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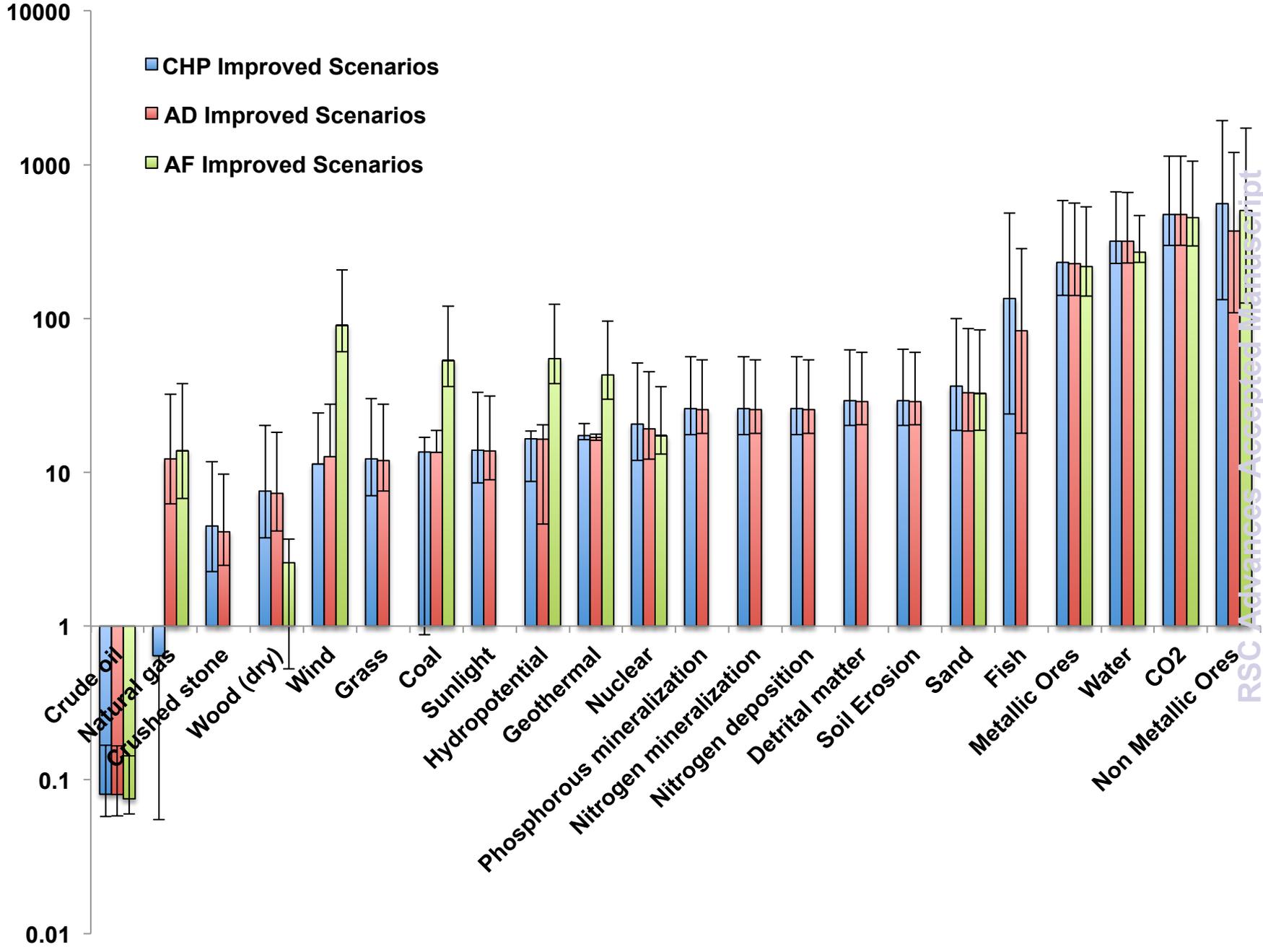
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Resource Intensity of Producing Microalgal Renewable Diesel
Relative to Petroleum Diesel



RSC Advances Accepted Manuscript

Textual abstract for the content page:

This pioneering study utilizes a hierarchical thermodynamic-based resource aggregation scheme to quantify the contribution of ecosystem goods and services to emerging microalgal biofuels life cycles.

Assessing the Critical Role of Ecological Goods and Services In Microalgal Biofuel Life Cycles

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Abstract

Microalgae bioenergy systems are gaining attention as a commercial biotechnical platform for producing renewable transportation fuels. In recent years, process-based life cycle assessment (LCA) has been extensively applied to understand the life cycle environmental impacts of emerging microalgal biofuel systems. However, conventional process-based LCA fails to account for the role of ecological goods and services within fuel and product life cycles. Additionally, traditional life cycle energy analysis suffers from several limitations such as ignoring the difference in quality and substitutability of resources, and accounting for only the first law of thermodynamics. To address these shortcomings, a hybrid Ecologically based-LCA (EcoLCA) model is developed to quantify the contribution of ecological resources within the algae-to-fuel supply chain and to compare the resource intensity of producing microalgal derived renewable diesel (RD) to that of petroleum diesel (PD). Multiple thermodynamic return on investment (ROI) metrics and performance indicators are used to quantify the consumption of ecological goods and services, environmental impacts, and resource intensity of producing microalgal RD. Results indicate that the quality corrected thermodynamic return on investment and renewability index for microalgal RD ranges from 0.17 to 0.44 and 3.51% to 6.36% respectively, depending on the choice of coproduct options and processing technologies. This work reveals that algae-to-fuel systems are highly dependent on non-renewable ecological resources reflected in their low renewability index; have a low quality corrected thermodynamic ROI (<1) and thus are not energetically viable; and are more ecologically resource intensive as compared to their petroleum equivalent—potentially negating their environmental benefits.

1. Introduction

Emerging issues of global climate change, domestic energy security concerns, and regulatory renewable fuel mandates are driving the production of low carbon biofuels¹. However, there is concern that the production of first generation biofuels—fuels derived from arable crops such as corn or soybean may displace or compete with cropland, potentially reducing the quantity of food crops available for human/livestock consumption. This could have major economic consequences including food shortages and inflation of global food prices^{2,3}. Previous analysis has also shown that first generation biofuels have marginal energy returns² and provide limited greenhouse gas (GHG) emissions reductions relative to petroleum fuels⁴⁻⁷. Additionally, the production of first generation biofuels may result in increased ecosystems degradation including impacts on biodiversity, water, soil and forest resources^{8,9}. Recently, liquid transportation fuels derived from microalgae have generated significant interest from leaders in academia, government, and industry¹⁰. Microalgae are considered a promising feedstock for conversion to liquid fuels due to their ability to capture waste carbon dioxide from industrial flue gas streams¹¹, high photosynthetic yield and lipid content¹², ability to be grown on marginal and non-arable land¹³, and potential for achieving policy mandated volumetric renewable fuel targets aimed at mitigating anthropogenic derived climate change and increasing U.S. energy independence and security.

