THESIS

BIOPLASTIC PRODUCTION FROM MICROALGAE WITH FUEL CO-PRODUCTS: A TECHNO-ECONOMIC AND LIFE-CYCLE ASSESSMENT

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ABSTRACT

BIOPLASTIC PRODUCTION FROM MICROALGAE WITH FUEL CO-PRODUCTS: A TECHNO-ECONOMIC AND LIFE-CYCLE ASSESSMENT

Concerns over depleting oil reserves and national security have spurred renewed vigor in developing bio-based products. One specific area of growing concern is the consumption of petroleum based plastics, which is expected to consume 20% of global annual oil by 2050. Algae systems represent a promising pathway for the development of a bioplastic feedstock but have many technological challenges. Algae-based plastics offer a promising alleviate that would decrease oil consumption, improve environmental impact, and in some cases even improve plastic performance. This study investigates the economic viability and environmental impact of an algae biorefinery that integrates the complementary functions of bioplastic and fuel production. The bioplastic and biofuel biorefinery modeled herein includes nine different production scenarios. Performance of the facility was validated based on experimental systems with modeling work focusing on mass and energy balances of all required sub-processes in the production pathway. Results show the minimum selling price of the bioplastic feedstock is within the realm of economic competition with prices as low as $970 USD tonne^{-1}. Additionally, LCA results indicate drastic improvements in environmental performance of the produced bioplastic feedstock, with reductions ranging between 67-116% compared to petroleum based plastics. These results indicate that an algae biorefinery focused on bioplastic feedstock production and fuels has the potential to operate both economically and sustainably. Sensitivity analysis results, alternative co-products (given that fuels represent minimal value) and product market potential are discussed.

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1. INTRODUCTION

A changing world is increasingly straining the precarious balance of the water-food-energy nexus. This strain has motivated researches to search for long term solutions that ensure the proper balance and use of all components of this nexus. Agricultural solutions such as no-till farming, managed grazing, and tree intercropping challenge the traditional techniques of agriculture in an effort to become more environmentally conscious. Energy solutions look to make the large transition from fossil fuel to renewable energy sources such as wind, solar and geothermal. Water, intricately connected to both agriculture and energy, is also reduced through improved practices such as those mentioned above. Algae biomass has received substantial interest because of its potential impact in the all three sectors. This potential stems from the inherent advantages of microalgae and include: high productivities, potential for year-round production, cultivation on non-arable land, utilization of degraded and saline water sources, integration with waste streams, and potential for genetic optimization [1–5]. Substantial investments evaluating the use of microalgae as a feedstock for biofuels have investigated improvements across the entire algal value chain [6–8]. However, despite these investments there is still no consensus on the realistic potential of algae. The range of economic results from algal biofuel studies reinforces this with minimum selling prices ranging from a low of $1.59 per gallon of biofuel to a high of $33.86 with the median landing at $8.77per gallon of biofuel [9–16]. This lack of consensus and high median value coupled with recent decreases in energy prices has resulted in an algae industry shift towards the identification of high value co-products in order to achieve economic competitiveness.

Co-products represent a promising avenue for improving the economics of algal fuel pathways. Some typical algal co-products being explored are fertilizers, animal feed, cosmetics, nutraceuticals, and other specialty chemicals. Co-products such as nutraceuticals have very high values upwards of $60,000 USD tonne^{-1} [17]) but also have small market sizes of around 38,000 metric tonnes per year on a global scale

[18]. A small market size carries the risk of possible market saturation at relatively small farm sizes. Conversely, large market products such as animal feeds do not have the same market saturation concerns [19] but suffer instead from dramatically lower product values ($350 USD tonne^{-1}) [20]. One co-product that has been minimally investigated to date and that has the potential to alleviate both of the above concerns is bioplastic production in an algal biorefinery. Considering that virtually all plastics in existence have been manufactured since 1950 [21], the rate of proliferation of their everyday use is astounding. The current global plastic production is greater than 300 million metric tonnes annually, with the majority being produced in the US, Europe, China and Asia [22]. If the current rate of growth in plastic manufacturing continues, plastics will account for over 20% of the world's total oil consumption by the year 2050 [23]. Considering the increasing population and economic prosperity of historically underdeveloped countries, this estimate is likely conservative [24]. Such a large market size and an optimistic market growth projection indicate that bioplastics have the potential to dramatically impact the global plastics supply chain.

A wide range of traditional plastics can be directly replaced with algae based bioplastics. These include commodity thermoplastics ($1,540-$2,200 USD metric tonne^{-1}), biodegradable resins ($2,640-$5,500 USD metric tonne^{-1}), and engineered resins ($1,540 and $8,800 USD metric tonne^{-1}) [25]. While widely variable and highly dependent on the application, even the lowest value reported above is substantially more lucrative than other large market algal co-products being investigated. Due to both the large market size and comparatively high value, bioplastics have the potential to positively impact the economic feasibility of algae based biorefineries. Bioplastic manufacturing does not come without its complications. Algae lipids emit unpleasant odors when present in the bioplastic product, reducing the number of applications of such bioplastics. Agglomeration tendencies caused by the carbohydrates/sugars in the biomass slow production and necessitate expensive and time consuming remedies. Notwithstanding these technological hurdles, algae based bioplastics have shown superior mechanical properties when compared with their petroleum based counter parts [25]. This improved performance comes from the proteins in the

algae, which lengthen during processing and become incorporated in the polymer matrix. Thus, a higher protein feedstock has the potential to produce higher quality bioplastics. The vast majority of algae based biofuel conversion strategies focus almost exclusively on utilizing lipids, to produce a diesel replacement, and/or carbohydrates, to produce an ethanol fuel. The removal of carbohydrates through fermentation and lipids through solvent extraction offers two-fold benefits for algae bioplastic production, either reducing or eliminating the manufacturing complications while simultaneously improving the quality of the final bioplastic product.

This study investigates the pairing of a dedicated algae biomass growth and fuel conversion facility with a bioplastic conversion process to create a synergistic fuel and co-product relationship. Three growth pathways are examined in an effort to determine the tradeoffs between performance and capital costs. Additionally, three biomass conversion scenarios are examined constituting different degrees of biomass processing. Nine total scenarios are examined as a result of the combination of these pathways. An engineering process model was developed in a modular fashion consisting of sub-process models that depict each aspect of the biorefinery. Inputs to the model are informed by experimental results and where necessary literature references. Each of the nine scenarios were analyzed through Techno-economic Assessment (TEA) and Life-Cycle Assessments (LCA) in order to understand both the economic feasibility and environmental impacts of each system. The process model serves as the foundation for both the TEA and LCA by calculating key inputs relevant to each. The purpose of such analyses are to determine if a dedicated algae biomass to bioplastic feedstock production facility has the potential for improved environmental performance over petroleum plastic resins and if added costs of coupling fuel production equipment to the algae growth system improve the economic outlook.

2. METHODS

Sustainability assessment of the biorefinery system included TEA and LCA which were based on a foundational modular engineering system model. The model included sub-process modules in Microsoft Excel spreadsheets and Visual Basic for Applications coding. Each sub-process model was developed and validated with collaborative partners and literature. The systems model encompasses a system boundary of algae biomass growth through biomass conversion to the sale of products, namely bioplastic feedstock (BPFS) and fuels (where applicable). It is assumed the plant is co-located with a coal fired power plant in order to directly utilize the CO_2 rich flue gas. Mass and energy balances were completed for each individual sub-process model to maintain high fidelity, however only flows that cross the system boundary of the entire process impact the TEA or LCA. These flows include any consumed materials, such as fertilizers or solvents, as well as energy requirements in the form of electricity and heat.

A total of nine scenarios were analyzed based off various combinations of the three different biomass growth architectures coupled with three different conversion pathways. The possible pathways and products of each of the scenarios as well as the fundamental mass flows across the system boundary are presented in Figure 1. The first sub-process encompasses the growth of the algae biomass, for which there are three options: Open Raceway Ponds (ORP), Cyclic Flow Photobioreactors (CF-PBR) and a combined CF-PBR/ORP system. The dewatering sub-process directly follows any growth system architecture and is constant across all scenarios analyzed. The biomass conversion sub-process has three options: drying only, lipid extraction and fractionation, each with varying degrees of processing intensity. The final sub-process analyzed is BPFS preparation, where the remaining biomass is further processed into a marketable state for bioplastic compounding. Each of these sub-processes are described in more detail below with a summary of the key inputs to each model in Table 1. Also shown in Table 1 are the sources for the major inputs, many of which are gathered from experimental work. Any assumptions not gathered

from experimental work is taken from applicable studies in literature. All of these assumptions are used across various sub-process models to calculate mass and energy balances which in turn provide the basis for the LCA and TEA. The sub-process diagrams for each individual sub-process across all options are shown in Figure A11 through Figure A17 of APPENDIX A.

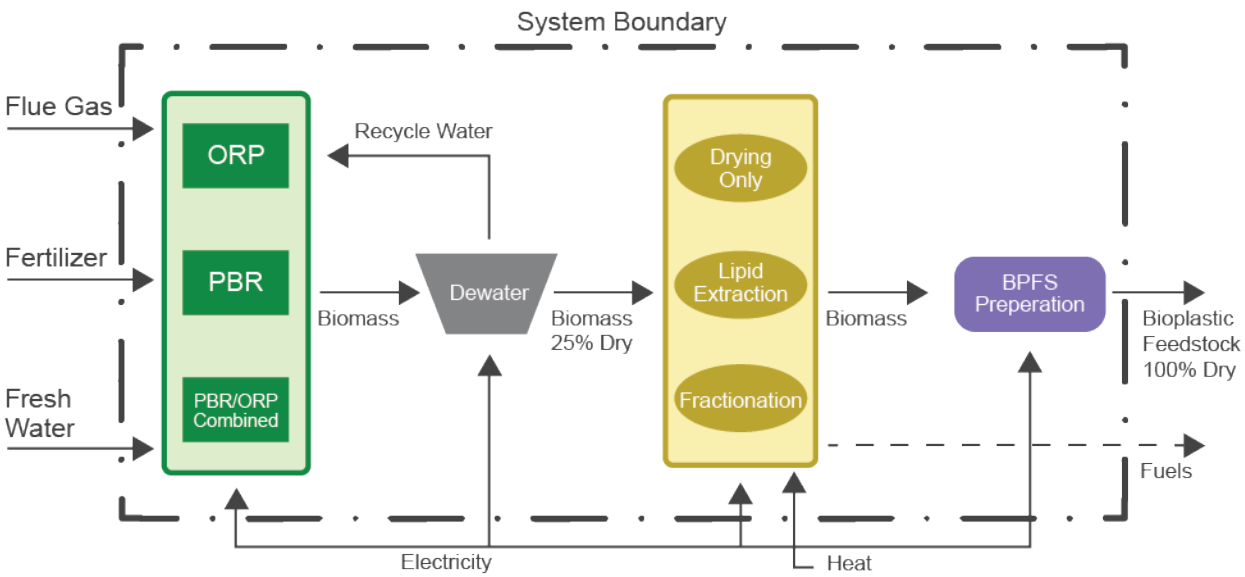

Figure 1. Process flow diagram depicting the three possible growth scenarios (ORP only, CF-PBR Only and CF-PBR/ORP combined) as well as the three possible biomass conversion strategies (Drying Only, Lipid Extraction and Fractionation) for a total of 9 different scenarios. The system boundary encompasses biomass growth to delivery of the high-protein bioplastic feedstock. Solid lines indicate mandatory flow paths while dashed lines indicate potential flow paths.

2.1 Growth Architectures

In this study, *Scenedesmus acutus* (UTEX B72) is the algae strain used for cultivation. This strain was chosen for the comparatively high protein content. Extensive experimental work has been completed on this strain, results from this experimental work being leveraged to inform the inputs to this model [26–28]. Experimental work has been completed with flue gas as the carbon feedstock , and is thus directly comparable to studies such as this, with results used as validation for the model [7,14,26,27,29–32]. The detailed performance assumptions across the growth architectures are detailed in the following sections.

2.1.1 Open Raceway Ponds

ORPs are the most commonly studied algae growth architecture in the literature [10,33]. This is due to their straightforward and simple design that translates to a low capital cost compared to other systems.

Additionally, their simple operation and long history in wastewater treatment has given rise to many commercial designs [34]. However, due to their open nature, culture contamination from foreign debris is a problem, as are culture crashes that drastically reduce the productivity of these systems. Considering an ORP reliability of 95% and that with every algal culture crash extensive clean up would be required as well as time for inoculum production, this work assumes an ORP growth system that has 300 operating days per year [35].

Economic considerations for the ORPs modeled are based on those outlined in Davis et al. (2016) with capital costs and labor based on the 10 acre scenario. Land siting is assumed to be low value, non-arable land that does not compete with agriculture [12,14]. Finally, fertilizer and energy prices were determined from current market prices as of March 2018 [36,37].

Average annual productivity for the ORPs was assumed to be 12.5 g m^{-2} d^{-1} with a CO_2 utilization efficiency of 37.5 percent. These are generally lower than that typically assumed in literature and were directly informed by experimental results from the specific process being examined [7,14,29–32]. Major energy expenditures for ORP operation were assumed to be the freshwater pumping power [14] which is mostly driven by evaporation losses, CO_2 delivery power [6], and the paddle wheel circulation power [38]. The combination of these assumptions results in an areal energy usage of 28 kWh ha^{-1} d^{-1}.

2.1.2 Cyclic Flow Photo Bioreactors

PBR growth systems are another highly researched growth structure, mostly because of the technical advantages they offer over ORP systems. The closed environment of the PBR systems result in higher quality biomass, reduced culture crashes, and lower evaporation losses [10,39]. The larger and more complicated material requirements and increased labor and engineering required for PBR systems result in them being typically much more expensive than ORPs both in capital and operational costs

[10,26,27,39]. In an effort to combat this conception, a new concept of PBR was developed by Wilson et al. [27]. Cyclic Flow Photobioreactors (CF-PBR) realize both energy and capital savings over more traditional PBR designs. The CF-PBR drastically reduces energy consumption by periodically filling and draining the tubes throughout the day rather using constant flow. This change realizes a 92% decrease in energy consumption over a continuous flow system, mainly attributed with the low duty cycle of the pumps. [27] Capital cost reductions was also a concern and was addressed through the use of low cost, commonly available components [26].

