phosphate (PO_4^-).³² The second step is gravity thickening (TH) settling process.³³

Flash Hydrolysis (Module 3). FH (Module 3) is a hydrothermal process that utilizes wet algae biomass in a continuous flow reactor and fractionates macromolecules into liquid and solid phases.^{17,21} The FH process utilizes water at subcritical conditions (280 °C; 1,200 psi) where water exhibits solvent like properties and quickly hydrolyzes algae biomass for 9 s in a continuous flow reactor. A 20% algae biomass slurry was assumed for the FH continuous flow reactor.³⁴ The fractionation at this short residence time preserves the proteins and soluble peptides into the liquid phase which can be used for nutrient recycle. FH is advantageous over an HTL system because the longer residence time of HTL^{35–37} causes the formation of unwanted tar, phenols, oxygenated hydrocarbons, and aromatic compounds,²¹ a fact that is nonexistent in the FH reaction. The solid phase is lipid rich, up to 74% reported,¹⁷ and is nonperishable.²¹

Hydrothermal Liquefaction (Module 4). The biofuel intermediate (BI) is processed to yield a suitable biocrude that is catalytically upgraded to a “drop-in” biofuel product. One of the methods for extracting the biocrude from the BI is with hexane extraction. An alternative method is with HTL. This model utilized HTL to refine the BI because hexane extraction has considerable environmental impacts due to the energy-intensive dewatering requirements and the significant burden associated with solvent use and recovery.^{38,39} The HTL process employed conditions of 350 °C; 3,000 psi; and a 20 min residence time.³⁷ All models utilized a rotary vacuum drum filtration system due to its relatively simple design, application, and operation and it can filter solids in a continuous mode at low labor costs.⁴⁰ The energy demand was estimated to be 5.9 kWh/m³.⁴¹

Hydrothermal Mineralization/Atmospheric Precipitation (Module 5a/Module 5b). This study evaluated HTM and AP as methods of solid nutrient precipitation. HTM is a hydrothermal process that recovers and stores the macromolecules as valuable coproducts in the form of hydroxyapatite through crystallization.^{42,43} The process requires the addition of a calcium mineralizer. The Ca mineralizer-to-phosphate ratio is 1.67, ideal for maximum phosphorus removal and hydroxyapatite (HAP) production.^{26,27,44} The HTM process in this study utilized 280 °C; 1,200 psi; and 1 h residence time in a continuous flow reactor. A heat exchanger operating at 85% efficiency was used to preheat the incoming hydrolysate into the HTM reactor using the heat recovered as a result of lowering the temperature from 280 to 99 °C. AP is executed at atmospheric conditions rather than hydrothermal conditions. The process requires addition of magnesium mineralizer at a 2:1 ratio relative to phosphate.^{26,27} The product from the AP mineralization is called struvite/dittmarite, a solid form of fertilizer which can be used as a nutrient source for the algae cultivation⁴⁵ or can be sold as a valuable coproduct.⁴⁶ The AP process does not require heating as is required in the HTM process, but has an energy demand associated with mixing the hydrolysate for the required 60 min reaction time. Following the HTM/AP process, the nutrient-depleted hydrolysate was recycled back to the cultivation pond.⁴⁷

Life Cycle Assessment. Life cycle models were created for each of the six compared systems (RDII-AP, RDII-HTM, RG-AP, RG-HTM, HRJ-AP, and HRJ-HTM). The system boundary for each modeled system was “well-to-pump” incorporating all processes upstream of the delivered energy product. These upstream processes have corresponding environmental impacts. These impacts were determined using materials and energy flows derived from the life cycle inventory (materials and energy accounting including infrastructure related costs⁴⁸) and impact factors obtained from either EcoInvent, GREET, TRACI, or any open source LCA databases. The functional (FU) utilized in this study was 1 MJ of usable energy.

The drop-in fuel can either be RDII, RG, or HRJ whereas the energy coproducts include naphtha, propane, etc. To calculate direct land use associated with each modeled system, the calculated per

hectare energy production (MJ/ha-yr) for each of the pathways was divided by the total energy produced (MJ/yr) for a small-sized refinery in the United States.⁴⁹ Each model was evaluated on two environmental end points: energy use in megajoules (MJ) and global warming potential (in kg CO₂-equivalents). Energy-based allocation method applied for coproduct handling was evaluated.

