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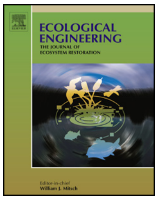

Editorial

Weeds in the algae garden – A source of biomass for the algae-to-biofuels program

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ABSTRACT

Despite decades of effort, viable algal biofuels remain a distant vision. High-lipid microalgae for biodiesel is plagued by low productivity, poor biomass quality, and pond instability, so conversion of non-specific algal biomass into other fuels is now the favored approach. Nevertheless, with low productivity and high costs, microalgae cannot provide the annual tonnage of biomass needed for fuel production. An alternative source of easily produced algal biomass has been available for decades. Algal turf scrubbing (ATS) robustly cultivates indigenous algae in an open flume photobioreactor. It is a proven, cost-effective, point- and non point-source treatment method for recycling the aquatic nutrient pollution whose levels threaten to exceed sustainable earth system boundaries. Using ATS to reverse nutrient loading in eutrophic waters would produce copious algal biomass at essentially no cost, for biofuel production or for development into other bioproducts.

1. Introduction

For more than thirty years, the United States Department of Energy (DOE) has been developing the capacity to convert algal biomass into replacements for diesel and gasoline (Sheehan et al., 1998), which, if successful, would expand energy security and could begin stabilizing net greenhouse gas emissions (Darzins et al., 2010; U. S. DOE, 2010; IPCC, 2011; OECD/IEA, 2011).

The first element of DOE's algal biofuels strategy involved prospecting for phytoplankton strains having potentially desirable properties. Dubbed the Aquatic Species Program (ASP), this project was active from 1978 to 1996 (Sheehan et al., 1998), and collected approximately 3000 algal species, from a variety of ecosystems and geographical locations (Sheehan et al., 1998; Knoshaug et al., 2009). Most of the collected strains were ultimately rejected, and only about 10% of the original candidates are preserved (Knoshaug et al., 2009).

The second element of the ASP strategy was to develop the chosen strains into crops that grow rapidly in outdoor ponds. The consensus design for a microalgal growth pond is an oval raceway, with a volume ranging from tens of thousands to millions of liters, and a water depth of up to 200 cm (Nurdogan and Oswald, 1995). The pond is equipped with a paddlewheel that operates continuously to provide mixing (Darzins et al., 2010) and a source of concentrated CO_2 to overcome the limited exchange of this essential nutrient between the atmosphere and the culture medium. A production run starts with a test tube of pure culture that is serially expanded in 100× increments, first in the laboratory and then outdoors; the final 100× expansion is harvested. Initially it was considered possible to harvest half the contents of a mature pond, allow the remaining half to re-expand by 2×, and repeat this cycle indefinitely. Unfortunately, it has proven almost impossible to cultivate defined phytoplankton monocultures outdoors reliably for more than a single harvest, as they are inevitably out-competed by unwanted exogenous algae, consumed by grazers, or infested by non-photosynthetic microbes (Darzins et al., 2010; Lane and Carney, 2014; Schenk et al., 2008).

The third element of the strategy was to focus initially on what appeared to be the most promising drop-in fuel, biodiesel, as demonstrating economically sustainable production of this biofuel would encourage a smooth transition from lower-productivity agricultural biomass (e.g. corn for ethanol) to higher-productivity algal biomass as a feedstock, while exploiting existing distribution infrastructure. Because lipids can serve as biodiesel precursors, algal strains that accumulate easily extracted lipids in laboratory culture were chosen for initial development. Initial analyses, using assumptions then considered conservative suggested that microalgal biodiesel was potentially economically feasible if production improvements could be implemented (Chisti, 2007; Wijffels and Barbosa, 2010; Chisti, 2013; Dassey et al., 2014; Rogers et al., 2014).

1.1. Issues with microalgae production

Microalgal production protocols have matured since they were first introduced. Currently a series of closed photobioreactors (PBRs) is required to incrementally expand microalgal seed cultures prior to production outgrowth, and these systems are costly to build and operate (Darzins et al., 2010; Schenk et al., 2008;

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Stephens et al., 2010; Walker, 2009). Harvesting and dewatering are also prohibitively expensive (Darzins et al., 2010; Lundquist et al., 2010; Coons et al., 2014). Furthermore, continuous production of microalgae – that is, harvesting half the biomass then allowing it to double again before each subsequent harvest – has proven difficult. During the single interval of outgrowth and harvest possible under currently achievable production conditions, the chosen algal strains do not accumulate large proportions of lipids as they do in laboratory culture (Lundquist et al., 2010; Schenk et al., 2008; Griffiths and Harrison, 2009; Henley et al., 2013), nor has biomass productivity in the field been as high as in laboratory or pilot scale projects (Lundquist et al., 2010; Stephens et al., 2010; Walker, 2009; Weyer et al., 2010).