Economic considerations for the CF-PBR system were completed based on detailed schematics of the system design. Costs for plastic components were assumed to be made out of PETG (polyethylene terephthalate glycol) for the clear tubing, PVC (polyvinyl chloride) for pipe fittings and PP (polypropylene) for feed tanks. Both the clear tubing and pipe fittings were assumed to be made from virgin resins whereas the feed tanks were produced from recycled resins. Costs per metric tonne of the plastic materials were assumed to be an average of a literature survey completed in 2018 [40–43]. Production costs were based off the mass of plastic resin needed, taking into account production costs with a molding cost factor of 1.5. A feed pump was specified (Barmesa Submersible Stainless Steel Vortex Sewage Pump, 5 HP) based off the calculated head and flow requirements of each module in the CF-PBR system. An installation factor of 2 based on US labor was also assumed. The culmination of these factors results in a CF-PBR areal capital cost of slightly above \$1 M-USD ha^{-1}. Fertilizer, energy and land prices were assumed to be identical across both CF-PBR and ORP systems.

The average annual productivity for CF-PBR systems is assumed to be 25 g m^{-2} d^{-1}, a CO_2 utilization efficiency of 50%, and an operating year of 360 days, all of which are higher than those assumed in the ORP systems. The large increase in operating days stems from the reduction of algae culture crashes and the more controlled environment of algae growth [44]. The increase in performance is attributed to the closed system nature of the CF-PBR, which in the case of operating days shows a drastic increase due to reduced algae culture crashes and more controlled growth environment. The energy consumption of the

CF-PBR system results in an areal energy usage of 17.75 kWh ha^{-1} d^{-1}. Again, all inputs to this sub-process model are heavily informed by experimental data and results gathered in testing conditions very similar to those assumed for this study.

2.1.3 Combined CF-PBR/ORP

In addition to the mono-structured growth systems described above, a hybrid CF-PBR/ORP growth system was also modeled. Adapting a hybrid approach could theoretically leverage the best attributes of each system, combining low capital costs with high productivities and culture quality. The CF-PBR was used to produce a robust inoculum of *Scenedesmus acutus* culture in sufficient amounts to inoculate the ORPs to 0.2 g L^{-1} after each ORP harvest. Whereas the ORP constitutes the bulk of algae growth and land area. The number of operating days is assumed to be 330 days yr^{-1}, an increase over the ORP architecture. This stems from a hybrid system offering improved culture health and stability, and reduction of rebound time after crashes in the ORP.

This growth model leverages both the CF-PBR and ORP models described above. As such, the same economic and performance assumptions stated are also applicable here. The combined growth model couples the two growth systems to capture the system dynamics described above. The most important calculation in this combined model is the CF-PBR:ORP growth area ratio. Based on the harvest densities, ORP inoculation density, and assumed growth rates (see Table 1) a size ratio of 0.167 m^2 CF-PBR m^{-2} ORP is needed.

2.2 Dewatering

This work employs a proven two stage dewatering technique developed by Groppo et al. [26,45]. First, a polyacrylamide flocculent is added to the harvested algae/water mixture at 6 ppm in order to induce flocculation of the biomass in a settling tank. This step realizes a concentration increase from 0.8 g L^{-1} at harvest to 25 g L^{-1} (2.5% TSS) at the exit of the settling tank. Such an increase results in the removal of 97% of the water at minimal energetic cost. The concentrated algae slurry then proceeds to a Vacuum Filter Belt (VFB) which utilizes multifilament filter fabric and a short pulse of vacuum to achieve an exit

concentration of 250 g L^{-1} (25% TSS). Clarified water exiting the flocculation and VFB processes is recycled at an efficiency of 98%. Recycled water is sterilized with Ultraviolet (UV) light treatment to eliminate any pathogens or contaminants. The sterilized clarified water is then returned to the growth system.

Total energy expenditure for this dewatering process model, including sterilization, is 0.063 kWh kg^{-1} algae, which is dominated by the VFB (97%). The energy consumption of the VFB is assumed to have an energy consumption of 0.9 kWh m^{-3} of algae slurry processed. The UV sterilizer uses 2.7 Wh m^{-3} of clarified water processed, which is based on flow rate and power demand [46]. This combines to give a total energy consumption for the delivery of 250 g L^{-1} dewatered algae of 0.14 MJ kg^{-1} algae, of which all is electricity.

2.3 Biomass Conversion

Three different biomass conversion pathways were examined in this work, Drying Only, Lipid Extraction, and Fractionation process. Each pathway represents different levels of biomass processing to extract and utilize different components of the biomass.

2.3.1 Drying Only

The drying only case represents the simplest pathway technologically and is based on current commercial practices. Specifically, whole biomass is dried and then used as a feedstock for bioplastic production. In this pathway, no conversion steps other than biomass drying is required. The product from this pathway is limited to a bioplastic feedstock with no fuels co-product produced.

2.3.2 Lipid Extraction

In lipid extraction the lipid component of the algae biomass is extracted and utilized for fuels with the remaining biomass being used as a bioplastic feedstock.

The specific Lipid Extraction process modeled in this work is based on that developed by Laurens et al. [47,48]. The dewatered algae is treated with HCl/MeOH followed by hexane to perform an *in-situ*

transesterification reaction to produce fatty acid methyl esters (FAMES). Three streams exit this reaction, a lipid extracted algae slurry (LEA) stream, an aqueous stream and, a fuel stream. This process results in extraction of lipids equal to 8% of the biomass by mass, of which 80% are recovered as FAMES. The vast majority (74%) of the biomass is recovered in the LEA stream which includes any un-extracted lipids, as well as all of the protein originally in the biomass. The remaining mass is recovered in the aqueous stream, consisting of MeOH and approximately 25% of the carbohydrates originally present in the biomass.

Due to the presence of free sugars resulting from chemical changes of the carbohydrates present in the LEA, a washing step must be performed to avoid any downstream bioplastic processing complications. Washing is done through dilution of the LEA to 25 g L^{-1}, followed by re-concentration through a VFB with the same performance as presented in the dewatering sub-process. This additional step removes 54% of the carbohydrates remaining in the LEA. Considering the large amount of sugar in the exiting wash water it would provide a highly favorable environment for bacteria growth. Therefore, to avoid any culture contamination or crashes the exiting wash water is considered to be a waste stream rather than being recycled back to the growth system.

Economic and energy assumptions for this process are based on the work completed by Dong et al. [49] and Mu et al. [30] respectively. The resulting streams of economic value exiting this process are FAMES at 5 Million GGE yr^{-1} and LEA at 0.18 million Metric Tonnes yr^{-1}. The FAMES stream can be sold directly as fuel, requiring no further processing. However, the LEA exits at a protein content between 48-56% and must undergo further preparation before becoming marketable as BPFS. These details are presented in the Bioplastic Feedstock Preparation section.

2.3.3 Fractionation

The Fractionation pathway represents the most intensive of the biomass conversion pathways examined in this work. Fractionation adds upon the Lipid Extraction process in that it utilizes both the carbohydrate and lipid constituents of the algae biomass for fuel production. Whole biomass is subjected to dilute acid

pretreatment that convert carbohydrates into sugars to be used for ethanol fermentation. The fermented ethanol is then distilled off before hexane solvent extraction is used to recover the algal lipids. Finally, the lipids are upgraded to a Renewable Diesel Blendstock (RDB) through hydrotreating.

This process model was developed based on the work of Dong et al. [49] with some sub-process steps excluded as they are not applicable for a bioplastic biorefinery. Specifically, Anaerobic Digestion (AD) and Combined Heat and Power (CHP) are not included as they rely on the residual protein rich biomass after the fuel conversion steps. Including AD and CHP in this work would eliminate the BPFS revenue stream under investigation and were therefore excluded. Process areas modeled include biomass pretreatment, fermentation, lipid extraction, and lipid upgrading, which model biomass conversion into fuels and a high protein BPFS. Capital and operational cost for each of the included process areas were scaled accordingly based off reference flows to the plant size modeled in this study. The Fractionation process produces fuel co-products which are directly sold and a high-protein BPFS stream between 55-66% wt. depending on the growth system. The resulting streams of economic value exiting this process are biofuels at 12.7 Million GGE yr^{-1} and a protein rich algae residue at 0.17 million Metric Tonnes yr^{-1}. Similar to the Lipid Extraction process the high-protein stream must also undergo further processing before becoming marketable as BPFS. These details are presented in the Bioplastic Feedstock Preparation section.

2.4 Bioplastic Feedstock Preparation

Incoming biomass to the BPFS preparation process has varying degrees of moisture content and composition dependent on the upstream processes employed. Regardless of the upstream processes, all biomass to be used as BPFS must undergo further processing before becoming marketable. The first consideration is the moisture content. Excessive levels of moisture promote decomposition of the biomass, releasing foul smelling compounds that render the biomass useless for further bioplastic compounding. As such, low temperature drying techniques are employed to reduce the moisture content to the range of 5-10% to provide an optimum shelf life for the material. Biomass moisture reduction in

this process is accomplished in two stages. Membrane filters are employed to dry the algae to 60% moisture. This removed water is assumed to be recycled back to the growth stage after passing through the UV sterilizer, after which microwave drying evaporates the remaining water to reach 10% moisture.

The second consideration in BPFS preparation is the particle size. Target particle size varies with the bioplastic application and composition. The model uses a fluidized bed jet mill to homogenize the particle size with very tight tolerances to produce a fine powder of BPFS suitable for the desired application. The resultant homogeneous fine powder is now in a marketable state and can be immediately used for compounding with petroleum resins, but also has a shelf life that allows for storage or transportation to a separate compounding facility. It is assumed the energy requirements for this step are agnostic to the different previous sub-process operations.

It should be noted that the BPFS sold is not a direct replacement for petroleum plastics. Rather, the produced BPFS is blended with petroleum based plastic resins at near equal ratios to product the final bioplastic product. While such a product does not eliminate dependency on oil resources it drastically reduces the dependency on such.

Table 1. Primary Model Assumptions

	Value	Unit	Reference
Cyclic Flow PBR			
Biomass Productivity	25	g m^{-2} day^{-1}	Experimental
CO_2 Utilization	50	%	Experimental
Harvest Density	0.8	g L^{-1}	Experimental
Evaporation Rate	0.1	cm day^{-1}	Experimental
Biomass Composition			Experimental
Carbohydrates	35%		Experimental
Proteins	40%		Experimental
Lipids	15%		Experimental
Ash	10%		Experimental
Circulation Power Demand	17.74	kWh ha^{-1} day^{-1}	[27]
ORP			
Biomass Productivity	12.5	g m^{-2} day^{-1}	Experimental
CO_2 Utilization	37.5	%	Experimental
Harvest Density	0.8	g L^{-1}	Experimental
Inoculation Density	0.2	g L^{-1}	Experimental

Evaporation Rate	0.4	cm day^{-1}	[14]
Biomass Composition			
Carbohydrates	31%		Experimental
Proteins	36%		Experimental
Lipids	13%		Experimental
Ash	20%		Experimental
Circulation Power Demand	28	kWh ha^{-1} day^{-1}	[38]
Dewatering			
Flocculation Target Concentration	25	g L^{-1}	Experimental
Vacuum Filter Belt	250	g L^{-1}	Experimental
VFB Power Demand	0.9	kWh m^{-3}	Experimental
Water Recycling Efficiency	98	%	Experimental
UV sterilization Power Demand	2.7	Wh m^{-3}	[46]
Fractionation			
Pretreatment			
Steam Loading	8	% wt of slurry input	[49]
Sulfuric Acid Loading	2	% wt of slurry input	[49]
Ammonia Loading	0.5	% wt of slurry input	[49]
Electricity Demand	44.73	kJ kg total $flow^{-1}$	[49]
Heat Demand	0.735	kJ kg $biomass^{-1}$	[49]
Fermentation			
Fermentable Sugars	74	% wt of total carbohydrates	[49]
Ethanol Yield	44	% total fermentable sugars	[49]
Algae Biomass Carbon	50	% wt of biomass	[49]
Electricity Demand	16.5	kJ kg total $flow^{-1}$	[49]
Heat demand	206	kJ kg total $flow^{-1}$	[49]
Lipid Extraction			
Lipid Yields	87	% wt of total lipids	[49]
Hexanes to biomass	5.9	g hexane g $biomass^{-1}$	[49]
Hexane recovery efficiency	99.5	% of total hexanes used	[49]
Esterfiable lipids	80 %	% wt lipids	Experimental
Electricity Demand	9.4	kJ kg total $flow^{-1}$	[49]
Heat Demand	4	kJ kg total $flow^{-1}$	[49]
Fuel Upgrading			
Phosphoric Acid Dosing	0.2	% wt of feed	[49]
Wash Water Demand	10	% wt of feed	[49]
Silica Dosing	0.1	% wt of feed	[49]
Clay Dosing	0.2	% wt of feed	[49]
Fuel-range Hydrocarbon output	80	% wt of oil feed	[49]

Electricity Demand	718.65	kJ kg fuel output^{-1}	[49]
Heat Demand	1700	kJ kg Lipids^{-1}	[49]
Lipid Extraction			
Mass of Recovered lipids	8	% wt of biomass	Experimental
Lipids Recovered as FAMEs	80	% of recovered lipids	Experimental
Mass Recovered as LEA	74	% wt of biomass	Experimental
Hexane: Methanol Ratio	1:1	Volume ratio	Experimental
Methanol Required	0.5	L kg algae slurry^{-1}	Experimental
Methanol Recovery	97	% wt Methanol	Experimental
Hexane Recovery	99.5	% wt Hexane	[45]
Homogenization Electricity Demand	0.246	kWh kg algae^{-1}	[30]
Electricity Demand	0.51	kWh kg lipids^{-1}	[30]
Head Demand	6.83	MJ kg lipids^{-1}	[30]
Bioplastic Feedstock Preparation			
Membrane Dewatering Power Demand	0.09	kWh kg LEA^{-1}	[25]
Microwave Dryer	0.485	kWh kg LEA^{-1}	[25]
Jet Milling	0.485	kWh kg LEA^{-1}	[25]

2.5 Techno-Economic Analysis

TEA is a powerful tool when estimating the economic potential of nascent technologies and is widely used across many industries. This analysis utilizes a Discounted Cash Flow Rate of Return (DCFROR) calculation to model an algae production facility of 3000 ha for each of the scenarios described above. Combining the capital and operational costs determined from the process model with the economic assumptions and methods described below allows for the calculation of the minimum BPFS selling price ($ kg BPFS^{-1}). The DCFROR is calculated for a 30 year plant life and solved to yield a Net Present Value (NPV) of zero based on a fixed internal rate of return by varying the BPFS selling price.