In recent years, life-cycle assessment (LCA) has emerged as the preferential method for modeling the energy and environmental performance of biomass-to-fuel systems, and has been extensively applied to emerging microalgal biofuel and bioenergy systems¹⁴⁻²². Existing LCA of microalgae biofuel production have focused on quantifying the life-cycle greenhouse gas (GHG) emissions and life cycle energy balance for different microalgal growth configurations and fuel conversion pathways²³⁻³⁰. Additionally, prior work has investigated the impact of microalgal biofuels on nutrient and water resources³¹⁻³³, and quantified the geospatial constraints and related impacts on microalgal fuel production³⁴⁻³⁷. However, traditional energy analysis suffers from several limitations such as ignoring the difference in quality and substitutability of different resources, and accounting for only the first law of thermodynamics³⁸⁻⁴². Hierarchical thermodynamic

based approaches and metrics have been suggested to address the limitations of traditional energy analysis while concurrently providing a methodological framework for quantifying ecological resource consumption from a life-cycle perspective⁴³⁻⁴⁶. However, these have not yet been applied to study emerging microalgal biofuels. Additionally, existing sustainability assessments have ignored the contribution of ecological goods and services (EGS) or natural capital within the algal biofuel supply chain. Natural capital extends the economic notion of capital to include goods and services provided by ecosystems and the natural environment, which are essential to sustaining human and ecological life—such as: timber, food, water, energy resources, clean air, minerals and ores, purification of air and water resources, flood and drought mitigation, pollination of crops and vegetation, maintenance of global biodiversity, as well as climate and disease regulation. Despite the critical importance of EGS to human and global welfare, most existing measures of sustainability do not account for the role/consumption of EGS within product or fuel life cycles^{39, 43, 44}.

Ecological Goods and Services

Pre-industrial revolution, the paradigm of environmental awareness operated under the assumption that the global ecosphere would be able to absorb the totality of anthropogenic-derived pollution and resource degradation without widespread negative consequences for human life or the environment. However, in recent decades research has reported accelerated degradation of numerous ecosystem goods and services as a direct consequence of economic development and human activity⁴⁷. There is increasing realization that anthropogenic-derived environmental impacts can cause irreparable damage to the world's ecosystems and strain the natural ecological functions that support human life⁴⁸.

In 2001, the United Nations (UN) initiated the millennium ecosystem assessment (MEA)—an international collaboration designed to assess the impact and widespread consequences of environmental change for human and ecological well-being. The MEA developed a scientifically rigorous framework for assessing the impacts of environmental change in coupled dynamic socio-ecological systems, and provided guidelines for policy

measures and human action required for the conservation and long-term sustainability of the earth's biosphere⁴⁹. Published in 2005, the findings of the MEA indicate that in the second half of the 20th century anthropogenic-derived resource degradation and overconsumption of natural capital have changed ecosystems more rapidly and extensively than in any comparable period in human history⁴⁹. Results from the MEA study indicate that 6 out of the 11 global ecological provisioning services, 7 out of the 10 ecological regulating services, and 2 out of the examined 3 ecological cultural services have been severely degraded over the past 50 years. Furthermore, the results of the MEA indicate that anthropogenic derived environmental impacts have resulted in loss of global biodiversity, and may impair the ability of the planet's ecosystems to sustain human life. Clearly, it is imperative that sustainability assessments consider the consumption of ecological goods and services within biofuel life cycles at early stages of research and development, so as to avoid or mitigate any potential widespread negative impacts for human and global ecological welfare that may result as a consequence of full-scale commercialization of these fuels.

2. Hybrid Ecologically Based LCA Methodology and Metrics

EcoLCA is an environmentally extended input-output model capable of accounting for the consumption/role of ecosystem goods and services in a life cycle framework^{38, 41, 50}. This work extends the EcoLCA framework developed by Bakshi and colleagues to study the environmental sustainability of emerging microalgal biofuel systems^{43, 44}. The hybrid framework developed in this study utilizes the 2002 EcoLCA model to quantify ecosystem/economy wide impacts, while a detail process inventory is used to assess direct material, energy, and ecological impacts of biofuel production. By integrating process and EcoLCA models, we quantify the total life cycle impacts of microalgal biofuel production. Figure 1 presents an overview of the hybrid EcoLCA framework utilized in the present study.

