



Managing nutrients and system operations for biofuel production from freshwater macroalgae



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ABSTRACT

Filamentous freshwater macroalgae have significant potential as a renewable source of bioenergy. However, the ultimate success of freshwater macroalgae as a biofuel feedstock will depend upon our ability to produce biomass at commercial-scale in a cost-effective and sustainable manner. Aquatic ecology can play an important role to achieve the scale-up of algal crop production by informing the rates of nutrients supplied to the cultivation systems, and by helping to create adaptive production systems that are resilient to environmental change. A review and analysis of data from the published literature reveals that the large-scale cultivation of freshwater macroalgae is feasible using currently available technologies such as the Algal Turf Scrubber® system (ATS™). In addition, graphical analyses of published data obtained from ATS systems of varying sizes in operation worldwide reveal that both macroalgal biomass productivity and nutrient removal rates are hyperbolically related to the areal loading rates of both total nitrogen and total phosphorus. The effectiveness and need for CO₂ supplementation of macroalgal production systems like the ATS has not yet been conclusively demonstrated, however.

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1. Introduction

Algae have long been viewed as a promising source for biofuel feedstock with the capacity for higher productivity per unit of land area than conventional terrestrial crops [1–6]. While the majority of algal biofuel research to date has focused on strain selection and optimizing the productivity of microalgae, macroalgae also have been proposed both as feedstocks for diverse biomass applications and as targets for liquid and solid fuel production [6–9]. However, these efforts have primarily involved marine seaweeds and filamentous cyanobacteria, with a much lesser focus on the use of freshwater macroalgae (primarily members of the eukaryotic Chlorophyta) [6,8–11].

Although freshwater macroalgae represent a largely overlooked group of phototrophic organisms, they can exhibit high rates of areal productivity, and their tendency to form dense floating mats or substrate-attached turfs imply significant reductions in harvesting and dewatering costs relative to microalgae [6,12]. In addition, freshwater macroalgae can play an important role in the removal of nutrients (particularly N and P) from wastewater and other surface water bodies

contaminated by agricultural and storm runoff while simultaneously producing biomass for biofuel feedstocks [13]. Moreover, the cultivation of freshwater macroalgae on non-arable land using wastewater or other excess-nutrient-loaded surface water sources as a nutrient feed would avoid the energy vs. food debate associated with some terrestrial bioenergy crops [12,14–16]. One of the tradeoffs of using algal turf biomass as a bioenergy feedstock, as derived, for example, from current Algal Turf Scrubber® (ATS™) cultivation and harvesting systems and practices used for water treatment, is that the harvested biomass can typically have higher ash content. The ash is a combination of biogenic (e.g., the presence of diatoms) and exogenous material (silt and other mineral “trash” from the environment). The use of fresh water sources will tend to favor the growth of green species of algae that can help reduce biogenic ash, while improvements in algal turf cultivation and harvesting system design and operation is expected to help increase biomass productivity and reduce exogenous ash. Such improvements have not been a priority with systems historically focused only on cleaning water, but concern for the quality of the harvested biomass as bioenergy feedstock can provide incentive. Investigations led by Sandia National Laboratories (SNL) are currently underway to better assess the potential of algal turf for biofuel feedstock [17–19]. These investigations include the processing and conversion of low lipid content algal turf biomass to liquid fuel intermediates using a tandem combination of biochemical and/or hydrothermal liquefaction (HTL) processes [17–19], along with more definitive techno-economic and resource assessments to determine the feasibility of affordable algal

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turf biofuel scale-up while also providing environmental water clean-up services in selected regions of the country [19,20].

The problem of relatively high algal turf ash content, based on current production and harvesting practice, is one of the issues being given close attention by the SNL effort. SNL has demonstrated that raw harvested algal turf samples with 52% ash content, from a freshwater system in Florida, could be reduced by simple rinsing to about 23% ash, which is approaching the level of biogenic ash for that particular turf consortia [19,20]. This level of ash reduction was accomplished without significant loss of non-ash biomass content. SNL has also demonstrated that simple biochemical pretreatment, expected to be both scalable and cost-effective, can solubilize and hydrolyze the relatively high carbohydrate and protein content of the non-ash algal turf biomass to enable effective separation of the ash from those fractions and allow efficient fermentation to liquid fuel products (e.g., ethanol and isobutanol) with high yields using raw wet algal turf material [17–20]. Furthermore, HTL processing of whole raw wet algal turf, even with 52% ash content, has also been successfully converted to biocrude at bench scale with over 40% yield efficiency based on the non-ash content and without any process optimization [17–19]. Reduction of harvested algal turf ash content is needed to reduce the cost and increase the efficiency of downstream conversion processes. Relatively little effort has been made thus far to improve both algal turf biomass productivity and quality for fuel production, leaving open the potential for considerable improvement through better understanding of the dynamics of algal turf system performance under different water qualities and environmental conditions coupled with the implementation of modifications in algal turf cultivation and harvesting systems and operations. The results of the SNL efforts are still underway and will be reported separately in papers currently in progress.