The fundamentals of the DCFROR are based in economic principles that are adapted for application in renewable energy technologies as detailed in Short et al. [50]. The standard nth plant assumptions gathered from literature are used to define the economic parameters [50]. Parameters include a 10% discount rate/Internal Rate of Return (IRR), 30 year facility lifespan, 35% tax rate, 7 year MACRS depreciation,

and a loan of 8% interest over a 10 year period with a debt to equity ratio of 60:40. Methods for calculating additional facility parameters such as Insurance and maintenance costs are done by applying the percentages given in Davis et al [6] and Jones et al. [15]. Capital cost and material pricing were transformed from the quoted year to a cost year of 2016 using the Chemical Engineering Plant Cost Index (CEPCI).

Table A5 in APPENDIX A: SUPPLIMENTARY INFORMATION shows a detailed capital cost table depicting the amount of capital investment required for the CF-PBR/ORP growth architecture and Lipid Extraction conversion pathway, which was chosen to be the representative scenario. The capital costs include relevant scaling functions, as well as cost year transformations into a common year. Table A4 shows the economic assumptions for the operational expenses such as material and energy costs. When coupled with material and energy flows the operational cost can be determined. Table A3 shows the labor assumptions used in this report. Similar tables for the remaining scenarios are available from the author upon request.

2.6 Life Cycle Assessment

The environmental impacts for each scenario were quantified through an attributional LCA in terms of greenhouse gas emissions. Process models for each scenario, which describe in detail all mass and energy flows, formed the foundation for the LCA. The system boundary of the LCA encompassed algae growth through BPFS preparation and includes the combustion emissions of any fuels production. With BPFS being the main product of interest, the functional unit was defined as 1 kg of BPFS resulting in a functional unit of kg carbon dioxide equivalent (CO_{2eq}) kg^{-1} BPFS. The mass of CO_{2eq} is determined using the global warming potential impact factors of each emitted gas from the International Panel on Climate Change (IPCC), which relate the impacts of such gasses to an equivalent emission of CO_2. Gasses accounted for include carbon dioxide, methane and di-nitrogen mono-oxide with equivalency factors of 1, 28, and 265 respectively [51]. Upstream emissions from consumed resources and materials in the process model were quantified through a life cycle inventory analysis (LCI). LCI data was sourced predominantly

from the EcoInvent 3.4 database [52] and supplemented with data from the GREET [53] and NREL LCI [54] databases. The combustion emission of fuels is well studied and assumed to be 73 g CO_{2eq} MJ^{-1} of fuel energy [29,53,55,56].

Co-product allocation of emissions from the process was completed through the displacement allocation method, where any generated co-products are assumed to displace an existing product, earning a credit to the system. Two of the conversion pathways produce a co-product of fuels during the biomass conversion stages. This fuel is assumed to displace an equal amount of petroleum derived fuel, thus earning a credit equal to the production emissions of the same amount of gasoline on a gallon of gasoline equivalent (GGE) basis. It is important to note that since both the produced biofuel and the petroleum fuel it is replacing would be combusted during their use, only credits equal to the production of petroleum fuels are applied in the displacement method. Alternatively, the fuel displacement credit could have been chosen to include both the production and combustion emissions of the displaced fuels. This larger displacement credit would essentially negate the combustion emission of the fuels, further reducing the net environmental impact of the system. Additionally, a carbon credit is taken associated with the CO_2 captured from the flue gas in the biomass during the growth stage. Because of this large credit for capture CO2 in the algae growth stage, it was deemed more appropriate to take the smaller fuel displacement credit to avoid misleading results.

Table A2 in APPENDIX A: SUPPLIMENTARY INFORMATION shows a detailed material and energy flow table depicting any material or energy into and out of the facility for the CF-PBR/ORP growth architecture and Lipid Extraction conversion pathway was chosen to be the representative scenario. A similar table for the remaining scenarios are available from the author upon request.

2.7 Sensitivity Analysis

Sensitivity analysis was used to identify high impact inputs to the TEA and LCA. The sensitivity analysis was done by varying each parameter independently by a determined percentage (± 20%) and recording the change in results. This was done for both TEA and LCA metrics to determine high impact variables in

both analyses. A student t-test statistical analysis was used to determine significant variables with a confidence interval of 95%.

3. RESULTS AND DISUSSION

The work integrated sub-process models validated with experimental data for the generation of a modular engineering process model. The modularity supported the evaluation of nine different production process pathways. This foundation was used with TEA and LCA to evaluate the economic and environmental impact of an algal based bioplastic and biofuel biorefinery concept.

3.1 Techno Economic Analysis

Economic evaluation of the system was performed leveraging the energy and mass balance outputs from the engineering processing model as inputs to the TEA. Nine different scenarios were evaluated with results presented in Figure 2. The contributions of each economic factor (capital cost, variable operating cost, fixed operating cost, taxes, and co-product credit) to the minimum selling price (MSP) are also shown to allow comparison of their respective impacts. Negative values shown are the value generated through the sale of fuel co-products. Figure 2D shows the net MSP across all scenarios.

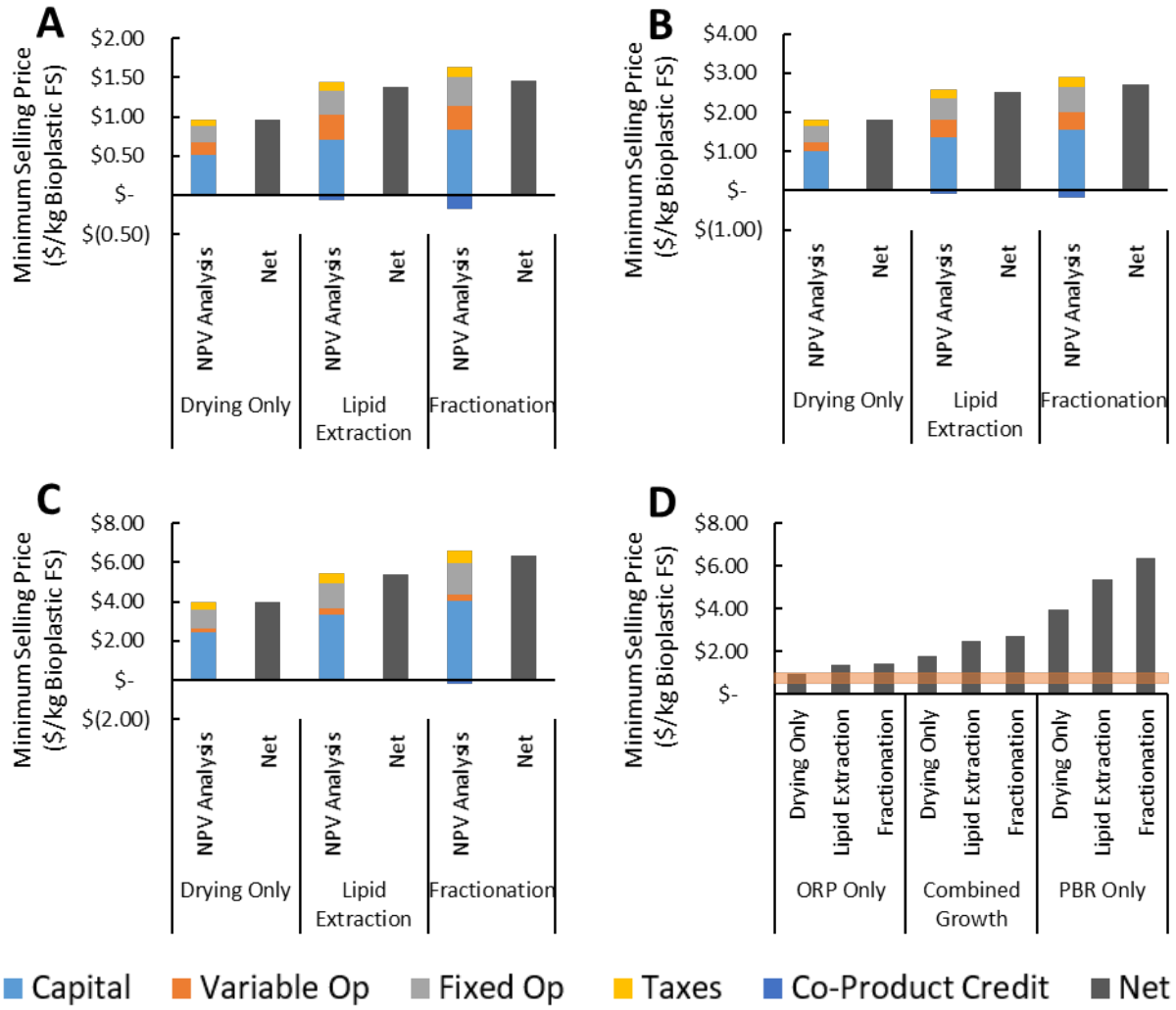

Figure 2. Economic results for the nine scenarios examined. Contributions of each sub-process are shown for the growth architectures ORP Only (A), Combined Growth (B) and CF-PBR Only (C). Plots include both net results as well as contributions from major economic categories. Credits are the value generated from the sale of the fuel co-product. Panel D is a summary of the net results of all scenarios presented in panels A, B, and C with shaded region representing the MSP range for profitability.

A direct comparison of the total costs across all processing scenarios highlights the impact of integrating CF-PBR systems into the growth systems, Figure 2D. While CF-PBR have many advantages they do represent capitally intensive investments [44]. Increasing the use of CF-PBR in the cultivation phase of the biorefinery results in reduced economic viability. This model takes into account the algae productivity and energy efficiency gains associated with the CF-PBR, thus representing a true depiction of CF-PBR economics including the inherent advantages. In order to draw conclusions about the growth systems care must be taken to view this trend only across identical conversion pathways. Each conversion

pathway varies the amount of algae biomass diverted to the BPFS main product and the fuels co-products. This directly affects the functional unit of the system and complicates growth system comparisons across different conversion pathways. Similarly, comparison between conversion pathways should only be done across identical growth structures when identifying trends. Moving from a pure ORP to CF-PBR production platform for the drying only pathway represents a 4X increase of minimum selling price from \$0.97 USD kg^{-1} to \$3.96 USD kg^{-1}. This trend is also observed across the other two conversion pathways, corresponding to 3X and 3.4X increases for the lipid extraction and fractionation pathways, respectively. These results illustrate the need for improvements if CF-PBR systems are to be utilized. These improvements could vary from engineering solutions related to reducing capital costs to biological improvements such as improved productivity.

The results show system capital costs to have the largest impact across all scenarios. This is a commonplace finding with n^{th} of a kind algae based systems [11,12,30,55,57]. This finding is independent of the growth architectures examined here, with both ORP and CF-PBR systems demonstrating this trend. The percent contributions of capital cost to the MSP ranges between a low of 51% for the ORP/Drying to a high of 64% for the CF-PBR/Fractionation. The capital cost includes growth systems, harvesting infrastructure and biorefining. The predominant contributor between these is the growth system. The growth system capital costs account for no less than 83% of the total facility capital costs for the ORP growth architecture, demonstrating the need for more cost effective growth systems. For the CF-PBR systems, the growth capital is ten times more intensive than ORPs per unit area and represents at least 97% of the total capital investment. These results highlight the need to decrease growth architecture capital costs. This can be achieved through alternative construction methods such as an earth and berm construction of ORP. For CF-PBR systems, reducing the costs to the same level of ORPs represents a significant challenge.

The results indicate that the added expenses needed for fuel production will not improve the selling price of the BPFS. Across all growth structures the drying only pathway provides the lowest MSP by a

minimum of 26% when compared to the other conversion pathways. While the additional fuel conversion equipment costs do increase capital costs, their impact can be mostly attributed to increased operational costs (both fixed and variable). These operational costs increase 44% and 68% over the drying only pathway for the lipid extraction and fractionation pathways, respectively. The increase stems in part from increased energy usage but, mainly from the requisite inclusion of the expensive solvents used in biomass processing. This is confirmed through the sensitivity analysis, which identifies hexane recovery efficiency as one of the more impactful parameters on MSP. Additionally, the production of biofuels causes a decrease in the amount of mass that eventually becomes bioplastics. Even in crude oil refining, the produced fuels represent only a small fraction of the profits while accounting for the majority of the production volume [58]. As such, the BPFS represents the more valuable of the revenue streams exiting the facility. Thus, as more fuels are produced, an increase in MSP is seen.

An important idiosyncrasy to consider is the quality of the bioplastic feedstock. While the results above show an increase in MSP across the more intensive processing pathways they do not represent the potential increase in the BPFS value. Therefore, the addition of fuel production does not result in a BPFS price reduction. However, some pathways may still be economically profitable due to increased value from quality improvements in the BPFS. The intensification of protein in the BPFS through the removal of other components, i.e., lipids and carbohydrates, potentially increases the quality of the product. This would allow for the targeting of higher value bioplastic applications and increase the marketable selling price for the corresponding BPFS. The dynamic between fuel production and BPFS value is difficult to capture in the results presented as the bioplastic industry is in its infancy. Thus, further work must to be done to quantify the additional value added to the BPFS through the production of fuels in order to truly determine the economic potential of the pathways examined.

For the three scenarios without fuel production, the BPFS can be directly compared to current practices allowing for more transparent conclusions about the economic potential of these scenarios. The results from these scenarios can be directly compared to current industry practices for bioplastic production.

Biomass is typically purchased between \$800-\$1200 USD tonne^{-1} [25], which allows for profitability in the bioplastic industry. The results above indicate that the ORP/Drying scenario offers an economically competitive pathway for a dedicated algae to bioplastics facility with a MSP of \$970 USD tonne^{-1}, which falls within the profitable feedstock price range. While this scenario represents the most favorable, other ORP based scenarios are within consideration as well, with MSP of \$1370 and \$1460 USD tonne^{-1} for lipid extraction and fractionation respectively. Technological improvements or increases in fuel value would result in these fuel producing scenarios becoming competitive with whole biomass BPFS, notwithstanding the potential value added from higher protein content in the BPFS. Another potential solution to reducing the selling price in scenarios with fuel conversion is to explore higher value chemical products.

3.2 Life Cycle Assessment

An attributional LCA was completed for each of the nine scenarios to quantify the environmental impact. Outputs from the engineering process model were used as inputs to LCA modeling with results presented in Figure 3. The contributions of each sub-process to the overall impact are also shown such that the large contributors can be identified. Negative values shown for the growth stage represent the credit associated with the biogenic uptake of atmospheric CO_2 from algae growth. In addition, co-product credits associated with fuel displacement are shown to be negative.