The need to use defined culture media to cultivate microalgae for biofuels requires large-scale production of sterile solutions of macro- and micronutrients and recycling of nutrients from fuel-production residue. To support rapid microalgal growth in raceway ponds, supplementation with concentrated CO_2 is necessary, requiring either co-location of production ponds with a source of this nutrient, which would require extensive reengineering of these installations, or transport via pipeline, which would compete with existing markets for this industrial gas (Gao et al., 2012). Most of the best solar resource for growing microalgae in the US is located in arid regions, making water supply challenging.

Achieving reliable year-round high productivity and lipid yield is thus likely to require further major effort, including ecological or genetic manipulation (Beer et al., 2009; Radakovits et al., 2010; Peralta-Yahya et al., 2012; Benemann, 2013; Shurin et al., 2013). Even with generous assumptions for annualized biomass productivity and lipid content, as yet undemonstrated, biodiesel production from microalgae is not likely to be cost effective (Lundquist et al., 2010; Richardson et al., 2014; Sikes et al., 2010). These obstacles to microalgal biofuel production are troubling, as the Energy Independence and Security Act of 2007 mandates that by 2022 – only seven years from now – the United States produce 21 billion gallons (80 billion liters) of non-corn-based biofuel annually (Energy Independence and Security Act of 2007). This target, 8.3% of the United States' 2013 gasoline consumption (U.S. Energy Information Administration, 2015), is unlikely to be achieved, either by exploiting microalgae grown in raceway ponds or by any source of non-algal biomass, and has been revised downward (Schnepf and Yacobucci, 2014).

1.2. DOE's new strategy

DOE is therefore now investigating alternative fuels produced via bio- and thermochemical conversion of non-specific algal biomass into fuels and fuel precursors (Biddy et al., 2013; Toor et al., 2011). These processes depend upon total organic content rather than the presence of one specific class of biochemicals, and thus the major relevant characteristic of the biomass is whether it can be produced reliably at a high rate. This decision relaxes some constraints by expanding the range of algal species worth considering. However, it imposes new hardships related to engineering the conversion processes, including more capital-intensive fermentation processes, the higher temperatures and pressures needed for thermochemical conversion, means for handling the high ash and salt content of the biomass, and the suitability of thermochemically produced biocrude as a refinery input.

2. Algal turf scrubbing

During the same three decades that DOE has been pursuing microalgal biofuels, a completely independent algal cultivation practice, conceived for purposes unrelated to biofuel production, has evolved from initial discovery to multi-hectare outdoor production. Algal turf scrubbing (ATS), as this practice is known, is used not for producing algal biomass per se, but rather to remove point and non point-source nitrogen or phosphorus pollution from contaminated waters (Adey et al., 2011; Stewart, 2004). ATS^{TM} is a trademark, and Algal Turf Scrubber® a registered trademark, of Ecological Systems Inc., the primary RT&D entity for the technology; these are licensed to HydroMentia, Inc., the primary commercial entity that deploys and licenses it. Figs. 1 and 2 depict ATS units of various scales; Table 1 provides a list of past and current ATS installations. ATS mimics the algal turfs that colonize tropical coral reefs by providing a growth substratum readily colonized by algal cells present in the input water, along with a flow regime that supplies continuous adequate nutrition. The algal cells attached to the stationary substratum develop into an immobilized mass of interwoven filaments and trapped cells (the "turf") whose rapid growth extracts nutrients and other pollutants from the water as it flows through the system.

Table 1
Representative algal turf scrubber projects.