Hybrid EcoLCA Framework

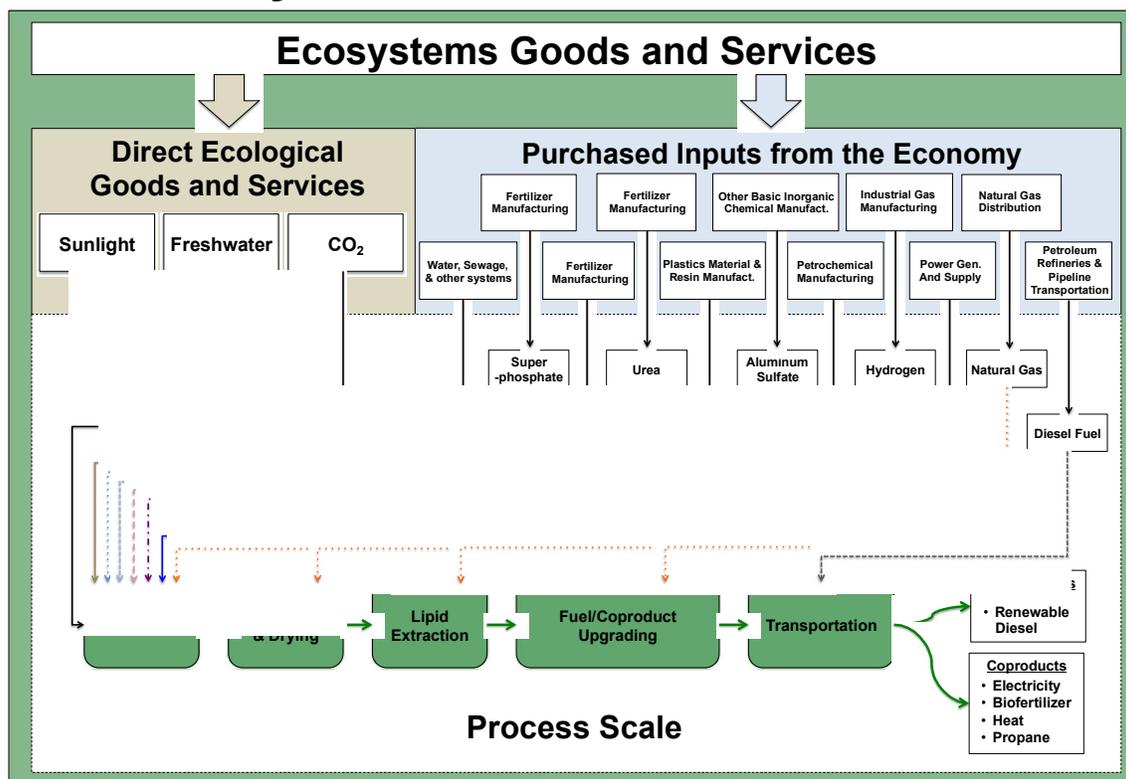


Figure 1 – Hybrid EcoLCA Framework for Microalgal Biofuels

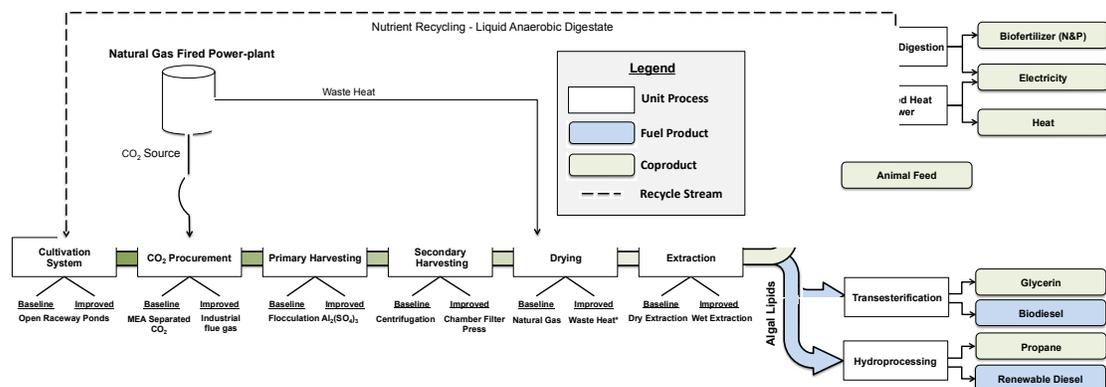
In this work, we develop a hybrid EcoLCA model to quantify the contribution of ecological resources within the algae-to-fuel life cycle, and to compare the resource intensity of producing microalgal derived renewable diesel and biodiesel to that of traditional petroleum diesel. Furthermore, a host of hierarchical thermodynamic metrics is utilized to address the shortcomings of existing life cycle energy analysis and provide novel insights into the environmental performance and sustainability of emerging microalgal biofuel systems. Renewable diesel also known as “green diesel” is an infrastructure compatible biofuel produced via hydrotreating of algal lipids. RD is attractive as a fuel product because of its high energy density, cetane number, and storage stability⁵¹. Furthermore, RD is fungible with petroleum diesel and as such can be used in current commercial vehicle fleets and fuel infrastructure. The main paper provides an in-depth analysis of microalgal derived RD; results for microalgal biodiesel are provided in the Supporting Information (SI).

Process model

A detailed process model was developed to quantify the direct material, energy, and ecological inputs for producing algal derived renewable diesel and biodiesel via a theoretical integrated open raceway pond (ORP) biorefinery operating in Phoenix, AZ^{23, 34}. Two technological routes, baseline and improved scenarios, spanning a large feasibility space were evaluated for biofuel production. Baseline scenarios represent current commercial day refining and processing technologies, while improved scenarios represent technological options which have undergone pilot scale experimentation but whose feasibility on a commercial scale has yet to be determined.

Algal growth rates were developed based on monthly average meteorological and climate parameters obtained from the National Solar Radiation Database (NSRD)⁵² and National Oceanic and Atmospheric Administration (NOAA)⁵³ as well as biomass composition and photosynthetic efficiency terms^{12, 34, 54}. The fractional composition of the algal biomass was assumed to be 25% lipids (L), 28% carbohydrates (C), and 47% proteins (P)⁵⁴. The molecular composition of the biomass fractions was constructed based on the work of Lardon et al. 2009¹⁵. It was assumed that the integrated ORP biorefinery operates for eight months out of the calendar year. Furthermore, the biorefinery is constructed on a 1000 hectare plot of land in which 500 hectares are allocated for open raceways ponds and 500 hectares for infrastructure requirements.

The modeled biomass-to-biofuel production chain consists of the following sub-modules: cultivation, CO₂ procurement, primary harvesting, secondary harvesting, drying, lipid extraction, coproduct and fuel conversion, and transportation. An overview of the biomass-to-fuel process chain along with technological routes examined in this work is provided in Figure 2.



*Waste heat from a colocated power plant is utilized to dry the residual deoiled biomass (RDB) prior to combustion via CHP as well as algal derived biofertilizer and animal feed prior to transportation.

Figure 2 – Microalgae to fuel process chain

It was assumed that the algal biorefinery would be co-located with a natural gas (NG) fired power plant, which would provide industrial flue gas as a carbon source for algal growth. In the biomass-to-biofuel model, two process options are evaluated for CO₂ procurement. In the baseline scenario(s) industrial flue gas is separated into pure CO₂ via monoethanolamine scrubbing, this pure CO₂ is then compressed and injected into the algae ponds. In the improved scenario(s) industrial flue gas is directly compressed from the NG fired powerplant and pumped into the ORP via low-pressure blowers. Process energy requirements for flue gas/CO₂ compression and transportation were constructed based on the work of Kadam 2002⁵⁵. While the use of industrial flue gas may reduce the high resource and energy demands associated with CO₂ procurement, there is high technological uncertainty regarding the feasibility of direct injection of industrial flue gas and its effects on the microalgal culture⁵⁶⁻⁵⁸.

Inputs for the cultivation of microalgae include: sunlight, freshwater, high density polyethylene (HDPE) pond liner, urea (N-fertilizer), super phosphate (P-fertilizer), potassium chloride (K-fertilizer), industrial flue gas, and electricity required for pumping and water movement as well as for the compression and transportation of industrial flue gas/CO₂. It was assumed that a HDPE pond liner would be used to line the ORP³², and paddlewheels are utilized for circulating the algal growth medium. Energy requirements for sourcing ground/surface water were developed based on the 2008 Farm and Ranch Irrigation Survey⁵⁹. Energy requirements for circulation of pond medium and pumping

between various system components was developed based on the Darcy-Weisbach equation. Additionally, factors such as water loss due to evaporation, pond leaking, pond blowdown, as well as the embodied impacts of the HDPE pond liner are also considered in the algae-to-fuel model³⁴.