The catalytic upgrade of the biocrude generated from HTL and necessary for drop-in fuels production was modeled using parameters associated with studies performed by Argonne National Laboratory which were incorporated in the GREET model.²⁸ The RDII production was based off of the hydrogenation process developed by Universal Oil Products (UOP), a wholly owned subsidiary of Honeywell International (Honeywell UOP). The process scheme was modeled and published by Argonne National Laboratory in 2008.⁵⁰ The RG production was modeled using catalytic cracking, also based upon UOP technology. The bio-oil was fed into the fluidized catalytic cracker (FCC) with inputs of vacuum gas oil (VGO), steam, and electricity. This stand-alone model uses algae oil as the feedstock rather than in combination with vacuum gas oil.⁵⁰ The hydroprocessed renewable jet (HRJ) fuel, also known as jet fuel from hydroprocessed esters and fatty acids (HEFA), was modeled utilizing processes and parameters in GREET, 2016.²⁸ The data and assumptions for energy use and emissions associated with HRJ fuel production were sourced from a study conducted by Pearson et al. in 2011.⁵¹ The hydrotreatment and catalytic treatment required a catalyst (5% Pd/C and 0.5% Pt/ZSM-22, respectively).⁵²

Techno-economic Analysis. The economic assessment was conducted over a 30-year project life assuming a likeliest 12% discount rate. The initial outlay and capital costs included infrastructure costs, major equipment costs, and miscellaneous expenses.⁴¹ Infrastructure costs are costs associated with establishment of physical assets including land, buildings, roads, and electrical distribution. Major equipment costs (MEC) are costs of procuring heavy machinery and other unit operations paraphernalia. The cost of land was based upon current economic data provided for commercial farmland in Virginia at a rate of \$1,590/ha,⁵³ the costs of utilities were determined from U.S. Energy Information Administration.^{54,55} Construction and major equipment costs were extracted from the study conducted by Resurreccion et al. (2012)¹³ and were updated using average inflation rate over the last 6 years (1.45%).⁵⁶ Process costs, indirect costs, energy costs, and depreciation represent total operating costs. Annual cash flows were calculated by subtracting the operating costs from the revenues which included the sale of the biofuel product and the associated coproduct. A prevailing statutory tax rate of 39% was assumed for this study which is equivalent to 23.6% as the effective marginal tax rate (EMTR). This is a suitable measure of tax rate because it applies to investment projects where the pretax return is just enough to break even after taxes.⁵⁷ Overhead costs were assumed to be 60% of labor costs, contingency costs were calculated to be 10% of total infrastructure costs, and annual maintenance and insurance was assumed to be 3.5% of the respective depreciable bases.^{13,30}

The three main materials for algae open pond cultivation were polypropylene (for the pond liner), aggregates (0.05 m thick under 5% of the base area), and polyvinyl chloride (PVC). Other equipment required were water pumps (1.5 kW rating), flue gas pumps (0.75 kW rating), and paddle wheels (cylindrical six-bladed PVC paddle³⁰). The FH systems (\$53 M per 221,920 Mg lipid extracted algae per year) and HTL/catalytic upgrade systems (\$117.8 M per 221,920 Mg per year) were modeled after the estimation based on Zhu et al. (2013).⁵⁸ Heat exchangers were utilized for the FH, HTL, and HTM systems and the associated costs were based upon the process design by Knorr et al. (2013)⁵⁹ and was inflated to a 2017 installed price of \$10.95 M per 200 Mg algae dry solids produced per day. These models assumed a heat exchanger system redundancy factor of 2. Although both industrial-scale FH-HTM or FH-AP systems are emerging technologies, all six modeled systems can appropriately be compared with established medium- to large-scale petrochemical refineries thereby foregoing the associated start-up and pioneering costs. Storage systems modeled for the biocrude lasts for 1 year, intermediate products for 30 days, and drop in fuels for 30 days at a rate of \$50/barrel.⁶⁰