Location	Water source	Area (m^2)	References
Florida	Indian River	18,535	(Hydromentia, 2010; Indian River County, 2014)
Florida	Runoff	10,000	(Hydromentia, 2005)
California	City of Patterson	1021	(Craggs et al., 1996)
Maryland	Bridgetown	300	[a]
Florida	Ft. Pierce	281	(D'Aiuto et al., 2015)
Maryland	Baltimore Harbor	200	[a]
Queensland	Aquarium Exhibit	144	(Adey and Loveland, 2007)
Maryland	USDA	120	(Mulbry et al., 2008)
Florida	Runoff	111	(Hydromentia, 2010)
New York	Jamaica Bay	65	(Jamaica Bay Research Symposium, 2011)
Florida	Powell Cr. Bypass	47	(Hydromentia, 2008a)
Florida	Santa Fe R.	47	(Hydromentia, 2010)
Florida	Lake Lawne	37	(Hydromentia, 2008b)
Maryland	Living classrooms	28	(May et al., 2013)
Arkansas	Spring Cr.	27	(Sandefur et al., 2011)
Virginia	York R.	25	(Rothman et al., 2013)
Virginia	Great Wicomico R.	24	(Adey et al., 2013)
Florida	Runoff	22	(Adey et al., 1993)
Pennsylvania	Susquehanna R.	19	[a]
Pennsylvania	Susquehanna R.	9	(Laughinghouse, 2012)
Maryland	Choptank R.	3	(Ray, 2014)
New York	Lake Erie	3	(Blersch, 2013)
Maryland	Patuxent R.	1	(Mulbry et al., 2010)
Maryland	Patapsco R.	1	(Mulbry et al., 2010)
Maryland	Bush R.	1	(Mulbry et al., 2010)

[a] P. Kangas, personal communication.

2.1. Discovery and initial development of ATS

Studies leading to development of ATS occurred in the 1970s and 80s, when one of us (Adey), sampling coral reefs in the Caribbean for the Smithsonian Institution's Marine Systems Laboratory, discovered that despite residing in what are essentially nutrient deserts, beds of benthic filamentous algae exhibited surprisingly high growth rates. This phenomenon was ultimately traced to efficient delivery of nutrients by wind-driven pulses of water (Adey and Steneck, 1985). The algal turfs were capable of rapid growth, up to 12 g of dry biomass per square meter of reef surface per day (ash included); because the reef surface undulates, this value can be extrapolated to 30 g per square meter per day, and this is demonstrated by measurements of oxygen concentration in the overflowing water (Adey and Steneck, 1985). In still waters, rapid algal growth would quickly deplete already low nutrient concentrations to their growth-halting lower limits, but in waters with an external supply of extremely dilute nutrients, un-depleted water

Fig. 1. Small-scale ATS. (A) A dual-floway system, with each floway 1 m × 100 m. Headworks are visible on the right. (B) Close-up of headworks, pulsing water into the system via tipping buckets. (C) Close-up of green filamentous algae (Ulva) growing in the floway. (D) Harvested biomass vacuumed from the floway being spread for solar drying.

flows continuously past the stationary turfs, providing continuous nutrition that supports rapid growth.

Through a series of experiments starting in Florida and the tropical Caribbean, Adey and others demonstrated that the growth of benthic filamentous algae indigenous to a local watershed can be facilitated by establishing a gently sloped (0.5–2% grade) open flume – the floway – supporting a high-surface-area growth substratum, and pulsing water over this surface in order to provide adequate mixing (Adey et al., 1993; Blersch, 2013). Indoor facilities were constructed that functioned as the sole water recycling systems for marine aquaria of up to several million liters, and ATS systems were ultimately scaled up to larger outdoor land based freshwater installations (Adey and Loveland, 2007; Craggs et al., 1996; Hydromentia, 2005; Huang et al., 2013) (Table 1). Several of these systems operated continuously for a decade or more.

2.2. Applications of ATS

In an outdoor system, the cleaned water is returned to the hydrology network enriched with oxygen and higher in pH. Because the water's residence time is low, and mixing and cell/water interaction are so efficient, no external source of nutrients or CO_2 is required, as growth is rapid even at low nutrient concentrations. For harvesting, temporarily interrupting the water flow allows the turf to drain via gravity flow, exposing a dense mass of bulk solids that is considerably less costly to remove and concentrate than the dilute suspension of microalgal cells that is the initially harvested product of microalgal systems (Darzins et al., 2010).