After cultivation, the algal biomass undergoes chemical flocculation via the addition of aluminum sulfate. In the baseline scenario the flocculated algae is further dewatered via a decanter centrifuge, resulting in a solids content of 22% (w/w). In the improved scenarios chamber filter presses are utilized as a means of dewatering the biomass; resulting in a final solids content of 25% weight by weight (w/w). It was assumed that the environmental impacts for the membrane replacement/regeneration are negligible as compared to operating costs, and thus was not considered in the analysis. Process requirements for the harvesting stage were developed based on prior pilot scale tests as well as peer-reviewed and technical literature⁶⁰⁻⁶². Post harvesting, in the base-case scenario thermal dewatering via combustion of natural gas is performed to dry the algal slurry to a 90% solids content¹⁵. Hexane extraction is then utilized to separate the non-lipid and lipid fraction(s) of the algal biomass. In the improved scenario(s), liquid-liquid (wet) extraction via countercurrent circulation of n-hexane is utilized to separate the lipid and non-lipid fractions of the biomass^{23, 63}. In both technological routes, the extracted lipids are either hydrotreated using hydrogen to produce algal derived renewable diesel as well as coproduct propane or transesterified to produce algal biodiesel and coproduct glycerin. Three process options are considered for the non-lipid fraction of the algal biomass: (1) use as an animal feed, (2) anaerobic digestion of residual de-oiled biomass (RDB) to produce bioelectricity as well as biofertilizer, and (3) cogeneration of RDB via combined heat and power (CHP) to produce bioelectricity and heat. Efficiencies were considered at each stage in the algae-to-fuel process chain including: 75% nutrient uptake efficiency³⁴, 70% CO₂ utilization efficiency²⁹, 5% harvesting product loss for centrifugation and chamber filter presses³⁰, 90% process medium recycling for 1st and 2nd stage harvesting³¹, 95% lipid extraction and conversion efficiency for wet extraction pathways⁶³ and 97% lipid extraction and conversion efficiency for dry extraction pathways⁶⁴, 5% nitrogen volatilization for recycling of liquid anaerobic digestate⁶³, and a

25% electrical and 56.3% heat conversion efficiency for combustion of RDB in a combined heat and power plant⁶⁵. Detailed process level inventory and model parameters are provided in the Supporting Information.

EcoLCA model

The EcoLCA model is constructed based on the 2002 input-output (IO) model of the U.S. economy. Input-output models, first developed by Nobel laureate Wassily Leontief, provide a mathematical framework for quantifying the inter-industry transactions between different sectors in an economy or a region. The EcoLCA model extends the IO framework to quantify the direct and indirect environmental impacts that result from economic activities via translating the monetary flows of purchased inputs from the economy to ecological and natural resource consumption, emissions, land-use, and other environmental impact categories via the use of monetary to resource use or emission ratios for industrial sectors⁶⁶. As such, information regarding sector-wide economic activity is required to run the EcoLCA model. The economic activity for specific industrial sectors was calculated by translating the resource flows as developed in the process inventory with their corresponding 2002 producer price and aggregating the results. If the 2002 producer price was not available a price inflator was used to convert to the 2002 price equivalent⁶⁷. Additionally, EcoLCA does not consider the use phase of purchased inputs from the economy as well as direct ecological good and services that are consumed at the process scale³⁸. Therefore, economy wide environmental impacts obtained from EcoLCA must be integrated with environmental burdens at the process scale to obtain data on a life-cycle basis. Price data for inputs, as well as detailed material and energy flows are provided in the Supporting Information.

Thermodynamic return on investment:

A host of metrics have been utilized in LCA to quantify and compare the energy intensity of producing transportation fuel(s) from petroleum and biomass feedstocks⁶⁸⁻⁷⁰.

Traditional energy metrics, such as energy return on investment (EROI), compare the quantity of primary energy required to produce a functional unit of transportation fuel energy—evaluated over the life cycle⁷¹⁻⁷³. As the primary function of biofuels lies in their

utility to displace petroleum-derived liquid fuels, a fossil-based EROI metric is relevant for measuring and benchmarking the performance and sustainability of emerging microalgal biofuel systems. In this study, $EROI_{fossil}$ is defined as the ratio of output fuel energy to the non-renewable primary energy required for its production, and is provided in equation 1:

$$EROI_{fossil} = \frac{(Lower\ Heating\ Value\ x\ Mass\ of\ Biofuel)}{\Sigma Nonrenewable\ Primary\ Energy} \quad (1)$$

Common energy metrics such as EROI and variants are often used due to their intuitive appeal and ease of comparison with existing studies. However, these traditional energy metrics implicitly assume that all forms of primary energy are fungible, i.e. the heating value of different primary energy resources such as crude oil, coal, natural gas, uranium, solar, wind, tidal, biomass, and geothermal are perfectly substitutable, have the same work-potential, and thus may be added together and represented via a single aggregate metric⁷⁴. This traditional aggregation of different primary energy sources has several limitations including: (1) accounting for only the first law of thermodynamics, (2) assuming perfect substitutability between resources, and (3) failing to account for resource quality; and thus has led some researchers to question the utility of the resulting metrics and their ability for informing decision making⁷⁴.

Exergy analysis has been proposed and utilized to address some of these shortcomings⁴⁰. Exergy represents the maximum amount of useful work that can be extracted from a system (or resource) when it is brought into thermodynamic equilibrium with the surrounding environment or reference state⁴⁰. The presence of exergy destruction in a system indicates the possibility of a thermodynamic improvement; thus exergy analysis has been widely used in process engineering for optimizing industrial operations and commercial processes⁴⁰. Exergy is appealing from a methodological standpoint since it considers both the first and second law of thermodynamics, and can aggregate material and energy resources using a common denominator (joules). As such, aggregating primary energy sources based on *exergy* provides a better representation of the ability of these resources to produce useful work—as compared to *energy*. The quantity of exergy consumed throughout the industrial supply chain is defined as the Industrial Cumulative

Exergy Consumption (ICEC). Analogous to $EROI_{\text{fossil}}$, the fossil exergy return on investment ($ExROI_{\text{fossil}}$) for a fuel is defined as the ratio of output exergy of the fuel product to the non-renewable ICEC required for its production and is provided in equation 2:

$$ExROI_{\text{Fossil}} = \frac{\text{Exergy of Biofuel}}{\sum \text{Nonrenewable ICEC}} \quad (2)$$

While traditional exergy analysis overcomes many of the shortcomings of energy analysis, it does not account for the quality of different energy or material resources, nor does it consider the contribution of ecosystems in making ecological goods and services available for human and industrial activities. As natural capital provides the basis for human made capital, quantifying the consumption of ecological goods and services across the life cycle is critical for determining the sustainability of emerging microalgal biofuels.

