

Algae biofuel from wastewater treatment high rate algal ponds

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Abstract This paper examines the potential of algae biofuel production in conjunction with wastewater treatment. Current technology for algal wastewater treatment uses facultative ponds, however, these ponds have low productivity (~10 tonnes/ha.y), are not amenable to cultivating single algal species, require chemical flocculation or other expensive processes for algal harvest, and do not provide consistent nutrient removal. Shallow, paddlewheel-mixed high rate algal ponds (HRAPs) have much higher productivities (~30 tonnes/ha.y) and promote bioflocculation settling which may provide low-cost algal harvest. Moreover, HRAP algae are carbon-limited and daytime addition of CO₂ has, under suitable climatic conditions, the potential to double production (to ~60 tonnes/ha.y), improve bioflocculation algal harvest, and enhance wastewater nutrient removal. Algae biofuels (e.g. biogas, ethanol, biodiesel and crude bio-oil), could be produced from the algae harvested from wastewater HRAPs. The wastewater treatment function would cover the capital and operation costs of algal production, with biofuel and recovered nutrient fertilizer being by-products. Greenhouse gas abatement results from both the production of the biofuels and the savings in energy consumption compared to electromechanical treatment processes. However, to achieve these benefits, further research is required, particularly the large-scale demonstration of wastewater treatment HRAP algal production and harvest.

Keywords Algae; biofuel; high rate algal ponds; wastewater treatment.

INTRODUCTION

Algae biomass has the potential to become an important biofuel feedstock, because these single-celled plants can be grown year-round at productivities (~60 tonnes/ha.y), that are nearly an order of magnitude higher than those of most terrestrial biomass crops (e.g. ~7 tonnes/ha.y for maize) (Sheehan et al. 1998; Benemann, 2003). Algae are typically produced using either closed photobioreactors or open, paddlewheel-mixed, raceway ponds called high rate algal ponds (HRAPs). Photobioreactors (enclosed transparent tubes, bags or similar vessels) are used to produce high-value algae food supplements (nutraceuticals) including essential unsaturated fatty acids and carotenoid pigments. However, high capital costs and engineering scale-up limitations make these uneconomical for biofuel applications (Weissman et al., 1988; Sheehan et al. 1998). HRAPs are also a well established technology for the production of algae for health food supplements (Borowitzka and Borowitzka, 1988). Earth-lined HRAPs have much lower capital costs than closed photobioreactors but it remains to be seen if even such simple production systems can be affordably used for algae biofuel production alone (Oswald and Golueke, 1960; Benemann and Oswald 1996).

Algae biofuel could also be a by-product of wastewater treatment, especially where nutrient removal is required prior to wastewater discharge (Benemann, 2003). However, the unmixed, ~1 m deep facultative ponds that are widely used throughout the world for wastewater treatment do not

consistently provide a high level of nutrient removal and have very low algal biomass productivity. For example, in New Zealand, such ponds average an annual production of only somewhat over 10 tonnes/ha.y (Craggs et al. 2003), well below that required for economical biofuel production. The higher algal productivities achievable in wastewater treatment HRAPs would provide algal biofuel feedstocks at much lower costs. HRAP were developed in the late 1950s for wastewater treatment and resource recovery by Oswald and co-workers (Oswald and Golueke 1960). A full-scale wastewater treatment HRAP was built at St Helena, California in 1967 and is still operating. HRAPs are used at several treatment plants around the world and are capable of treating a variety of organic wastes (Craggs, 2005).

ALGAL PRODUCTION IN HRAPS

New Zealand HRAPs treating domestic wastewater have been shown to have algal yields of about 0.2 tonnes/ML (million litres) of wastewater and productivities of almost 30 tonnes/ha.y, which is between two to three-fold that of facultative wastewater treatment ponds (Craggs et al., 2003). However, algal production in such ponds is severely carbon-limited due to the low C:N ratio of wastewaters (typically 1:0.5 for domestic wastewater) compared to algal biomass, which can range from about 1:0.1 to 1:0.2, depending, respectively, on whether N is limiting or not (Benemann, 2003). Thus domestic wastewaters contain insufficient carbon to remove all of the nitrogen by assimilation into algal biomass. Carbon-limitation in wastewater treatment HRAPs is indicated by the elevated daytime pond water pH, resulting from the use of bicarbonate ions as a CO₂ source for algal photosynthesis, releasing hydroxide ions which can increase pond water pH to >10.