Additionally, Roberts et al. processed wastewater-derived microalgae with hydrothermal liquefaction (HTL), and suggested that the ash content of the algae may help to catalyze HTL reactions and improve the oxygen content and average higher heating value (HHV) of the algal biocrude produced [21,29,49]. The wastewater-fed algae processed by Roberts et al. had a dry weight ash content of 29%. Finally, multiple Chlorophyte genera, including *Cladophora*, *Rhizoclonium*, and *Ulothrix*, contain species that exhibit broad salinity tolerances [22–24]. This breadth of salinity suggests that freshwater macroalgae could be grown not only in freshwater ponds but also in cultivation systems fed by high-salinity groundwater or seawater. Therefore, freshwater macroalgae are a promising component of large-scale biomass applications across a broad geographic range [12,14,25].

Macroalgal cultivation is typically synonymous with the growth and harvesting of seaweeds, with over 16 million dry tonnes produced annually worldwide [12,14,26,27]. However, several studies have explored the use of freshwater macroalgae for the bioremediation of high nutrient wastewater effluents derived from animal agriculture or human sewage [12,28–30]. In addition, Cole et al. demonstrated the utilization of industrial flue gas as carbon source for freshwater macroalgae cultivation in large outdoor tanks [12], and further attempts to integrate freshwater macroalgae cultivation systems with agricultural, aquacultural, and industrial facilities to remove excessive nutrients are underway [12,31,32].

The mass cultivation of algae for bioenergy applications has received considerable attention in the research community in recent years [1–3, 12,33,34]. Nonetheless, the degree of scale-up that will be required to achieve the bulk growth of algae for fuels poses a significant number of challenges, ranging from the high capital, energy, and other resource costs of establishing and maintaining the cultivation and processing systems, to problems associated with biological contamination by pests and non-target organisms [33,35,36].

It has long been known that the photosynthetic conversion of solar energy into biomass in large-scale algal cultures is influenced by the

availability of sunlight (solar insolation), water, temperature regimes (day/night and seasonal variations), carbon dioxide, and other nutrient availability [37,38]. Of these factors, more than 40 years of research in aquatic eutrophication science indicates that the availability of nitrogen and phosphorus will set the upper limit for algal production that can be attained in algal biomass cultivation facilities [39–41]. A remarkably consistent response of surface waters to nutrient enrichment has in fact been observed worldwide [42]. Moreover, measured rates of photosynthesis and the average growing season biomass of microalgae have both been demonstrated to be strongly and positively dependent upon water column concentrations of total nitrogen and total phosphorus [39–41].

Our goal in this review thus will be to explore the pivotal role of inorganic nutrients (nitrogen, phosphorus, and carbon dioxide) in determining algal biomass productivity by freshwater macroalgae. We will first briefly review recent experiences in the cultivation of freshwater macroalgae, and we will then examine how the supply rates of N and P to ATS systems control both biomass production and nutrient removal rates. In addition, we will briefly discuss the possible value of carbon dioxide supplementation. Because most large-scale cultivation of freshwater macroalgae is likely to utilize flow-through systems for nutrients and water exchange, we will also examine how the hydraulic environment mediates nutrient availability and ecological community structure in mass cultivation systems.

2. Mass cultivation platforms for freshwater macroalgal biomass production

Civilizations across the globe have harvested and consumed algae for centuries [43]. However, research on the mass cultivation of algal biomass successfully was not initiated until the late 1940s and early 1950s in the U.S., Germany, and Japan [43–46]. The two basic technological platforms currently used for producing algal biomass are open pond and closed photobioreactor (PBR) systems. [43] Closed systems typically have higher productivity and are more stable, but they are also generally more expensive to set up and operate than open systems [2,43]. Although decades of effort have focused upon developing efficient and cost-effective closed systems for the cultivation of microalgae [47], closed systems for macroalgae cultivation have been much less frequently considered [48]. We suggest that it is likely that the mass cultivation of macroalgal floating mats in closed systems will cause unacceptably high levels of light extinction as well as heterogeneous light transmission through the cultures, which may hinder the establishment of dense macroalgal culture [48]. Moreover, the algae-to bioenergy pathway is more favorable when nutrients in wastewater effluents are used in place of commercial fertilizers [49]. In addition, it seems unlikely that high volumes of wastewater can be efficiently used in a system requiring sterile conditions for macroalgal biomass production, and therefore the use of wastewater is unlikely to be a significant part of any successful large-scale closed system for macroalgal biomass production [49].

In contrast, open cultivation systems are much less expensive, and can be highly productive (up to 30 g DW/m²/day) [49–53]. Although open systems are considered the most feasible approach to produce algal biomass competitively [43,49,54], they nonetheless face significant technical and economic challenges for affordable bioenergy and other products and services stemming from the fact that they are exposed to unpredictable and uncontrollable meteorological conditions; are at risk from both abiotic and biotic contaminants; and are often poorly mixed [43].

Extensive research effort has focused upon the identification of monocultures or polycultures of algal species that can thrive in outdoor cultivation systems despite the presence of environmental fluctuations and contamination pressures, while producing high biomass yields with a desirable energy and biochemical content [55]. Lawton et al. recently identified the cosmopolitan freshwater macroalgal genus *Oedogonium*

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