Odum developed a methodological framework built upon principles and concepts from thermodynamics, general systems theory, and systems ecology to understand the dynamic transformation of energy and resource flows within human-ecological systems, in what is formally known today as *emergy*⁷⁵. Odum observed that, in regards to the ‘global energy budget’, incident solar exergy becomes concentrated in as it flows through human-ecological systems. Analogous to energy pyramids commonly used in traditional ecological and food-chain modeling, emergy analysis posits that a hierarchical energy structure exists in human-ecological systems in which dilute sunlight is converted to plant matter, from plant matter to coal, from coal to oil, to electricity and other products, and finally to human made goods and services⁷⁶. Therefore, the utility of a resource as well as the ability of an energy carrier to provide useful work are measured in respect to both quantity (MJ, kWh, BTU, kg, etc.) and quality—the amount of available energy of one kind of a lower grade required to develop the higher grade⁷⁶. Emergy is formally defined as “the amount of available energy of one kind that is used up in transformations directly and indirectly to generate a product or service”, and is typically expressed in terms of solar equivalent joules (sej)⁷⁵. Emergy analysis provides an objective basis for comparing energy and material resources by assessing the direct and indirect past solar

energy required for their production. The ratio of emergy input to exergy output of a product or service is defined as *transformity*, expressed in equation (3)

$$\text{Transformity} = \frac{\text{Emergy Input}}{\text{Exergy Output}} \quad (3)$$

By definition transformity evaluates the amount of emergy required to create a unit of available energy (*exergy*) of another form. As such, transformity provides a quantitative measure for determining and ranking the quality of different energy and material resources. The amount of past solar exergy that is consumed throughout the ecological and industrial supply chain is referred to as ecological cumulative exergy consumption (ECEC), and is equivalent to emergy if the same system boundary and accounting procedures are chosen³⁹. Furthermore, a fuels emergy return on investment (EmROI), analogous to the prior return on investment (ROI) metrics, is defined below in equation 4:

$$\text{EmROI} = \frac{(\text{Exergy of Biofuel}) \times \tau_{\max}}{\sum \text{ECEC}} \quad (4)$$

Where τ_{\max} is the maximum transformity for fuels with the same functionality or usefulness, and is used to adjust for the quality of the output fuel exergy so that it is comparable to other products within the same functional group or class⁴¹. In this study, the transformity of petroleum diesel is used for τ_{\max} . EmROI represents the amount of quality-adjusted thermodynamic work potential generated per unit work (sej) invested via the economy.

While the emergy methodology has distinct advantages over traditional energy and exergy analysis, uncertainty in reported transformity values and misperception regarding emergy accounting has limited its widespread adoption⁷⁷. Nevertheless, emergy intrinsically considers differences in the quality and substitutability of resources, and provides a consistent, scientifically rigorous, and eco-centric framework for valuing the contribution of ecological processes and natural capital⁷⁸. However, as energy, exergy, and emergy analysis all offer unique insights regarding the sustainability of a product or service, a hierarchy of sustainability and performance indicators based on these thermodynamic metrics may be preferable.

Thermodynamic based Sustainability Metrics:

In this work a variety of thermodynamic return on investment metrics, sustainability indicators, and renewability indices based off of energy, exergy and emergy analysis are used to quantify the consumption of ecological goods and services, environmental impacts, and resource intensity of producing microalgal derived fuels. Several performance metrics based on ECEC analysis including: ECEC Yield Ratio (EYR), Environmental Loading Ratio (ELR), Yield-to-Loading Ratio (YLR), and Renewability Index (R) are used to assess the sustainability of transportation fuel production and are formally defined and summarized in Table 1.

Performance Metrics	Formula	Definition & Implication
Direct Inputs (DI)		ECEC of direct inputs from nature. For microalgal biofuel systems direct inputs include: sunlight, water, and photosynthetic CO ₂ .
Indirect Inputs (II)		ECEC of purchased inputs from the economy. For microalgal biofuel systems purchased inputs from the economy includes fertilizers, electricity, natural gas, wastewater treatment, hexane, hydrogen, diesel, HDPE pond liner, and other material and energy products considered in the biomass-to-fuel process chain.
Inputs from Non-Renewable Resources (NR)		ECEC of direct and purchased inputs from non-renewable resources. Includes direct and indirect ECEC consumed via metallic ores: Fe, Cu, Cr, Au, Pb, Zn, Ag, Mo, Ti, Al; sand and stone; non-metallic ores: apatite, clay, gypsum, feldspar, garnet, potash, salt, soda ash, diatomite, barite, talc, pumice, perlite, mica, quick lime, and other non-metallic ores; and non-renewable energy: nuclear, coal, natural gas, and crude oil.
Inputs from Renewable Resources (REN)		ECEC of direct and purchased inputs from renewable resources. Includes direct and indirect ECEC consumed via ecological regulation and maintenance services: detrital matter, photosynthetic CO ₂ , pollination, nitrogen and phosphorous mineralization, nitrogen deposition from the atmosphere; ecological provisioning services: wood, fish, soil, grass, water; and renewable energy: hydropower, wind, geothermal, and sunlight.
Yield (Y)	$Y = DI + II$ $= NR + Ren$	Sum of ECEC consumed from purchased inputs from the economy and ECEC of direct inputs from nature. Yield is equivalent to the sum of direct and indirect renewable and non-renewable ECEC consumed in the ecological supply chain.
ECEC Yield Ratio (EYR)	$EYR = \frac{Y}{II}$	Ratio of total ECEC to ECEC embodied in purchased inputs from the economy. The EYR indicates how much work is invested by the economy in converting natural resources into goods and services. A large EYR (>1) indicates that less ECEC is provided via purchased inputs from the economy relative to direct inputs from the nature in the production of a good or service.
Environmental Loading Ratio (ELR)	$ELR = \frac{NR}{REN}$	Ratio of ECEC of inputs from non-renewable resources to ECEC of inputs from renewable resources. ELR provides a measure of the stress on the environment due to a transformation or process. Values for ELR greater than unity indicate there is a higher reliance on non-renewable resources as compared to renewable resources. Thus, an ELR less than one is desired as it indicates that a product or services is more dependent on renewable resources.
Yield-to-Loading Ratio (YLR)	$YLR = \frac{EYR}{ELR}$	Ratio of ECEC yield ratio to environmental loading ratio. The ratio of the yield ratio to environmental loading ratio has been suggested as an index for determining the sustainability of a product or service. YLR considers the contribution of a resource or process to the economy per unit of environmental loading, thus an YLR value greater than one is preferred.
Renewability Index % (R)	$R = \frac{REN}{Y} \times 100$	Ratio of renewable ECEC to Yield. Renewability Index provides a measure of the relative contribution of renewable ecological resources in the production of a product or service.

Table 1 – ECEC based Sustainability and Performance Indicators

3. Results and Discussion

Thermodynamic Return on Investment:

Figure 3 presents thermodynamic return on investment metrics for the production of microalgal RD via current day commercial technologies (baseline scenarios) and optimistic future technologies (improved scenarios) under several coproduct scenarios, and compares the results with petroleum diesel. For $EROI_{\text{fossil}}$, $ExROI_{\text{fossil}}$, or $EmROI$ a value greater than one is desirable as it indicates that more work is produced per functional unit via the fuel system relative to the work invested for its production. Comparison of these thermodynamic metrics across multiple microalgal biofuel processing technologies and coproduct options provides unique perspectives on the performance and environmental sustainability of current and future microalgal biofuel systems at both the industrial and coupled industrial-ecological scale.