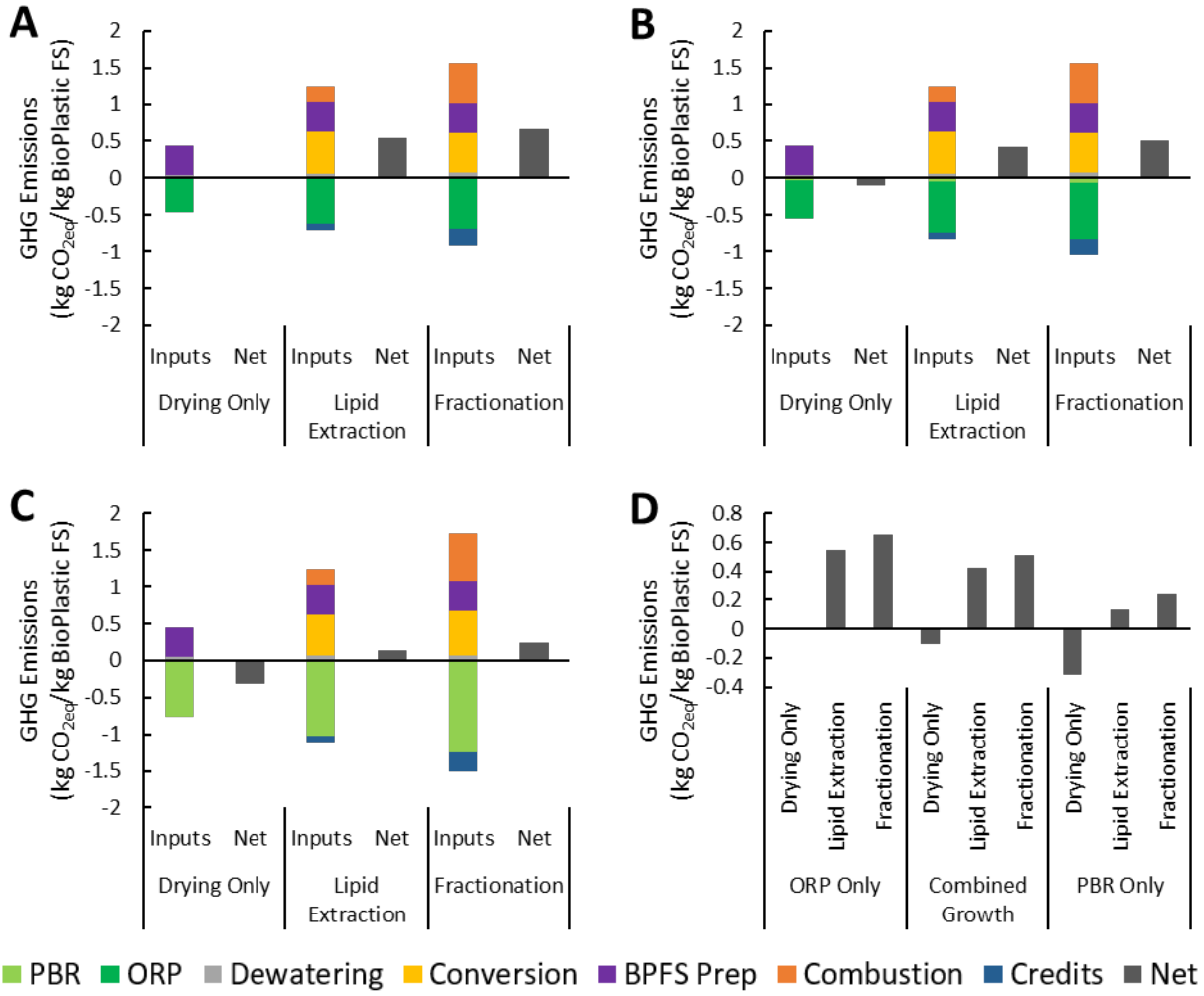

Figure 3. GHG results for the nine scenarios examined. Contributions of each sub-process are shown for the growth architectures ORP Only (A), Combined Growth (B) and CF-PBR Only (C). Plots include both net results as well as sub-process level contributions for each of the processing steps included from biomass growth to Bioplastic Feedstock (BPFS) Preparation, across the entire system boundary. Displacement credits are taken for the fuel produced as a co-product from the process and are shown as a negative value. Similarly, the CO_2 used in algae biomass growth is considered to be a negative value. Panel D is a summary of the net results of all scenarios presented in panels A, B, and C.

In the vast majority of previous studies, PBR growth systems have been found to be more energy intensive than ORP systems [26,27,39]. However, due to the low energy requirements of the CF-PBR system an interesting trend is seen in the results from this study. Comparing trends of growth system impacts across similar conversion pathways (Figure 3D) it can be seen that the environmental impact improves with increased CF-PBR usage across all conversion pathways. The most and least environmentally favorable scenarios had values of -0.315 and 0.656 kg CO_{2eq} kg $BPFS^{-1}$ for the CF-PBR/Drying and ORP/Fractionation scenarios respectively. The areal energy requirements for the two

growth structures were found to be 17 and 28 kWh ha^{-1} day^{-1} for the CF-PBR and ORP respectively. The CF-PBR represents a 58% decrease in energy requirements with these energy savings attributed to a combination of increased productivity, reduced need for fresh water pumping, less CO_2 delivery energy and lower culture circulation power demand. The growth energy requirements of the CF-PBR are the primary reason behind the promising environmental performance across all conversion pathways compared to pathways with an ORP.

Trends can also be observed for the conversion pathways examined. Within a common growth architecture the drying only pathway represents the best environmentally, followed by the lipid extraction and then fractionation. The fuels produced from both the lipid extraction and fractionation conversion pathways carry with them an associated combustion emission due to their inevitable use which dramatically impacts the GHG accounting. This combustion emission is more than triple the amount of co-product displacement credit allocated to the fuels, which is associated with only the production of petroleum fuels being replaced. Thus, the production of fuels results in a net increase of emissions as opposed to no fuel production. The fractionation pathway is the most affected by this as more fuels are produced, approximately 2.5 times more than in the lipid extraction pathway. In the fractionation pathway, the fuel combustion alone represents between 37-40% of all positive emissions from the facility across the different growth architectures. In this sense, similar to the TEA findings, fuel production has a large impact on overall facility results.

The above discussion relates back to the co- product displacement credit amount taken for the displaced fuels. It could be argued to include both the production and combustion of the displaced fuels in the fuel co-product credit taken, thus essentially negating the combustion emission incurred through the combustion of the produced fuels. The fractionation pathway would obviously see the greatest benefit from this change. However, making this change in the combined growth scenarios still results in the same conclusion, that fuels negatively impact the facility life cycle emissions, albeit to a lesser extent. With the larger fuel displacement credit drying only is still the most environmentally favorable conversion scenario

at -0.1 kg CO_{2eq}/kg BPFS followed closely by Fractionation and finally by Lipid Extraction at -0.03 and 0.21 kg CO_{2eq}/kg BPFS respectively. The increase in emissions from fuel production in this case is now dominated by the increased energy and other chemicals used for fuel production which are still substantial. Thus, while the increase of displacement credit results in less of an impact associated with fuel production it fails to drastically change the conclusions.

The combustion emission associated with the biofuels makes it difficult for a dedicated biomass to biofuel facility to achieve net negative emissions. In reality, the best these facilities could hope to achieve would be net zero emissions, as all carbon used during biomass growth would either be emitted during the combustion of the fuels or released with the decomposition or consumption of any biomass residuals. The biorefinery in this work realizes a unique potential to sequester carbon in the form of durable bioplastics. By blending the algae based BPFS into durable bioplastics all the carbon still present in the algae can be assumed to be sequestered as it will not be released through decomposition for hundreds of years, if at all [59]. Conversely, biodegradable plastics would capture the carbon present in the algae biomass for a short time, but eventually release the carbon back into the atmosphere during decomposition. Durable bioplastics offer the potential for a bio-product facility to obtain net negative emissions through sequestration of carbon. On the one hand, the potential integration of the same algae based BPFS into biodegradable plastics offer market security if a large scale shift from durable to biodegradable plastics is seen in the global market. On the other, moving to a biodegradable plastic would impact the carbon accounting.

Overall, these results indicate that the BPFS produced through any of the scenarios examined offer substantial improvement over petroleum based plastic resins. Quantifying the improvement requires understanding the environmental impact of the traditional feedstock being replaced. The BPFS has the potential to replace a wide range of plastic resins including PP and nylon which have an environmental impacts of 1.98 kg CO_{2eq} kg^{-1} and 8.03 kg CO_{2eq} kg^{-1}, respectively [52]. For discussion purposes the value for PP will be used as it represents a conservative assumption. Comparing this to the result of the

ORP/Fractionation scenario, which is the worst performing scenario environmentally at 0.656 kg CO_{2eq} kg $BPFS^{-1}$, the latter still represents a 67% reduction in emissions. The emission reductions reach as high as 116% in the best performing scenario of this study, CF-PBR/drying. This indicates that the major obstacle to wide scale implementation of this biorefinery concept is economic rather than environmental in nature.

3.3 Sensitivity analysis

Sensitivity analyses for each of the nine cases were completed to evaluate the impact of each variable independently. Variables were assessed through a statistical analysis at 95% confidence and only those variables that were determined significant are included. Figure 4 depicts all conversion pathways across a constant growth system (combined CF-PBR/ORP) and Figure 5 depicts all growth systems across a constant conversion pathway (Lipid Extraction). Only sensitivity results from six of the nine scenarios are shown in order to determine and discuss trends across the different growth and conversion pathways. All sensitivity results shown are for the TEA only, LCA sensitivity results and the three remaining TEA sensitivity results being presented in the supplemental information.

The sensitivity results support many of the findings from the TEA results. Growth system capital costs were found to be a major factor in the TEA results, as shown in Figure 5. As previously discussed, across all growth architectures the capital costs of the growth system were found to be impactful variables. Figure 5 also shows that biomass productivity is another critical variable as previously confirmed by other studies [12,14,55]. Algae productivity is directly related to the amount of revenue that is created, both in the form of fuels and BPFS. In addition, increased growth rate minimally impacts operational costs; the energy to mix the culture, for example, is a sunk cost and the increased amount of biomass produced results in a decrease of the impact when normalized to the biomass yield. In the case of this work the increase in biomass productivity allows for more BPFS to be sold, which represents the higher value of the products. This relationship is further enforced by the appearance of the washed algae biomass parameter on the lipid extraction pathway in Figure 5, which is the amount of residual biomass exiting the

lipid extraction sub-process. The increase in biomass recovered has a similar impact as improved productivity dramatically impacts the economics of the system.

Hexane recovery also represents a critical variable in fuel conversion pathways. This finding is not novel as solvent recovery has been regarded as a critical success criterion in the chemical processing industry for decades [60,61]. For any scenario that uses hexane the recovery efficiency is never less than the third most impactful parameter. Thus, it is critical to ensure that a very high hexane >99% [49] recycling efficiency is achieved for facility economic success. Additionally, algae biomass composition has an interesting effect on the facility. In many studies the carbohydrate and lipid components of the biomass are emphasized as critical components to a biomass to fuels facility success. Since the production of fuels is directly linked to these components, it is typically more favorable to maximize their fraction in the biomass, especially the lipid content as evidenced by the research on lipid accumulation through nutrient cycling [62–64]. However, in this facility these parameters are impactful because of their negative effect on the results. This is due to the higher value product being the BPFS rather than the biofuels; thus, a decreased amount of carbohydrates and lipids results in an increased amount of proteins and therefore BPFS. Thus, the sensitivity results can be used to direct the attention of future research to these critical areas.

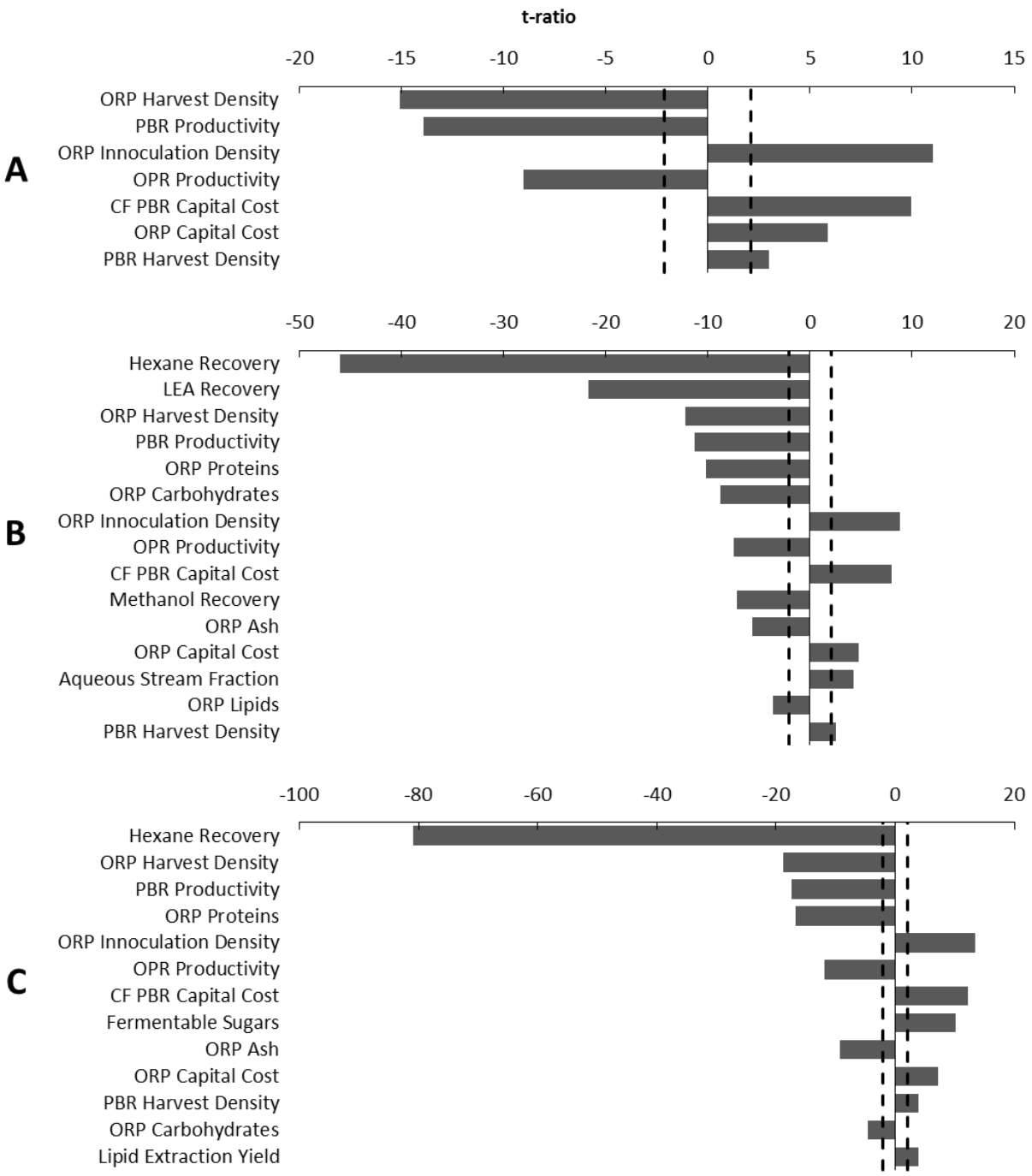

Figure 4. Sensitivity results shown were performed on the TEA work. The scenarios shown are for a constant growth architecture (combined CF-PBR/ORP) and conversion scenarios of Drying Only (A), Lipid Extraction (B), and Fractionation (C). A statistical analysis was used to determine significant variables at a confidence interval of 95%. Vertical dashed lines indicate the critical t-value for statistical significance. Only variables that were determined significant from this analysis are included.