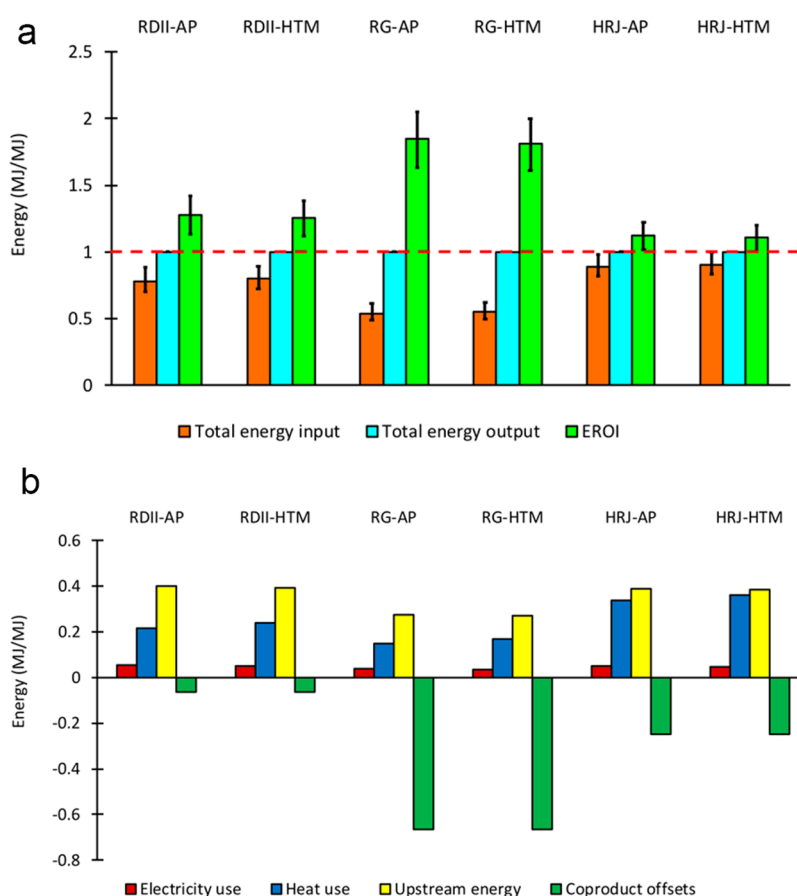


Figure 2. (a) Total energy input, total energy output and energy-return-on-investment (EROI) for all modeled flash hydrolysis-based renewable biofuel pathways: renewable diesel II (RDII), renewable gasoline (RG), or hydroprocessed renewable jet (HRJ). Nutrients recovery process includes atmospheric precipitation (AP) or hydrothermal mineralization (HTM). (b) Total energy use profile for all modeled flash hydrolysis-based renewable biofuel pathways: renewable diesel II (RDII), renewable gasoline (RG), or hydroprocessed renewable jet (HRJ). Nutrients recovery process includes atmospheric precipitation (AP) or hydrothermal mineralization (HTM).

Table 1. Functional Unit and Direct Land Use Calculations

Pathway	Product	Energy Allocation	Density (kg/L)	LHV (MJ/kg)	Total energy (MJ/ha-yr) ^a	Total energy (MJ/yr) ^b	Direct land use (ha)
RD II	RD II	93.6%	0.840	44.1	1,034,780	345,477,000	333.84
	propane (gas)	6.4%	0.002	43.2			
	weighted avg		0.786	44.0			
RG	RG	33.6%	0.745	43.5	1,495,642	267,704,000	178.99
	product gas	25.4%	0.002	42.6			
	LCO	19.0%	0.880	44.9			
	CSO	22.0%	0.890	43.6			
	weighted avg		0.614	43.6			
HRJ	HRJ	75.3%	0.810	44.1	1,089,572	301,840,000	277.03
	propane (gas)	14.5%	0.002	43.2			
	naphtha	10.2%	0.740	44.4			
	weighted avg		0.686	44.0			

^aTotal energy produced as biofuel in 1 ha in 1 year. ^bTotal energy produced as biofuel from a small-sized refinery in the U.S. in 1 year.⁴⁹

RESULTS AND DISCUSSION

Energy. For energy use, total life cycle energy input and energy output for all three pathways are presented in Figure 2a. Energy efficiency was evaluated in terms of the “well-to-pump” energy-return-on-investment (EROI), a ratio reported by other similar studies: Hall and Klitgaard (2006),⁶¹ Hall et al. (2009),⁶² Luo et al. (2010),⁶³ Clarens et al. (2011),¹⁴ and Resurreccion et al. (2012).¹³ These values are also presented in Figure 2a. EROI was calculated as the ratio of energy output

versus energy input. EROIs greater than one indicate net-energy producing systems (i.e., desirable from a life cycle perspective) whereas values less than one are net-energy consumers. Total energy input includes: *operations energy use*, specifically direct electricity and heat consumption, and *upstream energy use* or the energy/heat associated with electricity and nutrients delivery or the energy/heat associated with manufacture of materials of construction for each unit operation. Total energy output includes embodied energy in