Numerous outdoor ATS units have been built, several at hectare scale, for tertiary treatment of municipal water supplies, finfish aquaculture, and management of fermented dairy manure and agricultural runoff (Craggs et al., 1996; Mulbry et al., 2010; Pizarro et al., 2006; Higgins and Kendall, 2012; Kangas and Mulbry, 2014). With the exception of two systems that underperformed because of toxins in upstream water, due in one case to herbicide application, and in another to an undetermined toxin (Florida Department of Environmental Protection, 2012), no large-scale ATS project has been terminated due to a failure of algal growth (external factors such as power loss, pump failure, freezing of pipes, or vandalism have interrupted algal production, but these situations can

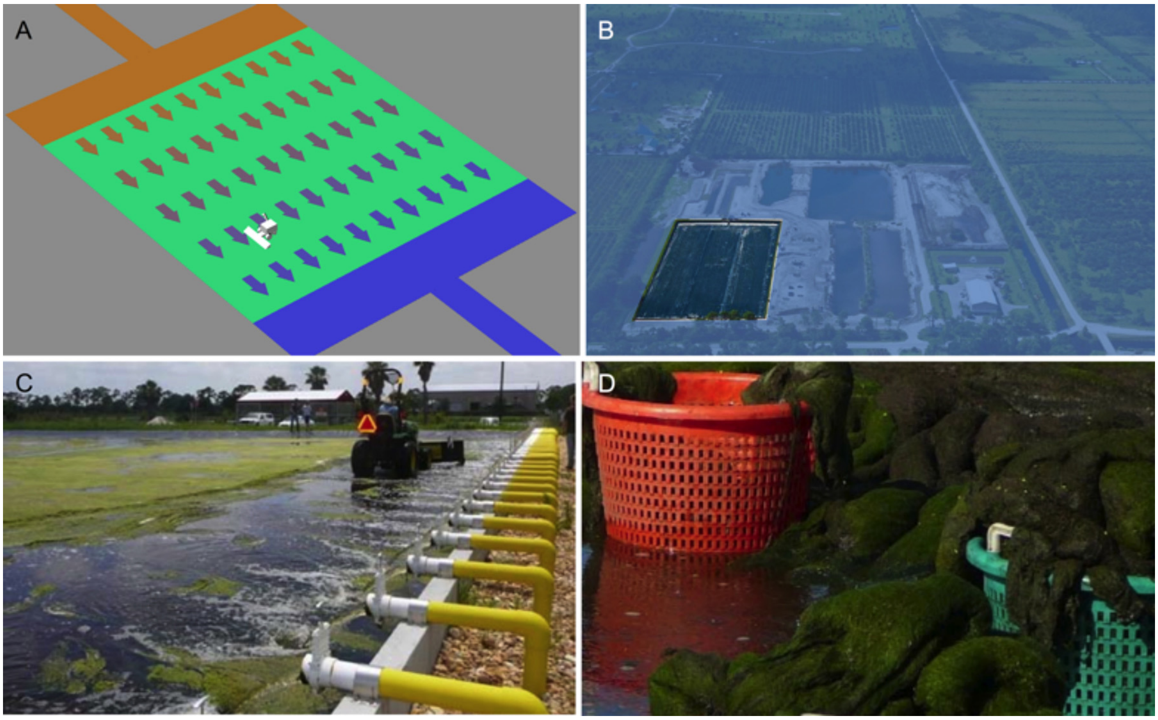

Fig. 2. Landscape-scale algal turf scrubbing. (A) Schematic aerial view of a landscape scale ATS system with 1 ha algal growth surface area (green). Input surface water (brown) enters the system, flowing down a gentle slope over an immobile, attached filamentous algal turf. Rapidly growing algal cells extract C, N, and P from the input water, oxygenate it, and raise its pH (arrows depict direction of flow and treatment level). The treated, upgraded water returns to the hydrology network. Frequent harvest, using agriculture-style equipment, represented by the combine (to scale) permanently removes contaminants from the system. (B) Aerial photograph of a landscape scale ATS installation with a treatment capacity of 10–40 ML d^{-1} (Egret Marsh, Indian River County, Florida, USA). Algal growth area is highlighted. (C) Photograph of Egret Marsh ATS floway headworks. Surgers providing pulsed input, in this case siphon breaks rather than tipping buckets, are shown on the right; a harvester is shown detaching algal biomass from the growth substratum. (D) Harvested algal biomass solids.

Photographs: HydroMentia, Inc.

be minimized through due diligence). ATS has operated outdoors over a broad geographic range, from freshwater systems in Florida (Hydromentia, 2005), Lake Erie (Blersch, 2013), Arkansas (Sandefur et al., 2011), California (Craggs et al., 1996), and Maryland (Mulbry et al., 2008) to mesohaline systems (Adey et al., 2013) in the Chesapeake Bay region. None of these operations required laboratory culture, nutrient or CO_2 addition, inoculation with defined strains, or genetic manipulation. Biomass productivity in the range of 15–50 t ha^{-1} y^{-1} (ash-free dry weight, AFDW) is routine for subtropical and temperate ATS units (Adey et al., 1993, 2013). Seasonal colonization by algae grazers such as Chironomid larvae can occasionally degrade productivity, but can typically be managed by temporarily increasing harvest frequency (P. Kangas, W. Adey, personal communication).