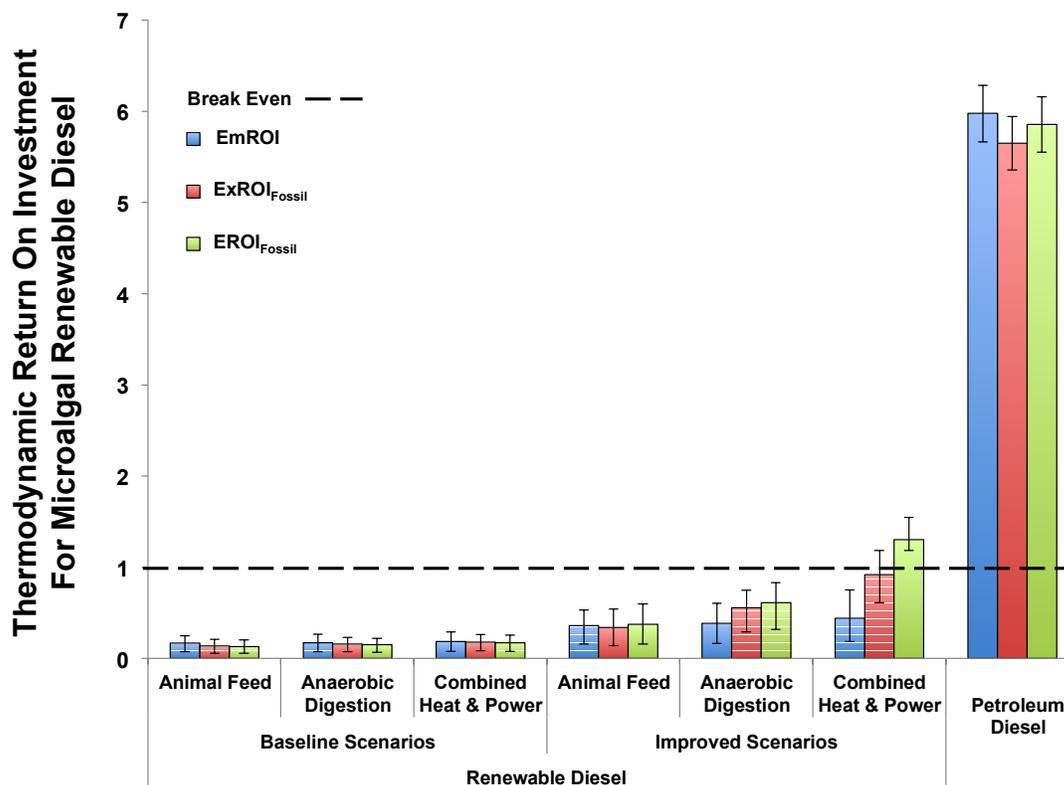


Figure 3 - Thermodynamic return on investment metrics. Error bars for baseline and improved scenarios represent the results for high (40% L / 50% C / 10% P) and low lipid (10% L / 20% C / 70% P) biomass composition. Error bars for petroleum diesel represent the range obtained via market and mass based allocation.

The results reveal that current day microalgal RD production has a low return on investment ($ROI < 1$) for all examined thermodynamic metrics and coproduct scenarios, and is a consequence of the exceedingly resource intensive stages in the algae-to-fuel process chain: including the high energy requirements for water circulation and pumping in the ORP system³², dewatering and harvesting operations⁷⁹, high upstream impacts of synthetic fertilizers⁸⁰, CO₂ procurement³⁴, and drying. Future and optimistic processing technologies (improved scenarios) offer superior ROI but are plagued with high technological uncertainty as these scenarios have yet to be effectively demonstrated at a commercial scale. Error bars for baseline and improved scenarios represent the results for high (40% L / 50% C / 10% P) and low lipid (10% L / 20% C / 70% P) biomass composition, while error bars for petroleum diesel represent the range obtained via market and mass based allocation. The results from Figure 3 indicate only one of the evaluated RD production pathways yields an $EROI_{fossil}$ greater than one (improved scenarios utilizing CHP). However, analysis reveals that by correcting for the availability of the energy (i.e. $ExROI_{fossil}$) the resulting ROI is less than unity. This value is further lowered when correcting for the quality of resources (i.e. $EmROI$). These results are compelling as they suggest that after accounting for the quality of resources, more useful work is invested via the economy in producing microalgal fuels than useful work generated from these fuels.

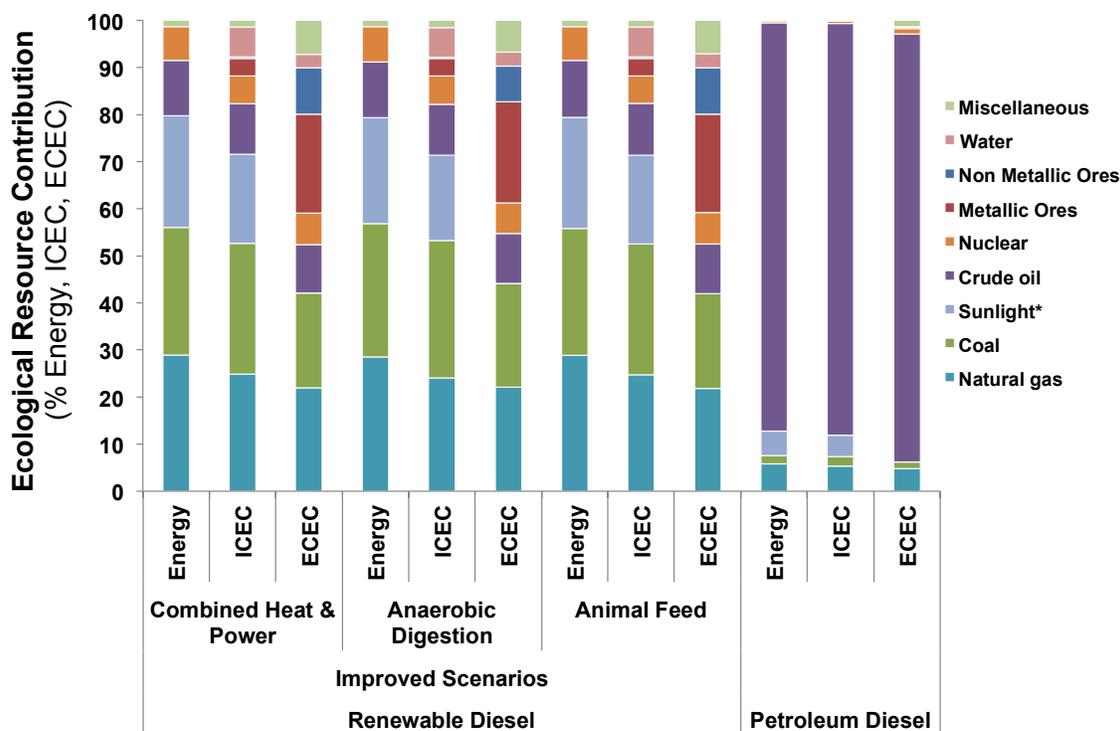
Although traditional energy metrics such as EROI are commonly used in the fuel and energy literature, this work has shown that these metrics fail to accurately measure the amount of useful work generated via microalgal biofuel systems as well as adequately quantify the amount of past ecological work required for their production, thus producing misleading and erroneous results regarding the environmental sustainability and performance of these fuel systems. These findings are significant, as traditional energy metrics such as EROI are frequently utilized to guide the course of fuel and energy policy and the sustainable adoption of fuel and energy resources.