At pond water pH of >8.5 the growth of both algae and the aerobic heterotrophic bacteria (which degrade the wastewater organic compounds) is increasingly inhibited, in part as a result of high free ammonia concentrations (Azov et al., 1982). Addition of CO₂ to wastewater treatment HRAPs would therefore enhance algal production and nitrogen nutrient removal by stimulating algal growth. Due to the large, almost ten-fold, range in N:P ratios possible with microalgae (from close to 4:1 to almost 40:1), N removal is the key issue in HRAP tertiary-level treatment (nutrient removal), since efficient P removal does generally not require additional algal biomass production above that needed for N assimilation.

There is little published information on CO₂ addition to wastewater treatment HRAPs, however, CO₂ addition has been shown to more than double productivity of algal cultures (Benemann et al., 1980; Azov et al. 1982; Benemann 2003; Lundquist, 2008) and is practiced at all commercial algae farms producing algal nutritional products. Initial trials of CO₂ addition to agricultural drainage waters were conducted by Gerhardt et al. (1991) and a large-scale trial was later successfully operated over several years. For wastewater treatment HRAP the source of CO₂ could be the flue gas from the power generated from the biogas produced by anaerobic digestion of solids removed from the wastewater, both as settled raw sewage sludge (during “primary treatment”) and the algal biomass harvested from the HRAPs. Further sources of CO₂ could be from the digestion of the biomass residues resulting from the conversion of algal biomass to other biofuels, such as ethanol or biodiesel. The use of HRAP to purify biogas (scrub CO₂ and H₂S) using cost-effective apparatus for mixing the gas into pond water has been demonstrated (Mandeno et al., 2005) and recent research in New Zealand has shown that CO₂ addition to wastewater HRAP doubled algal production (Yield: 0.3 tonnes/ML; projected productivity: 60 tonnes/ha.y) (Heubeck and Craggs, 2007; Heubeck et al. 2007).

A major disadvantage of wastewater treatment HRAPs is the relatively large land requirement compared with electromechanical treatment systems (e.g. activated sludge), however HRAP would

be smaller than conventional facultative wastewater pond systems. The algal biomass production potential from wastewater HRAP is limited by daily insolation and temperature, and hence the area necessary for effective year-round wastewater treatment increases with increasing latitude. Productivity increases are needed, and could be achievable through research on HRAP design and operation, and selection of algal strains that thrive in the HRAP environment.

WASTEWATER TREATMENT IN HRAPs

HRAPs can be used to oxidize organic matter and remove soluble nutrients in many types of wastewater (e.g., anaerobic pond effluents, domestic wastewater pre-treated to the primary or secondary level, agricultural wastewaters, etc.) Depending on climate, HRAPs should be designed with an organic loading rate of about 100-150 kg BOD₅/ha.d. Nutrient assimilation rates can reach 24 kg N/ha.d and 3 kg P/ha.d, based on typical algal nutrient composition and a maximum productivity of 30 g/m².d algae biomass (dry weight). These removals are achieved at much lower capital and operating cost compared to conventional mechanical treatment technologies (Owen, 1982; Craggs et al., 1999). HRAP integrated wastewater treatment amortized capital and operation costs (~\$450,000/ML) are only 25 - 33% of those of secondary-level activated sludge treatment (Green et al. 1995; Downing et al. 2002). HRAPs require power for gentle mixing, using about 0.04 to 0.15 kWh_e/kg O₂ produced depending on season, insolation and other factors, equating to 50 - 110 kWh_e/ML of wastewater (Benemann et al., 1980; Oswald, 1988b; Green et al. 1995). In comparison, activated sludge requires from 230 to 960 kWh_e/ML (based on 0.4 to 1.7 kWh_e/kg O₂) (Owen, 1982; Green et al. 1995b).