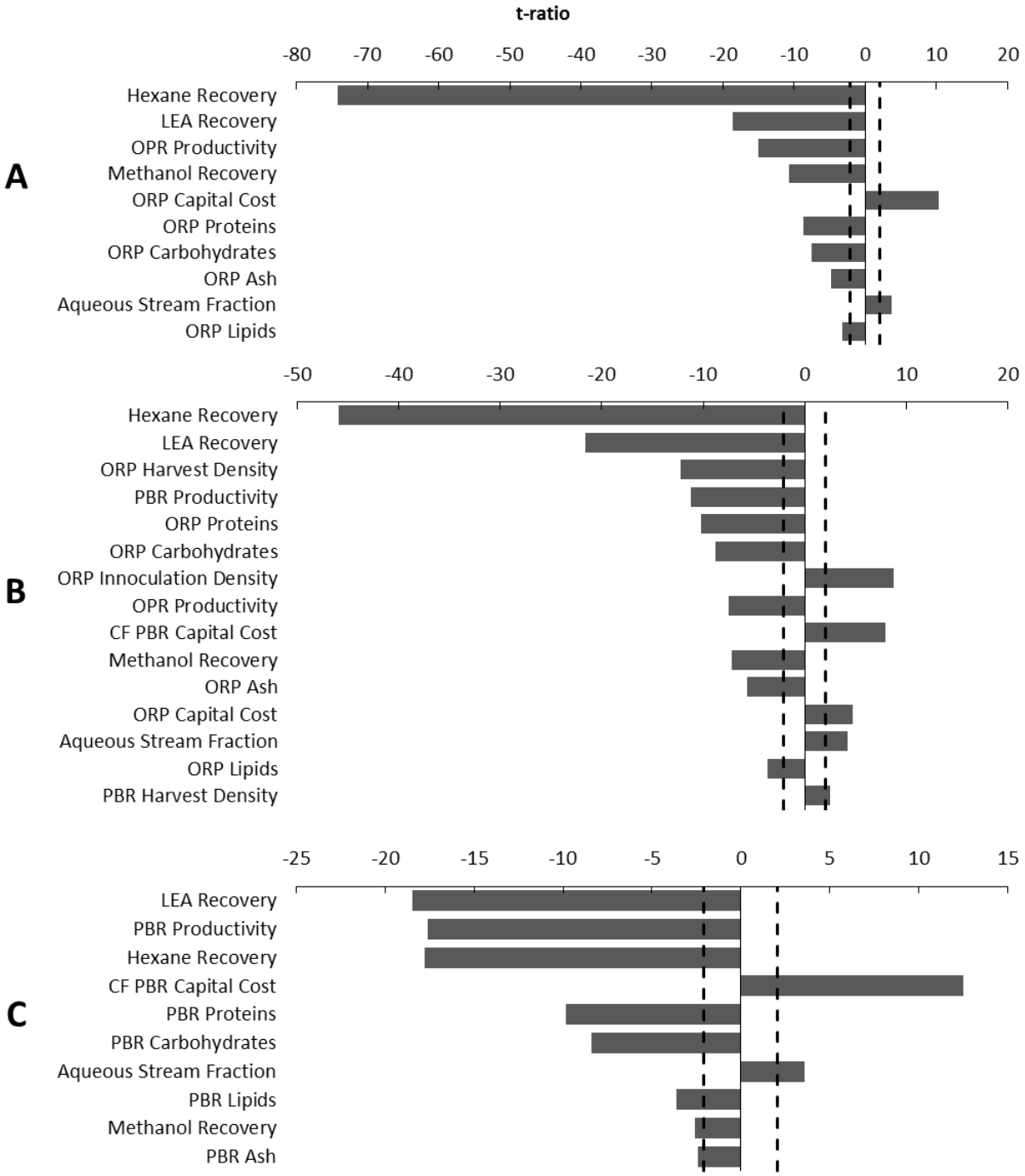

Figure 5.Sensitivity results shown were performed on the TEA work. The scenarios shown are for a constant conversion pathway (lipid extraction) and growth scenarios of ORP Only (A), Combined CF-PBR/ORP (B), and CF-PBR Only (C). A statistical analysis was used to determine significant variables at a confidence interval of 95%. Vertical dashed lines indicate the critical t-value for statistical significance. Only variables that were determined significant from this analysis are included.

3.4 Market Potentials

Realizing that the BPFS produced is not a standalone product, the potential impact of the BPFS is somewhat tempered. The algae based BPFS must be blended with petroleum plastics at near equal ratios in order to produce marketable products. This blending drastically improves the environmental impact of plastic product. Extending the system boundary to include the eventual compounding of the BPFS with petroleum resins results in a 23% (0.46 kg $CO_{2\text{-}e}$ kg^{-1}) decrease in emissions in the case of PP plastics. Considering the vast size and projected growth of this market, such an improvement in environmental performance would have far reaching positive impacts. While the introduction of algae bioplastics into the worldwide plastics market would not completely eliminate the dependence on oil it would severely reduce demand, helping to decrease the strain on finite oil reserves. Additionally, the inclusion of algae bioplastics offers a potential gateway for the transition to biodegradable plastics in the future.

The ORP/Fractionation scenario in this study has a fuel production volume of approximately 6 million GGE yr^{-1}, which is small compared to US national consumption. Thus, significant scale up would be needed to effect any change in the US production portfolio. Such a large scale up effort could cause concerns of market saturation in many co-products; however, such a market saturation is not concerning for the production of plastics. The Renewable Fuel Standard (RFS) is a federal program that requires transportation fuel sold in the United States to contain a minimum volume of renewable fuels. This minimum volume increases each year, with approximately 30 billion gallons being required in 2020 [65]. Of the 30 billion gallon requirement, approximately 10 billion gallons are required to be sourced from advanced biofuels and biomass derived diesel, for which algae fuels qualify. For the purposes of demonstration we will assume that all 10 billion gallons are produced using this facility, specifically the ORP/Fractionation scenario. For this massive scale up in fuel production, 321 million tonnes of bioplastics are produced, which is approximately 25 million tonnes less than the global plastic production [23]. Such a monopoly in biofuels production is highly unlikely, especially for a facility dependent on a point source CO_2 supply such as this. As detailed by Sommers and Quinn [66], taking into account the

number of point sources available that are located in acceptable algae growing locations reduces the fuel production potential drastically to 360 million gallons of fuel per year. Assuming 360 million gallons of fuel production in the ORP/Fractionation scenario results in a relatively small amount of bioplastics, 5.8 million metric tonnes. Thus, it can be assumed that the global plastics market is more than sufficiently large and an algal based plastic product would not saturate the market.

Furthermore, fuel production provides minimal value to the system due to stiff competition from petroleum fuel producers. A cost target of \$3 USD GGE^{-1} for bio-based fuels represents a conservative estimate. Historically, fuel prices in the US have exceeded \$4 USD GGE^{-1}. Increasing the value of the produced fuels from \$3 to \$5 USD GGE^{-1} improves the MSP for the ORP/Fractionation scenario by 8% from \$1.46 USD kg^{-1} to \$1.35 USD kg^{-1}. Comparison between fuels and other products on a per mass basis can be illustrative. The fuel co-product value of \$3 USD GGE^{-1} corresponds to a value of \$1 USD kg^{-1} for gasoline and even lower for ethanol. The potential for much higher value exists, especially in the case of carbohydrate fermentation. Replacing ethanol fermentation in the fractionation pathway (\$0.5 USD kg^{-1}) with fermentation to food grade additives such as citric or succinic acid (\$1.25-\$2.5 USD kg^{-1}) [67] offers a substantial increase in co-product value with essentially the same equipment. This change would result in a decrease in the BPFS MSP for the ORP/Fractionation pathway of 14% to \$1.26 USD kg^{-1}. These alternative products can also have sufficiently large markets; citric acid production was estimated at 1.6 million tonnes yr^{-1} in 2007 and is expected to grow [68]. Replacing biodiesel production with higher value products could similarly increase the value of the lipids extracted from the biomass in the lipid extraction pathway. This added value could drive the MSP of the BPFS into competitive ranges for scenarios with biomass conversion strategies.

Similarly in the LCA, a shift from fuels to non-energy co-products such as food grade acids offers significant benefits. Specifically, the co-product displacement credits could potentially increase: the credit allocation for fuels production in this study is taken to be 1.2 kg CO_{2eq} kg $fuel^{-1}$ [52], whereas the credits

for citric and succinic acid would be 3.85 and 3.3 kg CO_{2eq} kg^{-1} respectively [52]. This change would result in a decrease in the GHG emissions for the ORP/Fractionation pathway of 94% to 0.04 kg CO_{2eq} kg $BPFS^{-1}$. Such a substantial increase in the allocable credits could drastically alter the environmental impact of a system.

In addition to higher value co-products, other advancements could also aid in driving microalgal bioplastic systems towards economic competitiveness. Across all nine scenarios analyzed, results ranged from \$970 to \$6,370 USD $tonne^{-1}$ BPFS, corresponding to the ORP/Drying and CF-PBR/Fractionation scenarios, respectively. With a competitive price range being between \$800-\$1,200 USD $tonne^{-1}$, the ORP/Drying scenario was found to be immediately competitive, while the OPR and lipid extraction/fractionation scenarios were close enough to warrant discussion and further examination. A trend of increasing MSP with increasing CF-PBR usage was clearly seen across the results, indicating that despite the technological advantages CF-PBRs, the high capital costs are hard to justify. However, several technological improvements were analyzed to project a pathway for competitiveness of the CF-PBR. In the CF-PBR/Fractionation scenario, a 50% reduction of capital costs for the CF-PBR growth system represents a 40% decrease in the MSP of the BPFS from \$6.89 USD kg $BPFS^{-1}$ to \$4.24 USD kg $BPFS^{-1}$. A 50% reduction in operational costs represents a more modest improvement of 15% to \$5.86 USD kg $BPFS^{-1}$. Furthering the exercise, a doubling of the assumed productivity to 50 g m^{-2} day^{-1} yields a 48% decrease to \$3.58 USD kg $BPFS^{-1}$. Finally, combining all of these hypotheticals results in a 74% decrease to a low value of \$1.79 USD kg $BPFS^{-1}$ which is in the realm of the ORP scenario results discussed previously. These exercises provide potential future directions to improve on the economic and environmental performance of a microalgae to BPFS facility based on a CF-PBR growth system.

4. CONCLUSIONS

This study shows a potential path to improve the sustainability of the global plastics market. The LCA results show a decrease in GHG emissions of between 67% and 116% through the direct substitution of petroleum plastic resins with algae based BPFS for the production of bioplastics. Also shown is the economic potential of all nine scenarios examined in this work. Results show the Drying pathway for algae biomass conversion as the most economical pathway across all growth scenarios without accounting for increase in BPFS value through the removal of undesirable biomass components during fuel production. It was determined that for the specific scenarios examined in this study the added costs of fuel production does not result in a decrease of MSP. However, this was not enough to definitively conclude that the fuel conversion scenarios were uneconomical. The value added through the increasing protein content in the BPFS is not yet fully understood. Thus while the MSP of the fuel conversion scenarios are higher than the drying only pathways, a higher quality BPFS may allow for higher value bioplastic products to be produced, allowing these scenarios to become economically competitive as well.

Also demonstrated is the difficulty of these facilities in competing with petroleum based fuels for transportation. This has caused a standstill in the development of necessary technology and experience to progress towards cheaper biofuels. Alternative co-products offer the potential to more effectively utilize the non-protein components of the biomass in terms of economic viability. This points to a need for the algae industry to search out other, more valuable markets in order to gain economic feasibility, where first of a kind plants can be constructed to help drive future improvement and development.

4.1 Future Work

The work presented herein represents a strong foundation for continued research into micro algal based bioplastic biorefineries. The process model developed for this study provides the means by which

alternative scenarios can be easily modeled and examined. The furthering of this study can include work in the following areas.

A more detailed investigation into different co-product scenarios is warranted given the promising preliminary results discussed above. Such an investigation would include a literature review of possible fermentation candidates similar to that given by Deloitte [67] as well as a detailed process modelling effort to account for the differences from ethanol fermentation. It is estimated that yields, nutrient inputs and even processing equipment requirements could be different. Additionally, alternative lipid co-products should be examined for feasibility in algal systems. Several industrial applications for plant lipids are given by Tao that could provide a more lucrative use for algal lipids [69]. Detailed co-product investigations would help define a clear path for first of a kind algae facility implementation.

The high protein algae residue after any conversion steps should also be investigated for any higher value utilization avenues. This can be done through amino acid characterization to determine the nutritional value of the protein source. Given the amino acid profile, a value can be determined through the Protein Digestibility-corrected Amino Acid Score (PDCAAS) for comparison to traditional forms of proteins [70,71]. If the score is comparable to other protein sources used in human nutrition, a shift away from bioplastics could be warranted.

It could also be illustrative to examine the impacts of a carbon credit tax on a bioplastics facility. This would require the sequestration of CO_2 in the form of durable bioplastics, but could offer a pathway to inform policy on what levels of incentives would be impactful.

Finally, further work could be done to optimize and improve the hybrid CF-PBR/ORP growth system to fully capture the benefits of each. This would require experimentation with CF-PBR growth rates, harvesting densities and the like to reduce the CF-PBR:ORP ratio and lessen costs.