The results from Figure 3 reveal that petroleum diesel is thermodynamically superior to microalgal RD as indicated by its high ROI across all thermodynamic metrics relative to

microalgal fuels. The high ROI for petroleum diesel is a direct consequence of the fact that nature has performed most of the past work in making these resources available for human consumption. The low ROI for microalgae biofuels reflects the highly engineered and resource intensive nature of microalgal fuel production and has broad sustainability implications, as the large scale adoption of alternative fuels with lower ROI relative to petroleum transportation fuels could have long-standing societal consequences^{81, 82} as a greater portion of useful work must be diverted from the economy for fuel production and thus cannot be used to sustain other economic activities.

Figure 4 plots the fractional contribution of energy, ICEC, and ECEC by ecological resource type for microalgal RD production under different coproduct options and compares the results to petroleum diesel. Figure 4 shows that natural gas, coal, sunlight, and crude oil contribute the majority of total energy consumption in the algae-to-fuel supply chain, with similar trends found across the evaluated coproduct scenarios. ICEC analysis expands upon traditional energy analysis to consider both energy and material inputs; this is evident from the contribution of metallic and non-metallic ores, water, and other material inputs to overall resource consumption. However, the contribution of these resources is still small relative to other ecological resources (such as natural gas, coal, etc). As shown in Figure 4, the contribution of low-quality resources such as sunlight have a significant impact on overall resource contribution in traditional energy and exergy analysis. This is a direct consequence of the fact that low quality resources are weighted equitably with other energy and natural resources in traditional energy and exergy analysis. However, energy analysis corrects for the quality of resources by comparing them in terms of their solar equivalence. As such, their contribution is minimal when evaluated from an energy perspective. Furthermore, resources of higher quality (high transformity) such as metallic and non-metallic ores are found to comprise a larger fraction of total ecological resource contribution when evaluated via ECEC analysis. The results from Figure 4 show that crude oil constitutes over 85% of total resource consumption in energy, ICEC, and ECEC analysis of petroleum diesel production. As such, petroleum diesel requires less work from the economy for conversion to transportation fuel compared to microalgal biofuels, as the majority of past

work has been provided by nature via the formation of crude oil. Consequently, this results in a higher ROI for petroleum diesel relative to microalgal renewable diesel.



*2%-metabolized sunlight was considered for energy and ICEC analysis

Figure 4 - Fractional contribution of total energy, ICEC, ECEC by ecological resource for microalgal renewable diesel and petroleum diesel

Table 2 provides an overview of the ECEC sustainability and thermodynamic performance metrics for the scenarios considered in this work. The results show that petroleum diesel has a high ECEC yield ratio as a larger amount of past work has been performed by nature in producing crude oil as compared to the direct and indirect solar exergy of purchased inputs from the economy required for its extraction, refining, etc. However, microalgal biofuels require substantial material and energy inputs from the economy, and a comparatively minimal amount of past work from direct ecological good and services (direct sunlight, freshwater, and photosynthetic CO₂). As such, the EYR for petroleum diesel is larger than that of microalgal derived renewable diesel. The results from table 2 reveal that petroleum diesel has a low renewability index and low YLR, indicating that these fuels are not sustainable in the long-term. Additionally, the results

indicate that production of microalgal biofuels is highly dependent on non-renewable ecological resources reflected in the low renewability index and YLR, and high ELR. The high ELR for microalgal derived RD (ELR>1 for all examined production pathways) indicates that more non-renewable ECEC is utilized in the algal-to-fuel supply chain as compared to renewable ECEC. Additional results for microalgal-derived biodiesel are provided in the Supporting Information.

Transportation Fuel	Petroleum	Microalgal RD			Microalgal RD		
	Diesel	(Baseline)			(Improved)		
Coproduct Scenarios	N/A	AF	AD	CHP	AF	AD	CHP
Renewability Index (%)	0.13	3.62	3.51	3.63	6.34	6.23	6.36
ECEC Yield Ratio	6.34	1.02	1.02	1.02	1.04	1.04	1.04
Environmental Loading Ratio	760.19	26.62	27.53	26.57	14.78	15.06	14.72
Yield-to-Load Ratio	0.01	0.04	0.04	0.04	0.07	0.07	0.07

AF = Animal Feed; AD = Anaerobic Digestion; CHP = Combined Heat and Power

Table 2 – Comparison of ECEC thermodynamic performance metrics for microalgal renewable diesel and petroleum diesel

Figure 5 plots the ratio of ecological resource intensity of producing microalgal renewable diesel relative to petroleum diesel for a common functional unit, 1 mega-joule (MJ). The results indicate that microalgal RD consumes significantly more metallic/non-metallic ores and water resources, and generally have higher ecological resource intensity as compared to petroleum diesel on a functional unit basis. For animal feed pathways microalgal RD provides benefits in the following ecological resources categories: crude oil, crushed ore, grass, sunlight, phosphorus and nitrogen mineralization, nitrogen deposition, detrital matter, soil erosion, fish, relative to petroleum diesel. For anaerobic (AD) and combined heat and power (CHP) coproduct scenarios, microalgal derived renewable diesel has higher ecological resource consumption relative to petroleum diesel across all resource categories except for crude oil and natural gas. These findings are startling and suggest that the large-scale adoption of microalgae biofuels could result in heightened ecosystem degradation, potentially negating the environmental benefits of these fuels. It is important to note that ECEC analysis considers energy and resource flows in complex coupled industrial-ecological systems, and thus has a high degree of uncertainty relative to traditional energy and exergy analysis. Coupling the results

obtained via EcoLCA with dynamic ecological modeling⁸³ can provide a spatially and temporally explicit framework for quantifying the contribution of ecosystems goods, and potentially reduce uncertainty in the quantification of direct ecological goods and services. However, such an analysis is beyond the scope of this present study. Methods such as economic valuation of natural capital provide an alternative basis for valuing the contribution of EGS⁸⁴. However, economic valuation is sensitive to market distortions and price volatility, and may not capture environmental externalities. Furthermore, economic valuation intrinsically considers the value added via a service or resource in regards to its utility for mankind. This anthro-centric framework is diametrically opposed to the eco-centric framework utilized in ECEC or emergy analysis.