Nitrogen removal by nitrification-denitrification is a common nutrient removal process, but it is costly and requires additional energy ~400-1000 kWh_e/ML of wastewater with 30 g N/m³ (Owen 1982). HRAPs with CO₂ addition could provide energy efficient tertiary-level nutrient removal for little additional energy cost (Benemann et al., 1980; Woertz, 2007). Algal biomass can, as stated above, exhibit N:P ratios ranging from nearly 4:1 to almost 40:1 and therefore near-complete assimilation of both N and P into algal biomass from wastewater is theoretically possible (Benemann, 2003). A critical issue for tertiary-level nutrient removal is the maintenance of high algal productivity even when dissolved N has been reduced to low levels (e.g. <1 g/m³). This has been demonstrated in preliminary trials by supplying nutrients as required, but more research is required.

ALGAL HARVEST

Efficient and cost-effective harvest of algal biomass has been a major limitation to economical biofuel production from microalgae using HRAPs, including from wastewater (Benemann and Oswald 1996; Benemann 2003; Molina Grima et al. 2003). Algae harvesting is challenging due to (1) low and varying cell concentration (typically <500 g/m³); (2) cell densities similar to water; and (3) small cell size (5-20 μm). Various harvesting methods, including centrifugation (3 kWh_e/kg algae), filtration or microstraining, sedimentation, and dissolved air flotation (0.6 kWh_e/kg algae, in addition to the chemical flocculants required) can be used to remove algae from HRAP effluent. However, these processes are either not applicable (e.g. filtration, microstraining) or not economical for algae harvesting from wastewater treatment HRAPs or increase parasitic energy losses, as indicated. Chemical flocculation (e.g. with metal salts or polyelectrolytes) is the process currently used to enable algae recovery from facultative oxidation pond effluents. In wastewater treatment HRAPs often small colonial algae dominate (mostly *Scenedesmus*, *Micractinium*, *Actinastrum* and *Pediastrum* genera) which settle reasonably well under quiescent conditions (50-90% removal) (Benemann et al., 1980; Green et al. 1996; Craggs et al. 2003). This settling

phenomenon is characterized by self-flocculation of the algal cells (bioflocculation) which seems to be promoted by stress conditions, such as nutrient (e.g. N) limitation (Eisenberg et al. 1981; Sheehan et al. 1998). Bioflocculation can also be enhanced by recycling of a portion of the settled algae in a similar way to sludge recycle in the activated sludge process (Benemann et al., 1980). Further research is required on bioflocculation of wastewater HRAP algae, as this is the lowest cost harvest process available.

ALGAL BIOFUEL PRODUCTION

Oswald and Golueke (1960) first proposed the large-scale production of microalgae as a biofuel feedstock using HRAPs, with wastewater providing the make-up water and nutrients. Algal biofuels production was the main focus of research under the U.S. Dept. of Energy Aquatic Species Program (summarized in Sheehan et al., 1998). Biofuel conversion of algae biomass could involve one or a combination of four main pathways: (1) Anaerobic digestion of harvested algae biomass to produce biogas (methane); (2) Extraction and transesterification of algae lipid triglycerides to produce biodiesel; (3) Fermentation of algae carbohydrates to ethanol or butanol and (4) Gasification or other thermochemical conversions of algae, in particular super-critical water reactions to convert wet algal biomass to a crude bio-oil (Heubeck and Craggs, 2007). Some microalgae also contain potentially high value hydrocarbons (e.g. *Botryococcus braunii*) and some researchers have proposed genetically modifying algae to produce specific biofuel precursors.

Biogas methane

Oswald and Golueke (1960) found that algae could be digested to biogas (~60% methane) with an average yield of about 0.30 m³ (0.20 kg) CH₄/kg algal biomass with 50-60% volatile solids conversion. The relatively low yield can be attributed to both ammonia inhibition (due to the high N content algal biomass) and the relatively refractory nature of some algal cell walls. More recent laboratory work has demonstrated improved algae digestion through biomass pretreatment (Chen and Oswald, 1998) and co-digestion with low-N wastes (Yen and Brune, 2007) and a pilot-scale demonstration of anaerobic digestion of wastewater HRAP algae has been conducted (Sukias and Craggs, 2006). Co-digestion of HRAP algae biomass with the wastewater solids removed by primary treatment could potentially double the overall methane production from HRAP integrated wastewater treatment (Benemann and Oswald, 1996; Heubeck and Craggs, 2007).