2.3. *Ecology of and further improvements to ATS*

The algal turf in a floway self-organizes dynamically in response to the energy signature of its operating environment. The floway continuously samples the algal species present in the input water, acquiring an ever-growing bank of species, each with the potential to expand exponentially when conditions become ideal (Laughinghouse, 2012). As with an empty lot or an untended field, the species that dominate an algal turf are simply those that outperform their competitors under prevailing conditions. The community evolves over several years, becoming increasingly productive, predictable, and adaptive to seasonal variations (HydroMentia, Inc., personal communication). With ATS, species that would be unwanted in an open microalgae pond are the harvest, desirable because they outcompete all others.

An ATS installation can be viewed as a stationary, controlled, intentional algal bloom – the opposite of unwanted algal blooms that are increasingly afflicting our waters (Hallegraeff, 1993) – or perhaps more fancifully an “algal kidney” for ailing watersheds, referring metaphorically to renal dialysis. During uncontrolled blooms, planktonic algae first proliferate exponentially, potentially releasing algal toxins (Glibert et al., 2005). The algae then starve after incorporating most of the available nutrients. The dead and dying algal biomass feeds subsequent blooms of heterotrophs that lead to turbidity and hypoxic zones, with consequences such as fish and bird kills (Glibert et al., 2005). In contrast, during an ATS “bloom” – the week or two between harvests – the immobilized remnants of the previous harvest immediately resume rapid growth, extracting nutrients from the influent as it proceeds down the flume. The discharged water, higher in oxygen and pH (i.e. lower in CO_2) and lower in nutrients, thus offsets downstream hypoxia both directly by adding oxygen (during the day while photosynthesis is occurring) and indirectly by reducing the potential for unwanted blooms. Frequent harvest permanently removes nutrients and biomass from the system.

Algal turfs grow rapidly in typical surface waters, ranging from fresh to saline, whether pristine or polluted. The input water does not require sterilization or nutrient supplementation to achieve high growth rates, although managing nutrient content can optimize productivity (Yun et al., 2015), and pulse-induced turbulence provides sufficient mixing to support high productivity even in low-nutrient waters (Blersch, 2013). Depending on the influent chemistry, a sufficiently long floway can be limited by either N, P, or CO_2. Consumption of dissolved CO_2 can drive the carbonate/bicarbonate buffer system to a pH at which phosphate salts precipitate (Craggs et al., 1996; Hydromentia, 2005). The cleaned and upgraded effluent is simply returned to the water body from which it was withdrawn. Harvesting is easily accomplished by briefly interrupting the flow of influent, allowing the system to drain, and then scraping and/or vacuuming the biomass, producing material that is typically 7–12% solids. Increasing the solids content of the harvested algae has not previously been a concern for systems whose goal is nutrient removal. Thus dewatering can likely be improved with simple efforts directed at design specifications such as a favoring a higher slope and optimizing harvesting procedures. Ash content tends to be high (25–75%), but much of this is likely terrigenous rather than biogenic, and as with solids content ash content has never been a concern, thus simple optimizations in operations will likely address this issue.

Further improvements in ATS productivity are available. One of us (Adey) recently demonstrated that growth and nutrient removal rates more than double when a 3-dimensional growth substratum is used instead of the usual 2-dimensional mesh (Adey et al., 2013). The substrata used during this investigation were ad hoc, suggesting that they can likely be further optimized, improving the economics and potentially enabling expansion into regions where lower productivity would otherwise be an obstacle. Estimating 50% ash content, Adey's maximum productivity of $\sim 90\,\mathrm{g\,m^{-2}\,d^{-1}}$ is equivalent to $45\,\mathrm{g\,m^{-2}\,d^{-1}}$ AFDW, about 25% of the theoretical maximum (Weyer et al., 2010).

Increased surface area for algal cell adhesion is one likely explanation for increased productivity with 3D substrata, affording waterborne cells more colonization opportunities and thus yielding more multi-cellular filaments as the turf matures. Details of the hydrodynamics of the influent as it flows through the growth substrate, both during initial colonization and at various levels of turf maturity are also likely to be important. A second-order effect deriving from the higher density of attached filaments is increased retention of cells that would otherwise slough off the turf and exit the floway. All of these effects contribute to increased chlorophyll density, enabling a given areal region of turf to use a greater proportion of incident sunlight for photosynthesis. A countervailing effect of increased cell density may be a concomitant increase in shading; however, the pulsed flow of influent water causes the filaments to oscillate back and forth, allowing increased light penetration compared to steady flow conditions (Carpenter et al., 1991). The main question with 3D substrata is how close to the theoretical maximum can ATS productivity be driven.