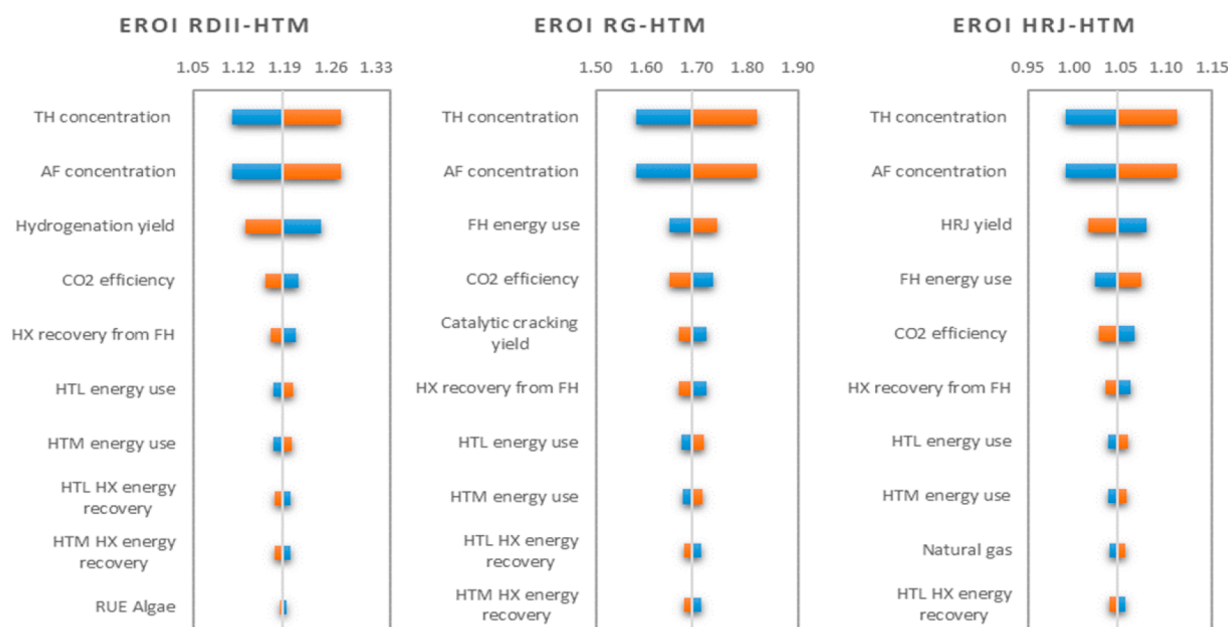


Figure 3. Tornado plots showing the sensitivity of hydrothermal mineralization's energy-return-on-investment, HTM EROI (output) from the three biofuel pathways: renewable diesel II (RDII), renewable gasoline (RG), or hydroprocessed renewable jet (HRJ) to inputs in these systems using flash hydrolysis. Bar widths indicate $\pm$ change from the model output's base value. Blue bars represent an increase and orange bars represent a decrease in input parameters.

each biofuel produced and each coproduct associated with the catalytic upgrade process. Table 1 shows the results of the weighted average for densities and lower heating values (LHV) for each of the renewable biofuel option.

The results of the EROI comparison reveal that the RG models have the most favorable energy efficiency. EROIs in all models are above the breakeven value of 1. RG's EROI (1.83) is 44% higher than RDII's (1.27) and 64.86% larger than HRJ's (1.11). The very slight increase in EROI median values for HTM models against AP models is attributed to hydrothermal heating conditions inherent to the hydrothermal operation, in contrast to AP models requiring only electricity for stirring at atmospheric conditions. Though EROI is a meaningful metric in assessing multiple emerging biofuel technologies for policy formulation and thus serves as a technical basis for subsequent commercialization, cautious use of the ratio must be exercised due to its inherent ambiguity as a result of incorporating coproduct energy.⁶⁴ This study therefore utilized EROI₁ recommended by Zhang and Colosi (2013) where energy outputs are explicitly accounted for in the numerator (including offsets) and energy inputs in the denominator.⁶²