Cost-effective anaerobic digestion could be achieved with covered anaerobic ponds, which could be fed with algal biomass harvested by bioflocculation (typically at ~3% solids concentration), compared to the 5-10% solids required for conventional, and more expensive, heated mixed digesters (Oswald, 1988a). Algal biomass remaining following lipid (oil) extraction or ethanol fermentation (see below) could also be anaerobically digested to produce biogas. Biogas methane can be used directly for heating (34 MJ or 9.38 kWh/m³ CH₄) or for electricity generation at 30% conversion efficiency (2.81 kWh_e/m³ CH₄). Essentially ~1 kWh_e can be generated from the biogas produced from 1 kg algae (Oswald, 1988a, b). Biogas may be cleaned (desulphurised, stripped of CO₂, and dried) and compressed (>20 MPa) for export into a natural gas pipeline or use as transport fuel. Each cubic meter of biogas has an energy value equivalent to ~1 L of petrol (34 MJ).

Biodiesel

Biodiesel production from oils extracted from algae grown in HRAPs was the main research focus of the 30 year U.S. Dept. of Energy Aquatic Species Program (Sheehan et al. 1998). The program concluded that in suitable climates, algae have higher oil yields than most terrestrial crop plants due to their high productivity, with between 50 and 100 tonnes algae dry matter/ha.y and a 25 to 50% oil (as triglycerides) content thought to be attainable, with the lower range being what is currently

thought to be feasible and the higher values projecting what is thought to be possible in the future by applying the modern tools of molecular biology to microalgae mass cultivation (Benemann and Oswald 1996). Algal oil content and quality varies between species and even strains within a species, and with environmental conditions, with nitrogen limitation often greatly increasing oil content (Borowitzka and Borowitzka, 1988; Benemann and Oswald 1996). A major issue is how to extract the oil from the algae, if drying of the biomass is required this will add significantly to the overall costs, even for sun drying (the only plausible method). The long chain polyunsaturated fatty acids which make up algal oil produce a viscous bio-diesel that may polymerize over time into waxy solids, reducing engine efficiency and clogging filters and injectors (Feinberg, 1984). In the case of algal biomass grown on wastewaters, maximizing oil content and yield would not be a priority, and, for the present, a yield of 0.12 L biodiesel/kg algal biomass would be a reasonable near-term goal for such wastewater grown algal biomass.

Bioethanol

Bioethanol is produced from the carbohydrate portion of algae biomass by yeast fermentation followed by distillation to separate it from the other fermentation products. However, bioethanol production from algae is limited by the carbohydrate content of algae biomass (typically 20% of dry matter) and the portion of the carbohydrate that can be converted to fermentable sugars and then to ethanol (typically half to two thirds of the carbohydrate fraction). Thus the fermentable carbohydrate content of algae biomass (~13% DM) is low compared with other bioethanol crops (e.g. ~65% DM for maize) (Sheehan et al. 1998) and an average yield of 0.13 L bioethanol/kg algal biomass appears reasonable. As in the case of algal oil production, a higher content of fermentable starch or other carbohydrates can be induced by means of nitrogen (and other nutrient) limitation. However, this option has received relatively little attention, compared to oil production and is unlikely to be a high priority for algal biofuels production in conjunction with wastewater treatment.

Crude bio-oil

A novel technology for the conversion of algal biomass to biofuel is the super critical water reactor (SCWR) that mimics processes that may have produced fossil oil by using intense heat (~374 °C) and pressure (~22.1 MPa) to disassociate water and degrade organic compounds (Yesodharan, 2002). SCWR conversion has similar advantages to anaerobic digestion in that the algal biomass does not have to be dried (5-30% solids) and conversion is of the whole algal biomass rather than just the lipid of carbohydrate fraction. The SCWR produces a 'crude' bio-oil (with a conversion efficiency of ~30%) from which a range of fuel products could be derived. An average yield of 0.4-0.5 L bio-oil/kg algal biomass might be achievable, but much more research is required to demonstrate the viability of this technology.