2.4. *ATS vs. open algal ponds*

Most of the algal species favored by ATS are not amenable to the usual laboratory microbiological cultivation techniques that depend on keeping isolated cells well suspended in defined liquid media, and would therefore have been rejected by the ASP. Every watershed possesses a unique complement of algal species, and thus the composition of species in an ATS floway is both biodiverse and unique, advantages for an open system that would be considered a flaw from the perspective of defined algal strain development. For reliably generating algal biomass at high productivity, the niche-filling complexity, variability, and redundancy of an ATS ecosystem outperforms the pure microalgal cultures or simple polycultures used in open ponds, as any given monoculture strain or collection of defined strains will perform optimally only over a narrow range of conditions (Smith and Crews, 2014). Scale-up simply magnifies these differences, as the precise management of microorganisms, unnecessary with ATS, is orders of magnitude more difficult outside the laboratory. ATS exploits the vigor of algal "weeds", whereas microalgal monocultures or polycultures, especially when scaled up, are potentially vulnerable to unwanted algal competition (Bull and Collins, 2012).

Input water for an ATS system is provided directly from the local hydrology network, and has a residence time measured in minutes before the treated water is discharged. The level of water treatment is a function of contact time between the water and the algal turf; floway geometry can be adjusted to the chemical problems inherent to the source waters. In a sufficiently long system, often ∼100 m, but dependent on the chemistry of the influent, quantitative removal of the limiting nutrient (N, P, or CO_2) can be engineered. Indeed, removal of CO_2 from the water as it flows through the system can increase the pH to the point that phosphate salts begin to precipitate within the turf (Adey et al., 2011).

None of these statements is true for PBR/open pond algae cultivation systems, whose comparatively strict media requirements necessitate expensive formulation practices, including control over sterility, salinity, and nutrient concentration, and typically require nutrient and water recycling – certainly so for large-scale projects imagined for construction in deserts. The need to keep microalgal cells suspended in closed reactors or comparatively deep ponds necessitates addition of exogenous CO_2 to encourage higher growth rates. Expensive dewatering procedures must be undertaken to concentrate PBR/open pond algae from its initially harvested solids content of $\leq$1% (Darzins et al., 2010) to a level closer to 10%. For example, much effort has been expended to develop methods to stimulate algal cells to flocculate and settle (Darzins et al., 2010; Wrede et al., 2014). Centrifugation is functional but expensive, and filtration problematic (Darzins et al., 2010). The use of electrical fields and sound waves have also been explored, but all of these methods require significant capital and operational inputs, and few, if any, studies have been published suggesting that economic scale-up of these proposed solutions is feasible. Dewatering is currently responsible for up to 40% of microalgal production costs (Biddy et al., 2013). As harvesting an ATS floway can easily achieve 10% solids at initial harvest, these are costs that simply do not apply to ATS systems.

3. ATS-based biofuels

Algae-derived lipid-based biofuels are thus not technologically ready and are not likely to be for years or decades. What hope is left for producing biofuels from algal biomass? The two most feasible methods appear to be fermentation and thermochemical conversion. Ethanol produced by yeasts via anaerobic fermentation of sugars is currently the only biomass-based liquid transportation fuel available at a large scale. In the US, annual ethanol production in 2013 was 13.3 billion gallons (50.3 billion liters) (U.S. Department of Agriculture, 2014). US production is to be capped, by mandate, at 15 billion gallons (57 billion liters) annually (U.S. Energy Information Administration, 2015), a rate that will require a large fraction of the country's annual corn production as feedstock. Ethanol has a lower energy density than gasoline, is hygroscopic, and can be blended into gasoline to no more than a 10% proportion (15% for flex-fuel vehicles).