The total energy use profile shown in Figure 2b shows that in both RD and RG models, operations energy (i.e., electricity + heat) is within 42–67% of their upstream energy whereas HRJ model's operations energy is 12% higher than its upstream energy. This is not surprising considering that the production of renewable biojet fuel necessitates the use of 1.5 times more heat than the production of renewable diesel or gasoline²⁵ and as a result, significantly increases its upstream energy burden. Coproducts differ across the biofuel pathways. RD pathway involves the coproduction of propane fuel mix, RG pathway cogenerates product gas, light cycle oil (LCO), and clarified slurry oil (CSO), and HRJ pathway cogenerates both propane fuel mix and naphtha as coproducts. It is for this reason that the gasoline coproduct as an energy equivalent is eight times that of diesel's or twice that of jet fuel's. Consequently, this makes the

net energy use for RG pathway to be negative (i.e., surplus energy) even when combined with energy associated with infrastructure materials and construction. This LCA uses an energy-based allocation method of treatment for the coproducts. Of RD's and HRJ's positive total energy use, the operations energy contributed the greatest share (RDII-86%, HRJ-88%) when compared to the infrastructure energy (RDII-14%, HRJ-11%), annualized over a 30-year life.

Of the operations upstream energy, nitrogen fertilizer contribution has the most impact of around 50% across all six modeled biofuel pathways whereas about 41–46% is associated with electricity. Previous studies have recommended the use of alternate sources of fertilizer such as nutrients derived from colocation with wastewater treatment, a potential viable source of water and nutrients for mass algal cultivation.⁶⁵ It is important to note that for each biofuel pathway (RD, RG, or HRJ), energy outputs are equivalent whether AP or HTM was employed due to the identical postprocessing catalytic upgrade parameters.

The allocation between drop-in fuel energy versus coproduct energy, as presented in Table 1, varies widely across all biofuel pathways due to significant differences in product streams. A HTL only model in lieu of FH was also evaluated in conjunction with AP or HTM, excluding any of the coproduct upgrading processes and maintaining the same energy/mass balance parameters and economic factors. Results showed that the EROI for the HTL only system increased by an average of 7.4% when compared to the RDII, RG, and HRJ systems. This is expected due to the reduced energy demand necessary for further processing of the hydrolysate coproducts.

Greenhouse Gas Emissions. The major operations contributing to LC-GHG emissions for all six modeled pathways include nitrogen delivery, electrification, natural gas use, and hydrogen delivery. Upstream LC-GHG impacts of nitrogen (1.34 kg CO₂ equivalents/kg), electricity (0.21 kg CO₂ equivalents/kWhr⁻¹), natural gas (0.00691 kg CO₂

equivalents/kg), and hydrogen (1.22 kg CO₂ equivalents/kg) were extracted from EcoInvent, GREET,²⁶ TRACI, or any open source LCA databases. Similarly, the use of polypropylene and polyvinyl chloride (as liner and paddle wheel material) contributed significantly to infrastructure LC-GHG emissions. Comparative LC-GHG emissions results are presented in Figure S2 of [Supporting Information](#). LC-GHG emissions has a direct relationship between total energy input and inverse relationship between EROI. Among the pathways, RD emits almost twice more CO₂ than RG and 12% more CO₂ than HRJ. The additional burden imposed by providing hydrogen to diesel processing is the main reason for this trend. GHG offset is calculated as the stoichiometric CO₂ requirement to produce a functional unit of algae energy. This work assumed that algae ponds are colocated with coal-fired power plants thereby harnessing the latter's CO₂ emissions. This assumption is reasonable given the considerable energy and cost of CO₂ compression, transportation, and delivery and allows for overall system sustainability improvement within the context of emissions avoidance. On a per hectare basis, algae consumes 112 Mg CO₂/ha across all pathways, using stoichiometric molecular weight of algae biomass via Redfield's molecular composition³⁰ and the calculated annual algae biomass yield. RD production has the largest footprint (333.84 ha/FU) compared to RG (178.99 ha/FU) or HRJ (277.03 ha/FU) as a result of renewable diesel's high energy density (RD = 0.786 kg/L; RG = 0.614 kg/L; HRJ = 0.686 kg/L). Consequently, RD is seen to have the lowest total GHG offset among the three pathways (Figure S2 of [Supporting Information](#)).