OTHER USES AND CO-BENEFITS

Feeds

Algal biomass also has potential for use as high-protein feed supplements for aquaculture and livestock (chickens, pigs and ruminants) (Borowitzka and Borowitzka, 1988). Microalgae contain over 50% crude protein with a yield that is 25-fold higher than soy beans, the highest yielding protein crop. Therefore an average yield of 0.5 kg protein/kg algal biomass is reasonable. Extraction of high value products such as β -carotene and the polyunsaturated fatty acids (PUFAs) or other high value oils could potentially increase the value to wastewater grown algae biomass (Borowitzka and Borowitzka, 1988).

Offset equivalent fossil fuel use GHG emissions

Production of one tonne of algae biomass in wastewater treatment HRAP assimilates approximately 1.8 tonnes of CO₂ (assuming an algal carbon content of 46% dry weight) (Benemann 2003). Once converted to biofuel, this offsets the CO₂ GHG emissions from equivalent fossil fuel use, which is dependent upon the type of fuel it replaces. For example, generation of electricity from methane abates 0.4 kg CO_{2EQV}/kWh_e from natural gas electricity generation compared to 1.0 kg CO_{2EQV}/kWh_e from coal electricity generation. Actual substitution depends on the marginal source of power. GHG emission abatement from the fuel use of biodiesel and bio-oil are 3.40 kg CO_{2EQV}/kg of biodiesel and 0.76 kg CO_{2EQV}/kg of bio-oil.

Reduced CO₂ emissions from wastewater treatment through lower electricity use

Low energy use HRAP wastewater treatment using sunlight energy through photosynthesis abates the CO₂ emissions of the fossil energy that would have powered electromechanical treatment (e.g., activated sludge; Green et al., 1995b; Benemann, 2003). HRAPs, in addition to BOD₅ reduction and nutrient removal, also promote solar disinfection decreasing the need for chemical or electromechanical disinfection (Davies-Colley 2005).

Fertilizer

As discussed, algal biomass is high in nitrogen (10% of dry matter for a non-limited culture), phosphorus (about 1% of dry matter), potassium and micronutrients. Algae recovered from wastewater HRAPs would allow the recycling of such fertilizers, and reduce fossil-fuel consumption required in nitrogen fertiliser synthesis (Oswald, 1988a). Typically, the manufacture of one kilogram of nitrogen (N) fertiliser requires about the equivalent of 16 kWh and the processing of one kilogram of phosphate fertiliser requires the equivalent of 4.47 kWh of energy (Wood and Cowie, 2004). Moreover, the manufacture of one tonne of nitrogen (N) fertiliser will release 3.15 tonne CO_{2EQV} from natural gas and the processing of one tonne of phosphate fertiliser will release 1.39 tonne CO_{2EQV} (West and Marland, 2001). Therefore the use of 1 kg of algae (7% N, 0.08% P) as fertiliser would reduce CO₂ emissions from inorganic fertiliser manufacture by 0.23 kg CO_{2EQV}/kg Algae. Thus even at 10% N content, the energy savings, and greenhouse gas abatement from the use of algae biomass biofuel residues as fertiliser would be equivalent to those from the use of the algae biofuel.

CONCLUSIONS

Algae biofuel production in combination with wastewater treatment using HRAP has several advantages over other approaches to microalgae biofuel production:

1. Provision of energy efficient and effective tertiary-level wastewater treatment with significant cost savings over electromechanical wastewater treatment technologies.
2. Wastewater treatment essentially funds the capital and operation costs of algal production.
3. HRAPs naturally select for productive colonial algae that easily settle.
4. Low-cost harvesting can be promoted through bioflocculation followed by settling.
5. Harvested algal biomass can be converted to biofuel through a range of pathways.
6. Recovered nutrients can be recycled as fertilizer.
7. GHG abatement from low energy wastewater treatment, renewable fuel production and fertiliser recovery provides additional financial and environmental incentives.

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