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APPENDIX A

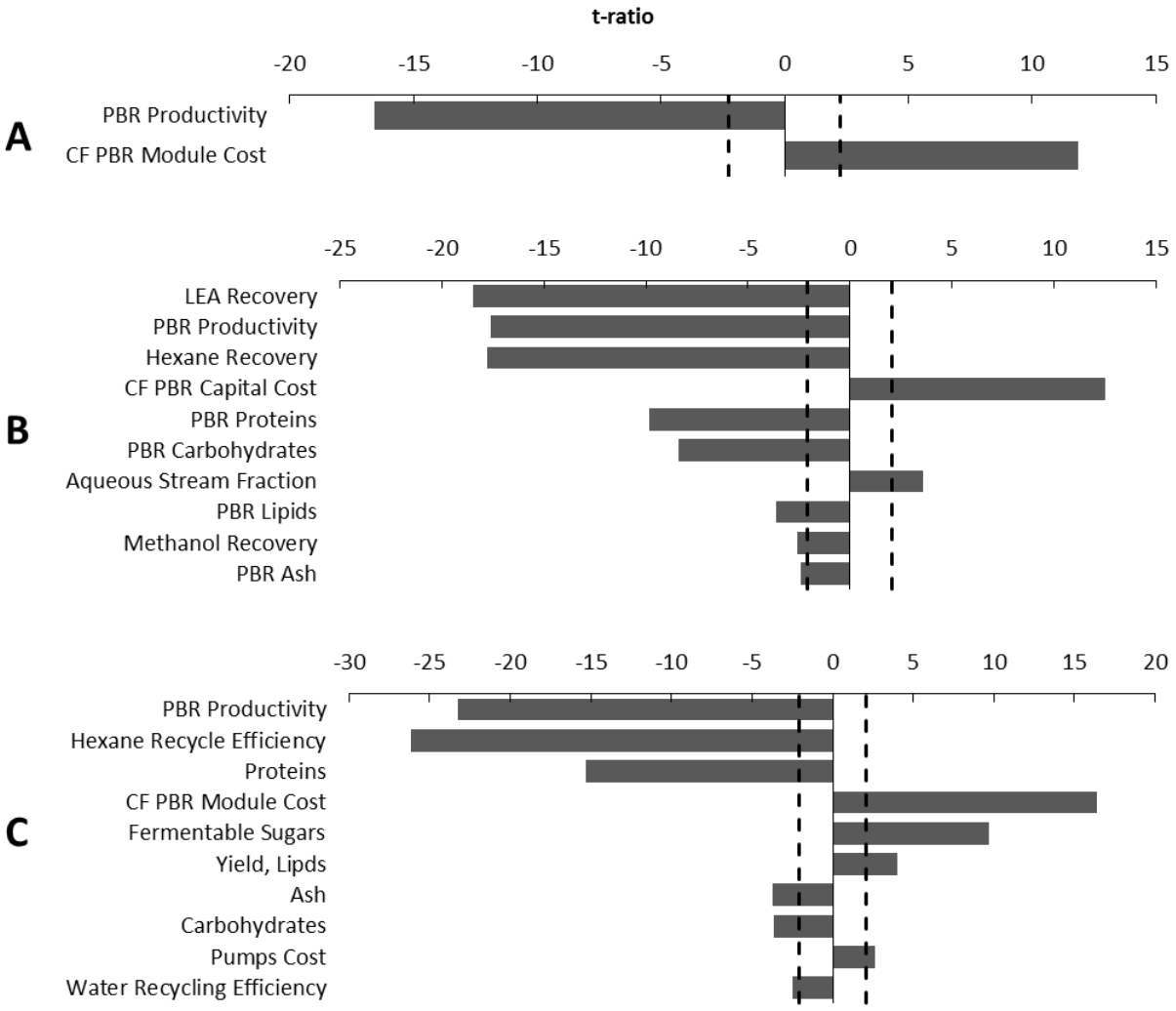

Figure A6. Sensitivity results shown were performed on the TEA work. The scenarios shown are for a constant growth architecture (CFPBR) and conversion scenarios of Drying Only (A), Lipid Extraction (B), and Fractionation (C). A statistical analysis was used to determine significant variables at a confidence interval of 95%. Vertical dashed lines indicate the critical t-value for statistical significance. Only variables that were determined significant from this analysis are included.

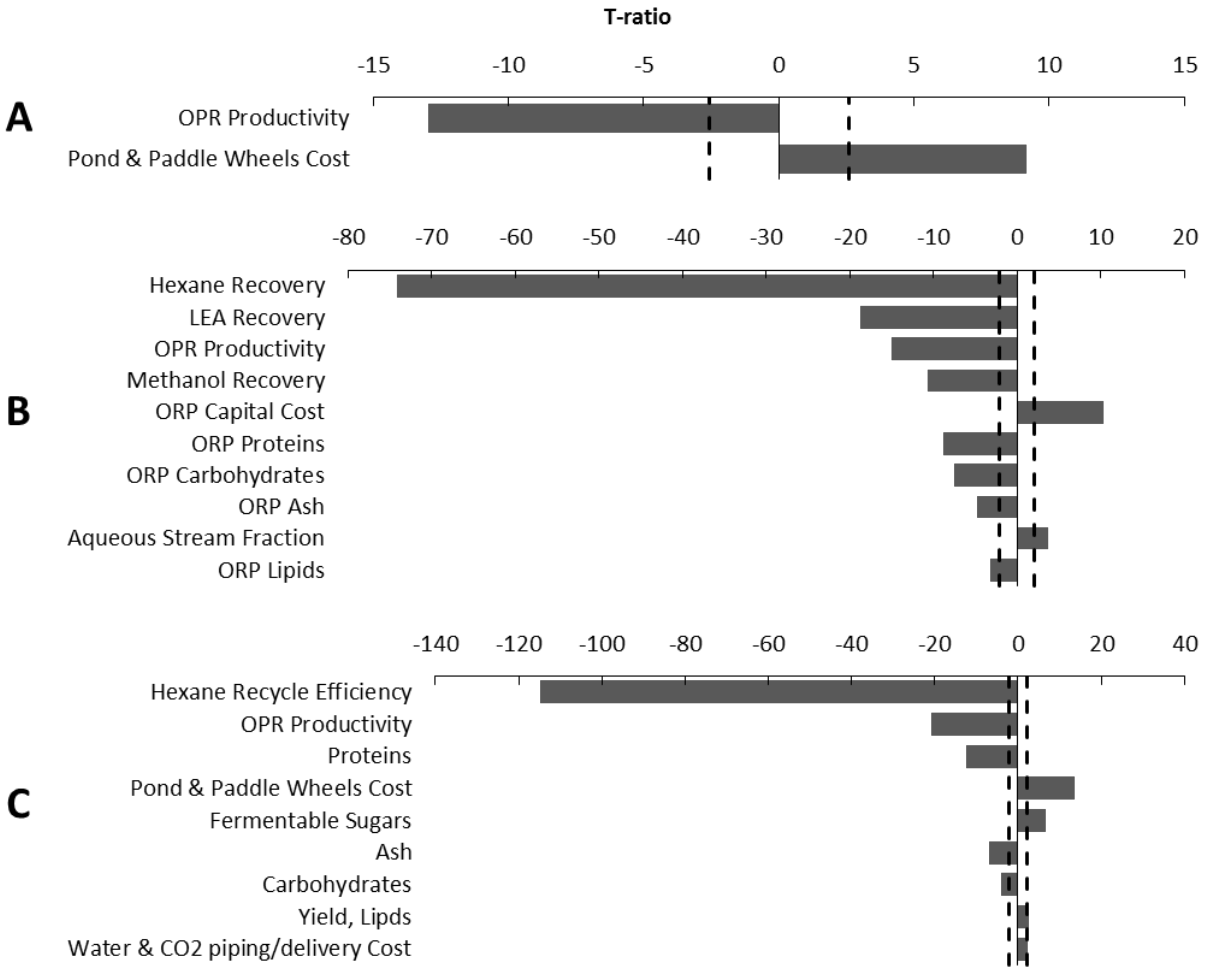

Figure A7. Sensitivity results shown were performed on the TEA work. The scenarios shown are for a constant growth architecture (ORP) and conversion scenarios of Drying Only (A), Lipid Extraction (B), and Fractionation (C). A statistical analysis was used to determine significant variables at a confidence interval of 95%. Vertical dashed lines indicate the critical t-value for statistical significance. Only variables that were determined significant from this analysis are included.

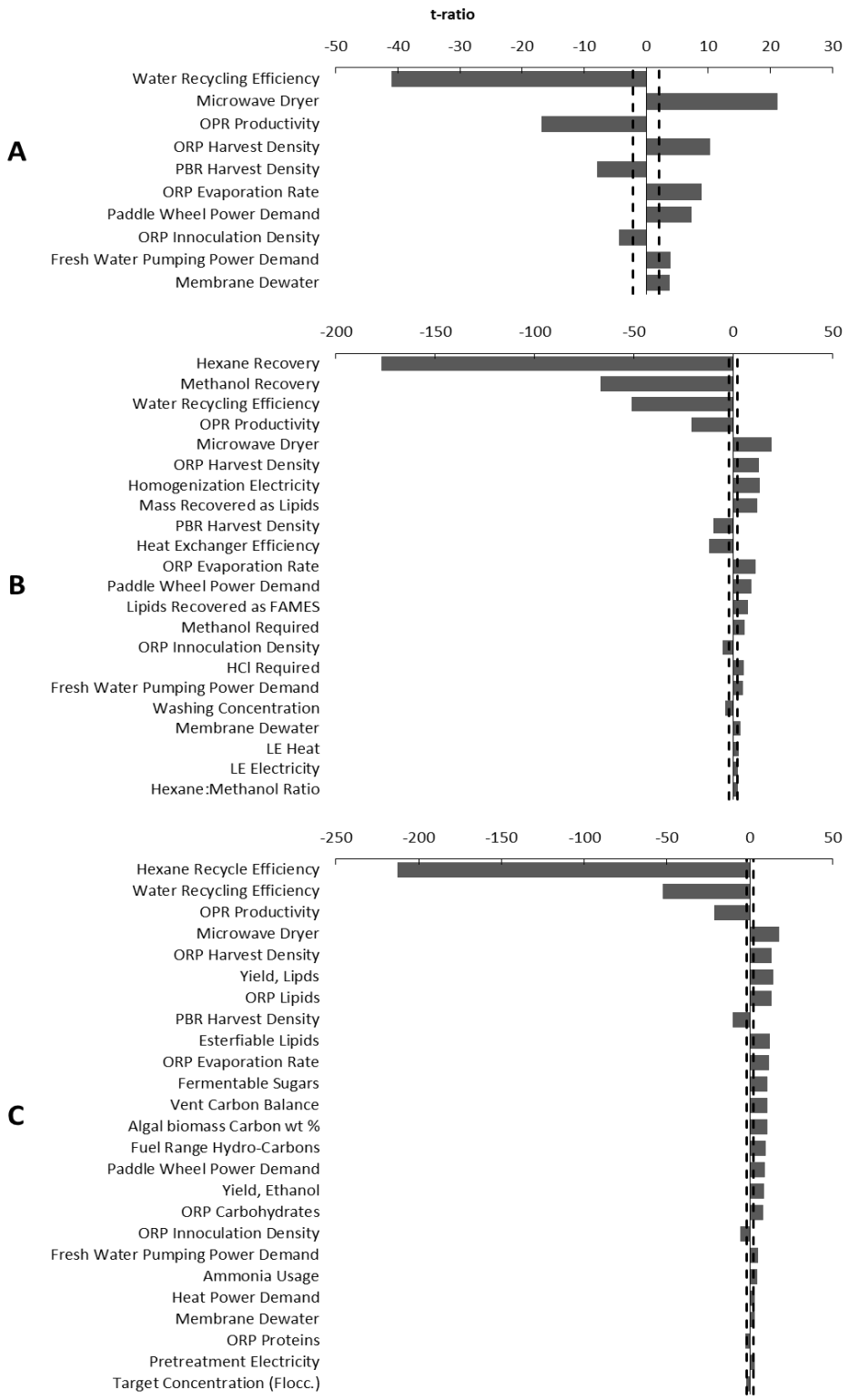

Figure A8. Sensitivity results shown were performed on the LCA work. The scenarios shown are for a constant growth architecture (Combined CFPBR/ORP) and conversion scenarios of Drying Only (A), Lipid Extraction (B), and Fractionation (C). A statistical analysis was used to determine significant variables at a confidence interval of 95%. Vertical dashed lines indicate the critical t-value for statistical significance. Only variables that were determined significant from this analysis are included.

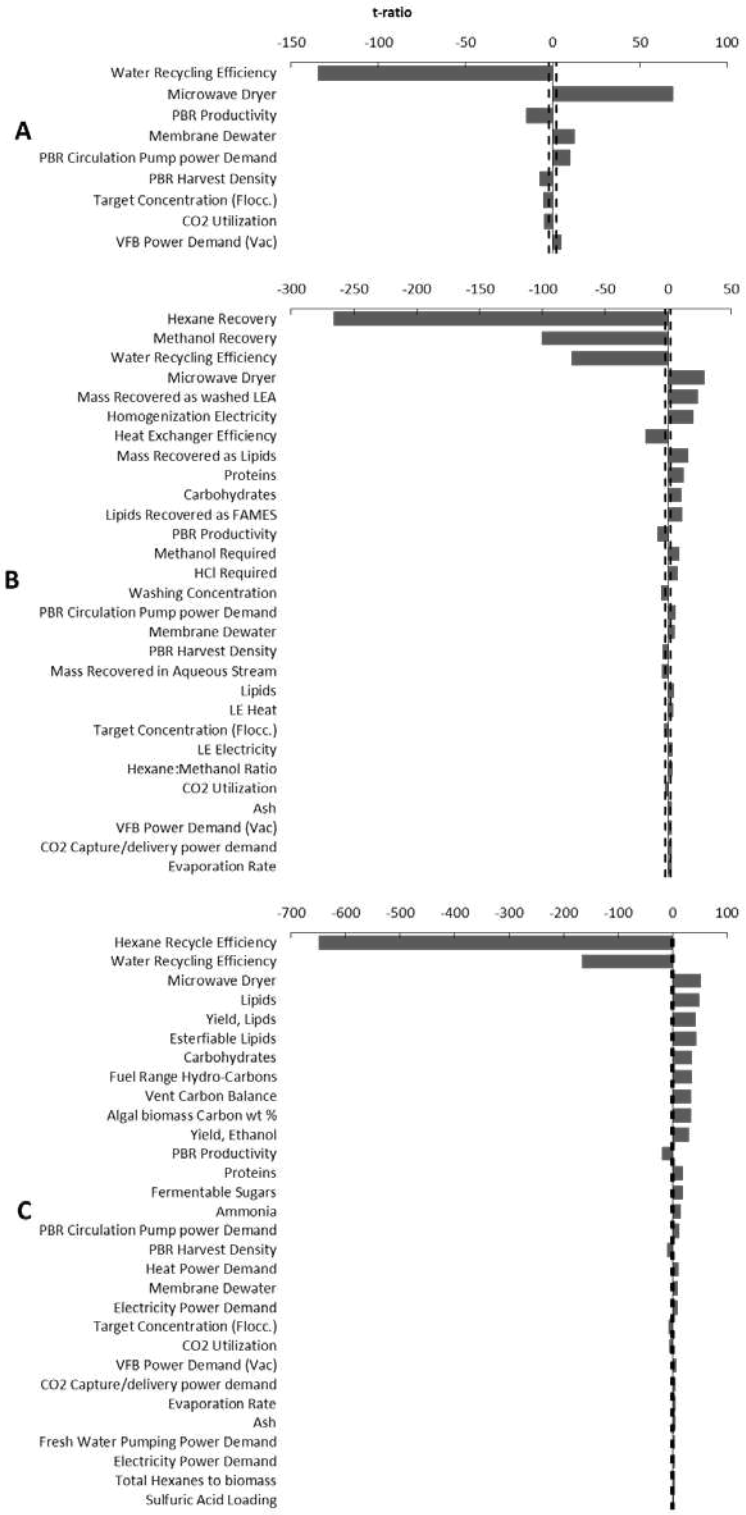

Figure A9. Sensitivity results shown were performed on the LCA work. The scenarios shown are for a constant growth architecture (CFPBR) and conversion scenarios of Drying Only (A), Lipid Extraction (B), and Fractionation (C). A statistical analysis was used to determine significant variables at a confidence interval of 95%. Vertical dashed lines indicate the critical t-value for statistical significance. Only variables that were determined significant from this analysis are included.