Impacts Sensitivity. A sensitivity analysis was conducted on EROI and Profitability Index (PI) for the HTM models. All input parameters in [Figure 3](#) were adjusted by $\pm 10\%$ for the sensitivity range. The AP models for each drop-in fuel is considered to be relatively similar as seen from the results of previous analyses. The most significant drivers to EROI included thickening concentration (TH) and autoflocculation (AF). The results of Monte Carlo analysis can be seen in [Figure 3](#).

Effect of Dewatering Concentration Factors. The concentration factor for both the AF and TH was set to 10%. Increasing either of these factors by 10% reduced the EROI by approximately 6% and the PI by approximately 14% for all models. The concentration factors effectively determine the amount of mass that will enter FH reactor. Although initially it could be inferred that more mass entering the reactor would result in more product and resultantly, more profit, infrastructure costs and heat exchange reactions associated with the aqueous phase of the algae slurry offset additional profits resulting in total system losses.

Effect of CO₂ Uptake Efficiency. CO₂ pumping energy use from flue gas source to the open pond system represents approximately 45% of the total electricity use in the total system operations. The models utilize a value of 72% efficiency of CO₂ uptake by the algae in the open pond.³¹ This requires that extra CO₂ is pumped into the open pond due to losses associated with nonutilization of the flue gas. Increasing the utilization efficiency of the CO₂ by the microalgae by 10% reduces the energy consumption by an average of 2.2% for all models. Although utilization efficiency of algae in open pond systems can vary considerably, it should be noted that a $\pm$ decrease in efficiency does not alter the EROI significantly.

Techno-economic Implications. The working capital (around 20% of the total initial outlay) of the systems

represents 25% of the total direct capital.^{13,30} This is the largest cost driver in the initial outlay. Similarly, engineering and contingencies is calculated to be 15% of the total infrastructure cost and total cost for construction and major equipment. This represents 9.6% of the total initial outlay. The infrastructure costs associated with the FH, HTL, and catalytic upgrade systems represent either second or third most significant cost drivers within all models. These costs were derived from Zhu et al. (2013)⁵⁸ and appropriately scaled to the models in the study represented by their individual functional units (Figure S4 of [Supporting Information](#)). This model assumes n^{th} plant economics⁶ where the processing plant technology is mature and several units have already been established in order to avoid the risk associated with longer start-up costs (5% of total infrastructure cost AND total cost for construction and major equipment) in this study,^{13,30} pioneer investment risks, and equipment design modifications/redesign/overdesign. It should be noted that neither commercial-scale HTL nor FH facilities have been established in private industry. Detailed initial outlay accounting can be seen in Tables S12, S14, and S16 of [Supporting Information](#).

Results from the simulation gave the following baseline values for HTM cash flows (annual operating costs, annual revenues) and total initial outlay, respectively: RDII, \$4.1 million, \$8.5 million, and \$55.4 million; RG, \$2.2 million, \$4.0 million, and \$29.7 million; HRJ, \$3.4 million, \$7.4 million, and \$46.0 million. From these cash flows and total initial outlay, profitability index (PI) is derived. PI is calculated as the ratio of the net present value (NPV) of the expected future cash flows and the total initial outlay. This ratio is meaningful insofar as it reflects the relative share of expected income throughout project's life as a percent of total expenditure incurred at the beginning of the project. An economically feasible project has $PI > 1$. Projects with $PI < 1$ are considered not profitable. A Monte Carlo analysis was performed on the HTM PI for all biofuel pathways and results showed that PIs are controlled by dewatering concentration factors (AF and TH), investment discount rate, carbon dioxide utilization efficiency, the yield ratios of energy end products including energy coproducts, the infrastructure costs associated with major hydrothermal systems (FH and HTL), and the selling price of hydroxyapatite. These results are found in Figure S5 of [Supporting Information](#).

The algae dewatering factors (AF and TH) are the top cost drivers for all models. This trend is similar to that of EROI's, which is expected due to energy usage and its relation to profit. The minimum selling price of the drop-in renewable transportation fuel product in order to reach a \$0 NPV was determined to be \$4.10 for RDII, \$5.64 for RG, and \$3.43 for HRJ. Adjusting the AF or TH concentrations by $\pm 10\%$ on the RDII, RG, or HRJ processes has a considerable impact on minimum fuel selling price, resulting in a raise or lower of fuel selling price by 13.4%, 18.3%, or 18.1% for RDII, RG, or HRJ, respectively. This is related to processing costs and associated labor, overhead, and miscellaneous costs. The price of HRJ could potentially be reduced to \$2.81, which is \$0.57 higher than the market value utilized in this study.