3.1. *Fermentation of algal biomass*

However, yeasts are not the only fermenters, nor are sugars the only fermentation input, nor is ethanol the only major product of all fermentations (Fortman et al., 2008; Wackett, 2008; Demain, 2009). One example of a non-yeast, non-sugar, non-ethanol (only) fermentation is the ABE (acetone/butanol/ethanol) process (Nimcevic and Gapes, 2000; Gapes, 2000), which can exploit bacteria of the genus *Clostridium* to ferment non-specific biomass into various energy-dense products, and which has recently been improved to produce primarily butanol (Ramey, 1998) and demonstrated using ATS biomass as an input (Adey, 2010). Butanol, denser in energy and less hygroscopic than ethanol, has combustion characteristics similar enough to gasoline's that only minor design changes, if any, would be needed to develop internal combustion engines that use it in any proportion (Szulczyk, 2010; Ibrahim and Okunola, 2014). It should thus be relatively straightforward to gradually displace corn-based ethanol production with ATS-based butanol production, increasing production with new plants to satisfy the 2007 mandate and retiring corn as an energy crop. Land once used to provide corn for biofuel could then be returned to food production or banked, enhancing food security as a byproduct of enhancing energy security.

3.2. *Beyond carbohydrate fermentation*

Fermentation by yeasts or *Clostridium* is capable of converting only the carbohydrate component of biomass into fuel compounds, leaving proteins and lipids in the residue. Thermochemical conversion of algal biomass into biofuels, whether algal tissue or fermentation residue, is thus receiving significant attention, in particular hydrothermal liquefaction (HTL) (Peterson et al., 2008; Fortier et al., 2014). For HTL, biomass with 10–20% solids content is sealed within a reaction chamber, and the temperature is raised to 280–380 °C for up to 30 min, producing a pressure of 7–30 MPa. The products comprise an organic phase (the "biocrude"), an aqueous phase containing dissolved salts and some organics, CO_2, H_2O, and some combustible gases, and a solid phase derived from the ash component of the biomass (Peterson et al., 2008). While HTL has been applied to microalgal biomass having approximately 20% ash composition (Biller and Ross, 2011), little work has been published on ATS-derived algae, which is often high in biogenic silica from diatoms and in exogenous silica and other refractories originating from suspended particulate matter in the influent that becomes trapped in the algal turf (Adey et al., 2013). Marine-derived biomass can contain carbonate from calcareous organisms that form a minor component of the algal ecosystem. Even when grown in clean water with liquid dairy manure as a nutrient, ATS-derived algae dominated by chlorophytes tends to have a relatively high ash content (~20%) (Mulbry et al., 2008). Larger reaction volumes and energy inputs would be needed to produce biocrude at the same rate from higher-ash than from lower-ash biomass. The effect of the ash on reaction chemistry and reactor engineering also needs to be further investigated (Peterson et al., 2008). Ash content has only recently become a consideration for ATS biomass production, and its possible reduction has therefore not received significant attention; there may be low-cost operating methods that reduce input of unwanted material (such as upstream settling ponds) or removes it from harvested biomass (such as rinsing).

Biocrude produced from algal biomass via HTL has a heteroatom content too high to be used as refinery input (especially N atoms) (Barreiro et al., 2013), requiring either removal of unwanted atoms prior to conversion, improvements in the HTL process itself, or chemical modification of the bio-crude prior to refinery insertion. One possible biomass pre-treatment step uses *E. coli* that have been genetically engineered to ferment protein into ammonia and mixed high-carbon alcohols (Huo et al., 2011). This protein fermentation requires lysis of the algal cells, which in the case of diatoms may be more difficult than for cells without silica in their walls. A possible post-treatment step, heating biocrude in the presence of hydrogen, can displace heteroatoms from the mainly hydrocarbon molecules, but requires high temperatures and pressures and a source of hydrogen. To date, modifications to the HTL process that produce low-N bio-crude from high-N inputs have not been reported.

An alternative to HTL is integrated hydrocracking/catalytic hydropyrolysis (IH2). This procedure was developed to convert dry biomass such as wood directly into a drop-in gasoline substitute, and has been tested in pilot plants capable of processing up to 50 kg biomass per day (Gas Technology Institute, 2012). This process has not been tested using either microalgae or ATS-derived algal biomass, and imposes significant preprocessing costs for algal biomass, which would have to be further dewatered to 50–80% solids. The ash issue would also require investigation for IH2, for volumetric considerations as well as for its effect on process chemistry.

4. Global impact of scaled-up of ATS

To produce both fuel and other potential algal bioproducts, it is possible that the best long-term strategy is to engineer microbes that perform direct photosynthetic conversion of carbon, nutrients, and light energy into the desired commodities or high-value products, secreted in self-harvesting vesicles or otherwise easily separated from the biomass. However, the technological readiness for such scenarios has not been demonstrated and may be several decades away. Thus it is likely that today's agricultural biofuel crops will first be displaced by non-specific high-productivity biomass cultivation such as ATS. As specific alternative technologies mature, carbon-neutral or -negative production from genetically engineered algal or other cell types would replace these interim methods product by product.