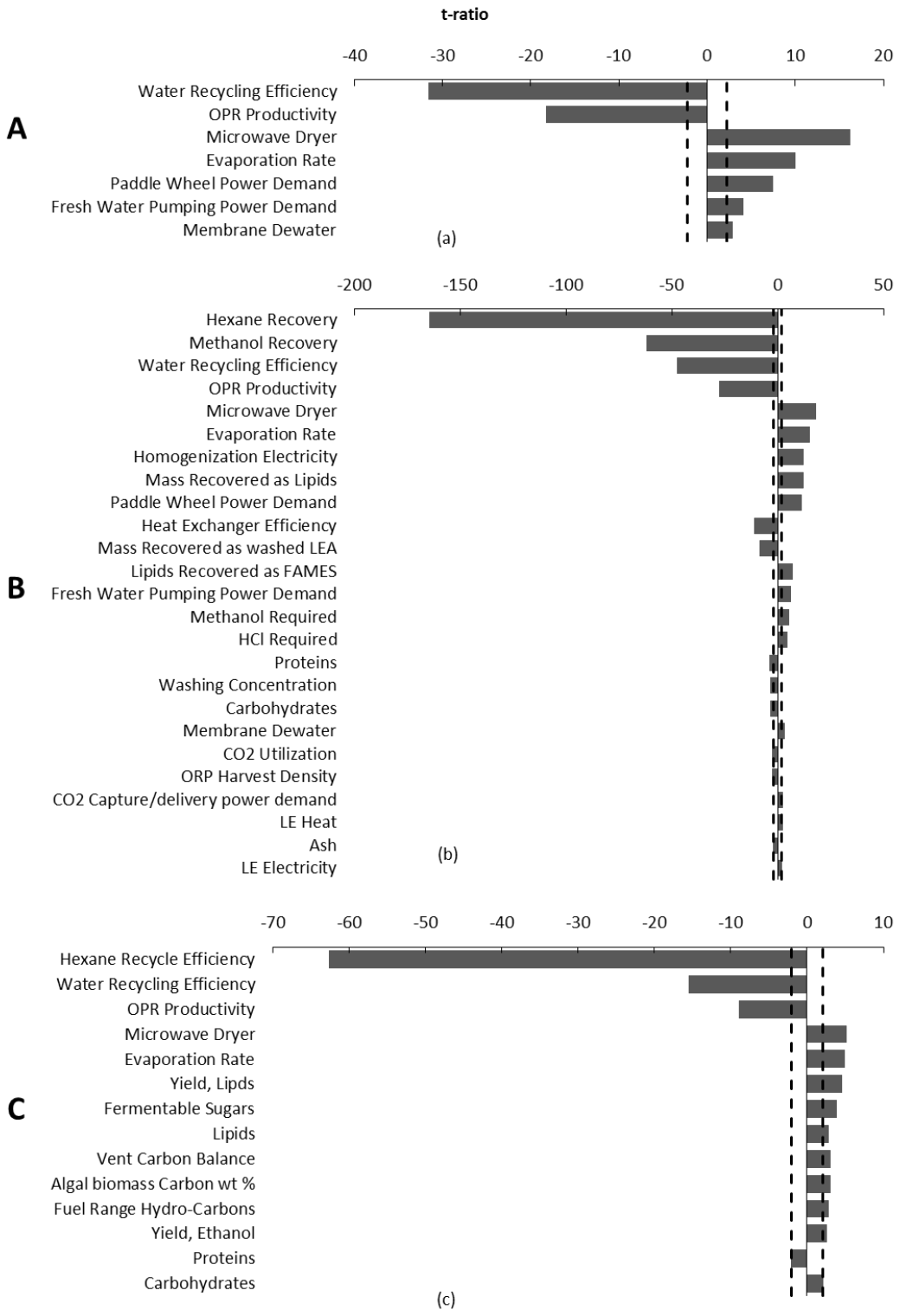

Figure A10. Sensitivity results shown were performed on the LCA work. The scenarios shown are for a constant growth architecture (ORP) and conversion scenarios of Drying Only (A), Lipid Extraction (B), and Fractionation (C). A statistical analysis was used to determine significant variables at a confidence interval of 95%. Vertical dashed lines indicate the critical t-value for statistical significance. Only variables that were determined significant from this analysis are included.

Table A2. A table depicting the material and energy flows for the Combined CF-PBR/ORP-Lipid Extraction scenario. Material consumption and production is presented on a sub-process basis.

Material and Energy Flows						
Material	Units	*PBR*	*ORP*	*Dewatering*	*Conversion*	*Bioplastic Compounding*
Cultivation Water	m3/day	129,632.03	-	-	-	-
TSP	kg/day	9,059.72	27,200.91	-	-	-
Urea	kg/day	18,155.24	54,509.34	-	-	-
Potash	kg/day	1,674.02	5,026.08	-	-	-
Flocculant	kg/hr	-	-	133.94	-	-
Methanol	kg/hr	-	-	-	848.83	-
HCl	kg/hr	-	-	-	714.50	-
Sulfuric Acid (93%)	kg/hr	-	-	-	-	-
Ammonia	kg/hr	-	-	-	-	-
DAP	kg/hr	-	-	-	-	-
n-hexane	kg/hr	-	-	-	351.00	-
Wash Water	kg/hr	-	-	-	588,391.71	-
Natural Gas	kWh/yr	-	-	-	45,460,578.89	-
Electricity (kWh/yr)	kWh/yr	16,522,532.84	28,733,062.56	5,571,734.22	46,663,943.43	60,007,815.29
CO2	kg/day	(182,342.15)	(547,464.53)		-	
Biomass Produced	kg/hr	4461.22	13397.96	-	-	-
Fuels Produced	GGE/hr	-	-	-	358.01	-
BPFS Produced	kg/hr	-	-	-	-	14,686.97

Table A3. A table depicting the assumptions for labor costs used in the work. These assumptions are taken from Davis et al. for use in this report [6].

Labor Considerations		
Parameter	Value	Units
Plant Manager	0.0003	per Ha
	155400	$/yr 2011
Plant Engineer (Civil/Env.)	0.0007	per Ha
	82590	$/yr 2011
Maintenance Supervisor	0.0003	per Ha
	60257	$/yr 2011
Maintenance Technician	5.06263E-09	Operator/ $ installed capital
	0.004	Operator/ Ha
	42286	$/yr 2011
Lab Manager	0.0003	per Ha
	59200	$/yr 2011
Lab Technician	0.0003	per Ha
	42286	$/yr 2011
Shift Supervisor	0.0013	per Ha
	50743	$/yr 2011
Module Operator (production)	0.1000	operator/pond
	35455	$/yr 2011
Module Operator (Dewatering)	5.34125E-06	operator/(m3/day)
	38523	$/yr 2011
Module Operator (Conversion)	8.44911E-08	Operator/ $ installed capital
	42286	$/yr 2011
Yard Employees	1.68982E-08	Operator/ $ installed capital
	29600	$/yr 2011
Clerks and Secretaries	0.25	person/management personel
	38057	$/yr 2011

Table A4. The assumed material and energy costs used in this report.

Material and Energy Cost Assumptions			
Material	Cost	Units	Source
Water	$ 0.32	$/m3	[49]
TSP	$ 355.00	$/tonne	[36]
Urea	$ 391.52	$/tonne	[36]
Potash	$ 376.00	$/tonne	[36]
Polyacrymalyde Flocculant	$ 2.50	$/kg	[72]
Methanol	$ 440.00	$/tonne	[73]
HCl (35%)	$ 200.00	$/tonne	[72]
Sulfuric Acid (93%)	$ 99.85	$/ton	[49]
Ammonia	$ 499.27	$/ton	[49]
DAP	$ 1,098.38	$/ton	[49]
Hexane	$ 1,078.85	$/ton	[49]
Silica	$ 2,000.00	$/ton	[49]
Clay	$ 600.00	$/ton	[49]
Hydrogen	$ 1,367.51	$/ton	[49]
Phosphoric Acid	$ 720.00	$/ton	[49]
Natural Gas	$ 0.02	$/kWh	[49]
Electricity	$ 0.06	$/kWh	[37]

Table A5. The capital costs for the CF-PBR/ORP-Lipid Extraction scenario. Other capital cost tables available upon request.

Capital Costs for Combined/LE Scenario		
Equipment	Purchased Cost	Installed Cost
Growth		
CF-PBR Modules	$ 238,952,180.71	$ 442,002,377.63
ORP		$ 203,268,951.21
Piping/Delivery		$ 36,207,281.93
Dewatering		
Recycle Water Pumps	$ 1,832,015.70	$ 2,106,818.05
Primary Settling Tank	$ 3,138,441.07	$ 3,138,441.07
Filter Press	$ 3,986,189.21	$ 3,986,189.21
UV Sterilizer	$ 4,260,029.54	$ 4,899,033.97
Lipid Extraction		
Methanol preheat HEX	$ 42,886.53	$ 128,659.59
Hexane preheat HEX	$ 263,057.49	$ 420,891.99
Pretreatment reactor	$ 7,935,641.40	$ 11,903,462.10
Pretreatment balance	$ 378,073.49	$ 378,073.49
Extraction column	$ 805,385.50	$ 1,610,770.99
Solvent recovery column	$ 250,997.99	$ 602,395.17
Solvent recovery re-boiler	$ 5,273.07	$ 17,401.12
BPFS Preparation		
Hollow-fiber Membrane Separation Unit	$ 609,228.77	$ 609,228.77
Microwave Dryer	$ 15,137,160.79	$ 19,678,309.03
Jet Mill	$ 1,224,261.29	$ 1,591,539.67
Total	$ 514,064,641.74	$ 727,678,406.63

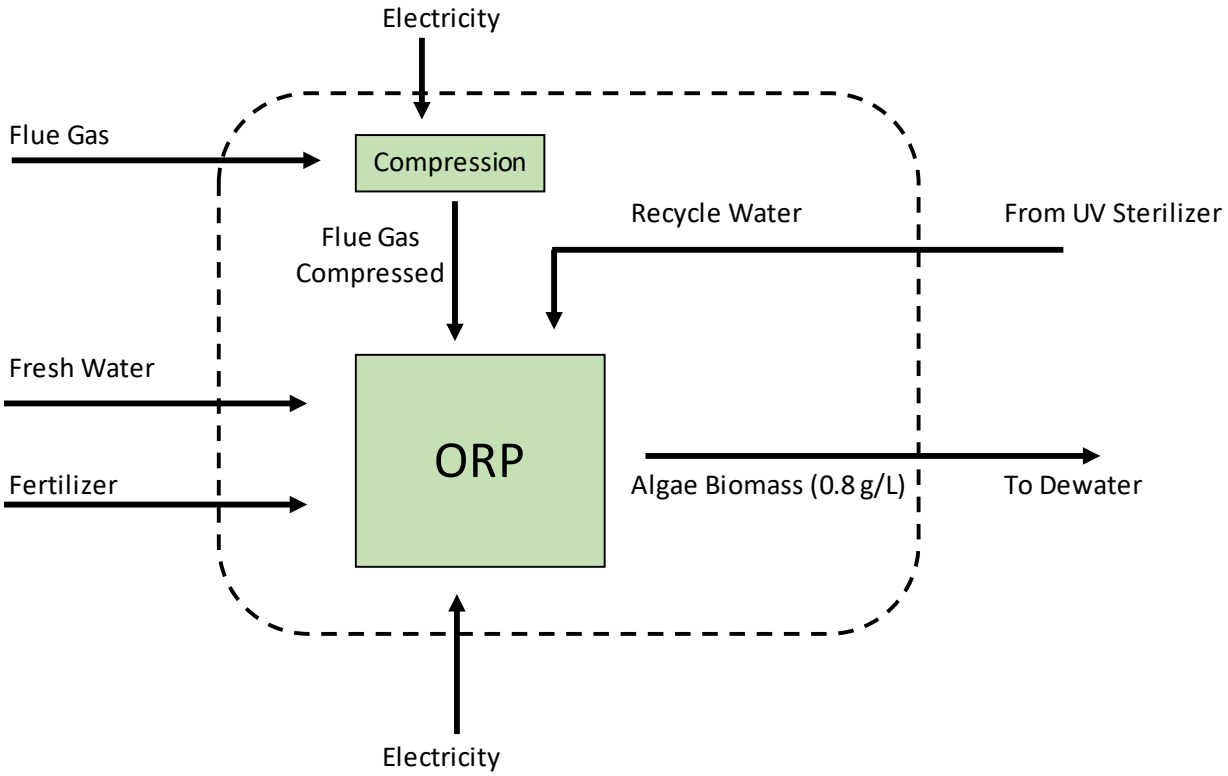

Figure A11. Sub-process flow diagram for the ORP growth scenario.