The discount rate proved to be the next most influential techno-economic parameter. Although the outlook for US biofuels, particularly algal biofuels, is less promising than other bioenergy sources, these economic results provide benchmark data on commercialization aspects of algae biomass conversion technology while overcoming technical barriers in large-scale biofuels deployment. The discount rates at \$0 NPV are 7.8%,

5.9%, and 8.6% for RDII, RG, and HRJ, respectively. The baseline discount rate was assumed to be 12%; however, reduced rates above are shown to increase profitability to acceptable investment standards given national strategic alignment with renewable transportation fuel technology and production. Figure 4 shows the relationship between NPV and

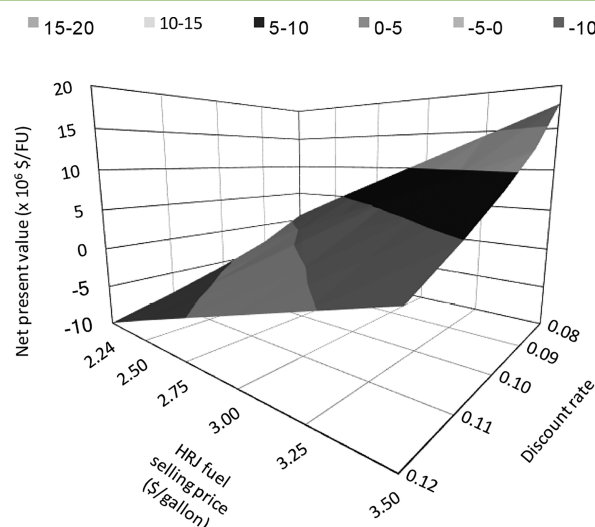


Figure 4. Relationship between net present value (NPV) to discount rate and hydroprocessed renewable jet (HRJ) fuel selling price using hydrothermal mineralization (HTM) as method of nutrients recovery.

the variance between discount rate and fuel selling price for the HRJ-HTM model. It is evident that the NPV is significantly increased by gradually reducing the discount rate or increasing biojet fuel selling price. The 2017 Annual Energy Outlook by the U.S. Energy Information Administration projects that the North Sea Brent oil price will rise from its current selling price of \$50/barrel to approximately \$75/barrel by the year 2020 and \$100/barrel by around 2030.⁶⁶ It is likely that transportation fuel costs will increase over the near future. Increased production of petroleum fuel products has momentarily reduced the cost of gasoline and diesel fuels. However, this scenario is considered temporary and long-term solutions such as this technology has the potential to sell renewable transportation fuel at a competitive market cost.

The relationship between fuel selling price and PI/NPV are presented in Figure S6 of Supporting Information for all HTM models. Though it is apparent that increasing the selling price increases both PI and NPV, the HRJ-HTM model has the highest PI and NPV among the three models. At approximately \$2.25/gal, the PIs of both RDII and RG are 0.5, after which the values diverge. The PIs of HRJ are higher than those for RDII and RG regardless of fuel selling price. The break-even fuel selling price (i.e., selling price at NPV = \$0 or PI = 1) for HRJ-HTM is at \$3.43/gal, lower than RDII's at \$4.10/gal and RG's at \$5.64/gal. Taken together, this observation indicates that although FH-based algae transportation fuel is an emerging technology, economics favor the early commercialization of biojet fuel compared to renewable diesel or gasoline. A standalone HTL model was compared to this study's FH-HTL-HTM model. Results indicate that PI for HTL is 4% lower. In a similar manner, the PI of the standalone HTL model was found to be 16% below RG PI and 8.6% below RDII PI. PI comparison is critical because it determines if the additional hydrothermal processing of FH hydrolysate to produce HTM

hydroxyapatite is a good investment compared to producing biocrude via HTM. In this study, additional heat requirements and infrastructure capital costs afforded by HTM-based biofuel pathways are offset by coproduct market value.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acssuschemeng.7b03912](https://doi.org/10.1021/acssuschemeng.7b03912).

Model development specifics, life cycle inventory data, material and energy balances for each unit operation and associated first-principles calculations, details on biocrude conversion and postprocessing, characteristics for each distillate fraction, life cycle metrics calculations, and capital costs and annual cash flows for each modeled system (PDF)

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The authors declare no competing financial interest.

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