In the near term, recycling the mineral component of algal biofuel production residue could displace equivalent quantities of high cost, energy intensive industrial fertilizers, removing these damaging materials from our waters and removing the atmospheric CO_2 loading derived from their manufacture. This large scale recycling of agricultural fertilizers would begin to reverse transgression of the biogeochemical planetary boundary, as described recently (Steffen et al., 2015). The cited authors rank biogeochemical changes, especially the release of nitrogen and phosphorus to the global environment, as more critical and more advanced than the climate effects of increasing atmospheric carbon and the effects ocean acidification, both of which extensive ATS deployment would also begin to remediate.

Application of ATS for biofuel conversion at a scale large enough to replace petroleum-derived fuels, even only in the US, will require extensive surface area for algal growth and other infrastructure required for handling the influent, effluent, and produced biomass. With ash-free biomass productivity using two-dimensional growth substrata already larger than local high-performance agriculture, productivity improvements available from switching to three-dimensional substrata will only improve the land-use situation. While ATS need not consume arable land, it does require the ability to construct large gently sloped expanses. A network of ATS units of sufficient size to completely clean excess fertilizer pollution from US rivers would still not provide enough biomass to completely displace fossil fuels; additional capacity would need to be installed, likely along southern shorelines of the Pacific and Atlantic, as well as the Gulf of Mexico. Unknown is how many years of service can be expected from the growth substratum and thus how often it will need to be repaired or replaced, a significant operating expense. Also unknown, either for ATS-based biofuels or for other bio-based fuel concepts, are the ecological and social impacts of large-scale production (Firbank, 2008; Richard, 2010; DeCicco, 2013). Finally, seasonal fluctuations in productivity would require either storage of biomass or temporary decreases in conversion capacity, additional encumbrances that need further study.

To estimate the relative extent of ATS deployment needed for biofuel production, consider a scenario in which the excess fertilizer and manure-based P applied in the Mississippi basin, which would otherwise be discharged into the Gulf of Mexico, is reclaimed by ATS, and the resulting biomass is converted to biofuel. Assume that the 16% (Potter et al., 2010) of the 14.2 Tg of annually applied

P that drains into the Gulf of Mexico (Bouwman et al., 2013) is reclaimed as algal biomass with 0.3% P composition (a conservative estimate) (Bouwman et al., 2013). If 50% of the biomass carbon is ultimately converted to butanol, approximately 282 billion liters (75 billion gallons) of butanol would be produced from 7.6 million ha (19 million ac) of algal growth area, 2.6% of the watershed's surface area. While this calculation is obviously simplistic, it provides a rough estimate of the scales involved. This production rate would nearly satisfy the US federal biofuels mandate, and also suggests that complete replacement of liquid fossil fuels with biofuels will require going beyond merely reclaiming nutrients from continental runoff, as the mandated volume is but a fraction of total demand. One possibility for expanding production would be to utilize marine waters as influent, by establishing extensive estuarine and ocean shore ATS infrastructure or possibly even large "floating islands" for producing ATS biomass.

5. Conclusion

The encumbrances of seasonal fluctuation and socio-economic impact of large-scale production afflict microalgal production even more so than they afflict ATS. Algal turf scrubbing is a mature and easily managed technology that combines elements of two ancient disciplines, road construction and agriculture. It is already economically viable for certain types of water treatment, even under conservative regulations whereby in some jurisdictions credit can be claimed for reducing either N or P. No other farming practice, algal or otherwise, is available that can be readily scaled to produce the millions of tons of biomass needed annually to satisfy the US federal government's mandate for biofuel production. A comprehensive regulatory scheme that paid for both N and P removal, carbon sequestration, water oxygenation, acidification reversal, and biomass would create a financial positive feedback loop that could ultimately cleanse the planet. A profitable, rapidly expanding worldwide network of ATS installations could grow until all continental runoff is treated to pre-industrial water quality levels. This expansion would counter many of the impending violations of planetary boundaries, starting with the most imminent, supporting an initial major increment of biofuel production capacity. Further maturation of ATS technology to address the operational issues offers the potential for ATS to expand sufficiently to completely displace petroleum-based liquid fuels.

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