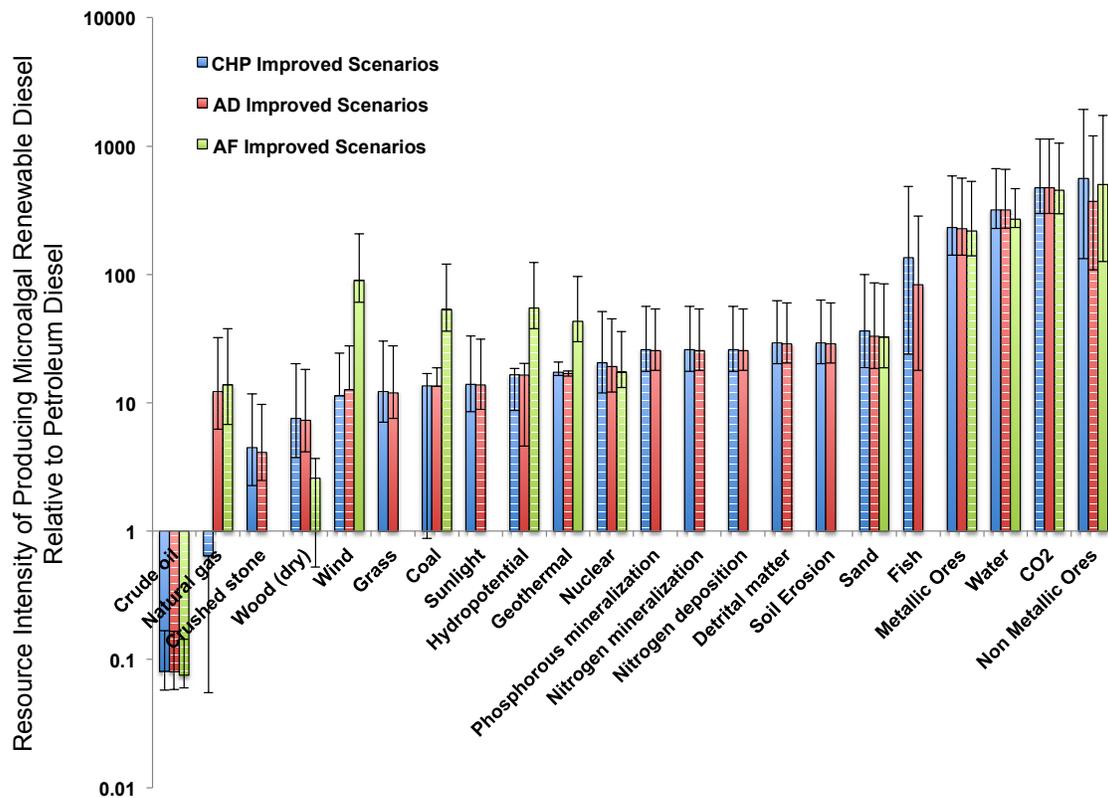


Figure 5 - Ecological resource intensity of producing microalgal RD relative to petroleum diesel. Resource intensity ratios were developed via taking the ratio of ECEC of resources required to produce one MJ of RD to the ECEC required to produce one MJ of PD. Coproduct(s) were accounted for via system boundary expansion, i.e. ECEC from coproduct(s) were subtracted from total resource use. Some columns are not shown on the logarithmic graph due to negative value(s) that occur as a result of displacement.

Two strategies exist to enhance the performance and sustainability of microalgal biofuels: (1) reduce the amount of purchased inputs from the economy required for microalgal fuel production, or (2) leverage natural ecological processes to increase the amount of past work provided by nature in making microalgal biofuels available for human consumption. The first option can be met with increases in technological maturation and commercial optimization of algae-to-fuel conversion processes. Multiple strategies such as genetic modification⁸⁵, hydrothermal liquefaction^{86,87}, cross flow and membrane based filtration/separations⁸⁸, and industrial symbiosis⁸⁹ via the use of wastewater^{90,91} and other synergies are being explored for increasing the performance of emerging microalgal biofuel systems. However, it is important to recognize that microalgae biofuel production is ultimately constrained via the 2nd law efficiency, i.e. the minimum thermodynamic work required for fuel production⁹². For the second option, it is possible to envision a scenario in which microalgae are consumed via predators at a higher trophic level in the ecological food chain (such as fish). Assuming that the lipid fraction of the microalgae be absorbed and retained via these predators, it may be possible to harvest and utilize these organisms for conversion to liquid transportation fuels⁹³, effectively allowing nature to perform the work traditionally required via energy intensive dewatering and conversion processes. Additionally, alternate microalgal processing options such as solar drying of the biomass may reduce the amount of human made work required for biofuel production. However, the high land-use requirements for solar drying may limit its commercial applicability.

4. Conclusions:

Failure to consider the impacts of emerging technologies on ecological goods and services before their widespread adoption and use could result in unsustainable choices and dramatic consequences for the earth's ecosphere including heightened depletion and degradation of the global ecological resource base, potentially straining the ecological functions that support human life. Thermodynamic analysis based on exergy and emergy provides a scientifically rigorous approach for valuing the contribution of ecological goods and services in product life cycles, and concurrently addresses several existing

problems in traditional energy analysis including accounting for the quality, substitutability, and useful work provided via material and energy resources. This study highlights the fallacies of traditional energy analysis, and shows that exergy and emergy analysis can provide valuable insights into the sustainability and performance of emerging microalgal biofuel systems. This work has shown that in the best-case scenario microalgal fuel systems are marginally energy positive, and more ecologically resource intensive as compared to their petroleum equivalent on a functional unit basis. However, technological maturation/optimization of the algae-to-fuel production chain as well as coupling microalgal biofuel production with ecological processes have the potential for reducing the amount of human made work required for biofuel production while concurrently increasing the sustainability of these emerging fuel systems. The hierarchical thermodynamic-based resource aggregation scheme utilized in this work can be extended to other nascent fuel and energy platforms and thus help guide the sustainable development and adoption of next-generation biofuels.

Term	Abbreviation
Anaerobic Digestion	AD
Animal Feed	AF
Arizona	AZ
Combined Heat and Power	CHP
Carbon Dioxide	CO ₂
Ecological Cumulative Exergy Consumption	ECEC
Ecologically Based Life Cycle Assessment	EcoLCA
Ecological Goods and Services	EGS
Environmental Loading Ratio	ELR
Energy Return on Investment	EROI
Exergy Return on Investment	ExROI
Emegy Return on Investment	EmROI
ECEC Yield Ration	EYR
Greenhouse Gas Emissions	GHG
High Density Polyethylene	HDPE
Industrial Cumulative Exergy Consumption	ICEC
Input-Output	IO
Life Cycle Assessment	LCA
Millennium Ecosystems Assessment	MEA
Mega-Joule	MJ
Natural Gas	NG
National Oceanic and Atmospheric Administration	NOAA
National Solar Radiation Database	NSRD
Open Raceway Pond	ORP
Petroleum Diesel	PD
Renewability Index %	R
Residual De-oiled Biomass	RDB
Renewable Diesel	RD
Return on Investment	ROI
Supporting Information	SI
United Nations	UN
United States	US
Yield to Loading Ratio	YLR

Appendix – Terms and Abbreviations

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