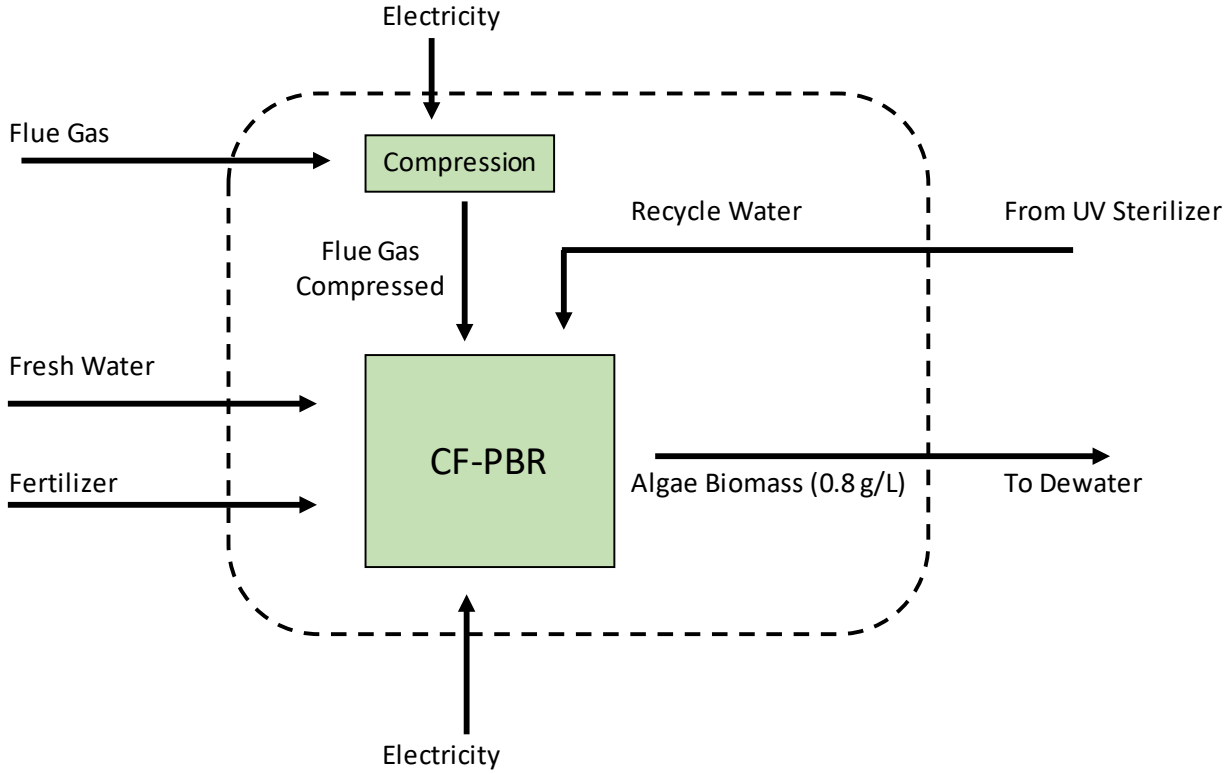

Figure A12. The Sub-process flow diagram for the CF-PBR growth architecture.

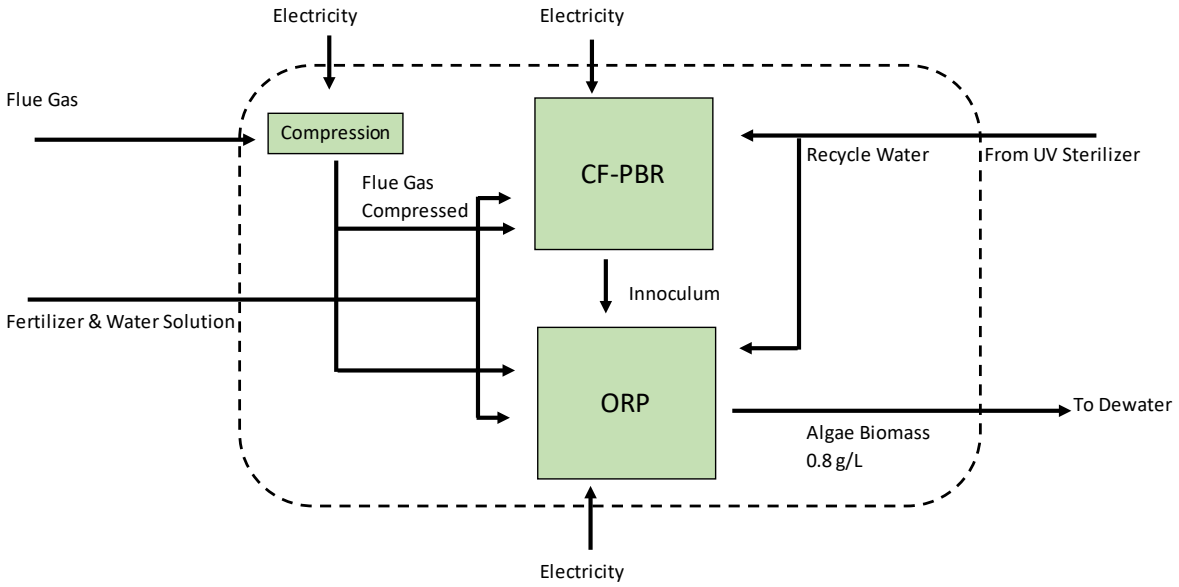

Figure A13. The sub-process flow diagram for the CF-PBR/ORP combined growth scenario.

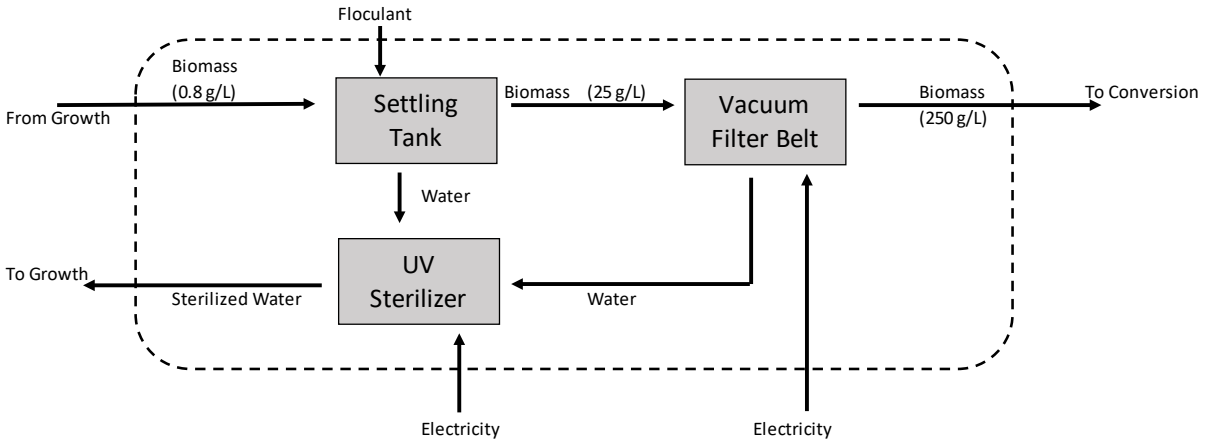

Figure A14. The sub-process diagram for biomass dewatering exiting the growth stage.

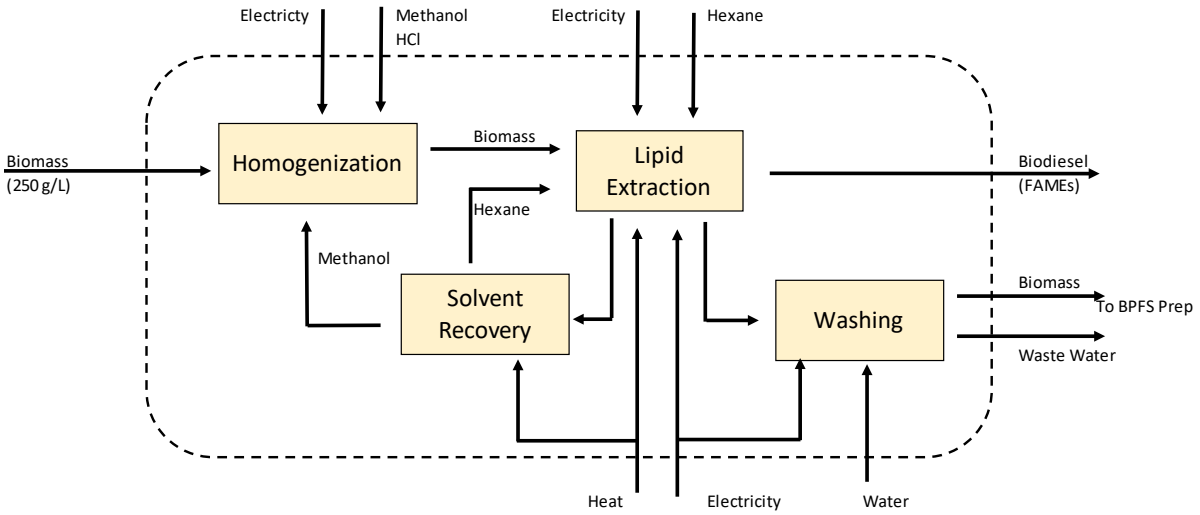

Figure A15. The sub-process diagram for the Lipid Extraction fuel conversion pathway.

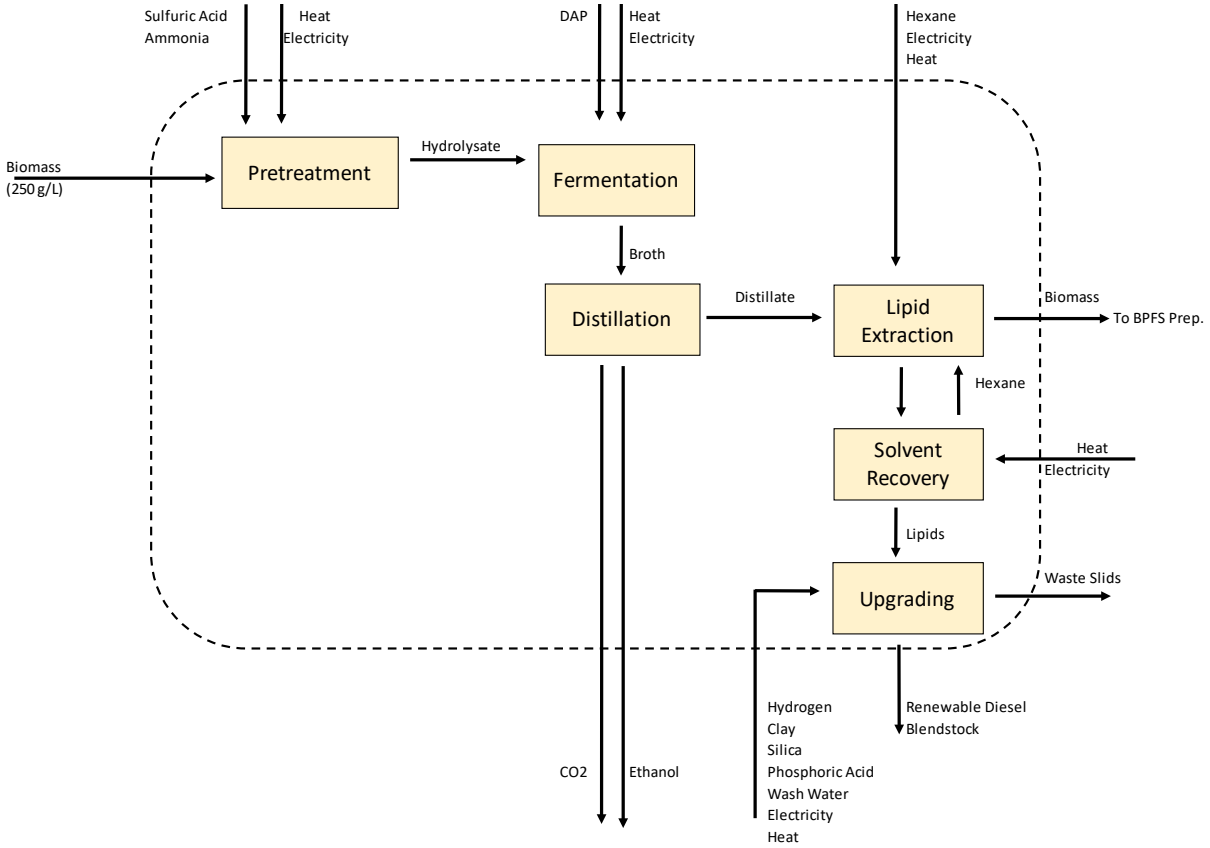

Figure A16. The sub-process diagram for the fractionation fuel conversion pathway.

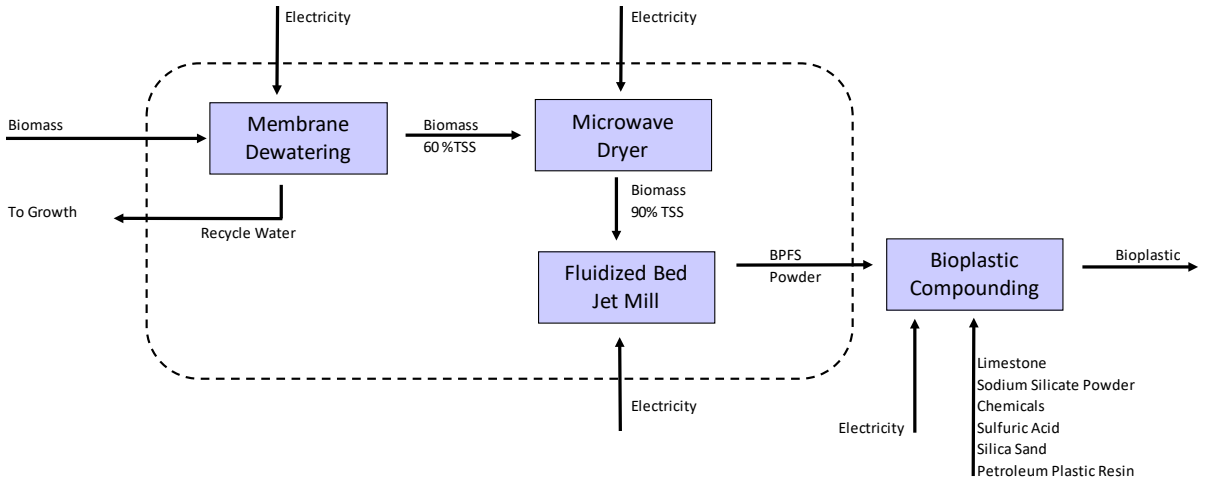

Figure A17. The sub-process diagram of the BPFS preparation process. Note how bioplastic compounding resides outside of the system boundary.