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Biogas Production from Algae Biomass Harvested at Wastewater

Treatment Ponds

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Abstract. Waste-grown microalgae are a potentially important biomass for biofuel production. However, most of the 7,000 wastewater treatment ponds systems in the US do not use algae harvesting. Those that do, typically return the biomass to the ponds, where it decomposes on the pond floor, releasing methane to the atmosphere and degrading water quality. Instead, the algae biomass could be processed in anaerobic digesters. Algae typically yield less methane than wastewater sludge (~0.3 vs. 0.40 L CH4/g volatile solids introduced). Ammonia toxicity and recalcitrant cell walls are commonly cited causes of the lower yields. Ammonia toxicity might be counteracted by co-digesting algae with high-carbon organic wastes. This paper describes the state of the current literature on algae digestion and presents new data on co-digestion with organic wastes. The focus of the project is to identify the essential information required for full-scale implementation of algae co-digestion at wastewater treatment plants, including the optimal conditions to maximize the methane yield, the volumetric methane productivity, and net energy production.

Keywords. Algae, anaerobic digestion, co-digestion, wastewater treatment.

Introduction

Waste-grown microalgae are a potentially important biomass for biofuel production. However, most of the 7,000 wastewater treatment ponds systems in the US do not use algae harvesting. Those that do, typically return the biomass to the ponds, where it decomposes on the pond floor, releasing methane to the atmosphere and degrading water quality. Instead, the algae biomass could be processed for lipid extraction to be used in transportation fuel, or it can be anaerobically digested to make biogas (US DOE 2009, Brune et al. 2009). Waste-grown algae have widely varying lipid contents, and the technologies for lipid extraction are still under development (Woertz et al. 2009). Thus, anaerobic digestion is likely to be the near-term, appropriate use of algae biomass at wastewater treatment plants. However, algae typically yield less methane than wastewater sludge (~0.3 vs. 0.4 L CH_4/g volatile solids introduced). Ammonia toxicity and recalcitrant cell walls are commonly cited causes of the lower yields. Ammonia toxicity might be counteracted by co-digesting algae with high-carbon organic wastes. Carbon-rich feedstocks that are available near major wastewater pond systems include primary and secondary municipal sludge, sorted municipal organic solid waste, waste fats-oils-greases (FOGs), food industry waste, waste paper, and various agricultural residues. Acclimation of the digester microbial community to algae digestion may also improve the yield.

Microalgae have two major advantages over higher plants with respect to biofuels production. First, biomass productivities are significantly greater for microalgae, with productivities projected at about 70 metric tons per hectare-year of ash-free dry weight (i.e. organic matter) in specialized growth reactors, such as high rate ponds (Sheehan et al. 1998). This productivity compares well with terrestrial temperate crops (e.g., 3 MT/ha·yr for soybeans, 9 MT/ha·yr for corn, and 10-13 MT/ha·yr for switchgrass or hybrid poplars [Perlack et al. 2005]). Second, the cultivation of microalgae does not require arable land or fresh water - it can be carried out in shallow ponds on hardpan soils, using saline or brackish water.

Relatively few studies have been published on the anaerobic digestion of microalgae (reviewed recently by Sialve et al. 2009). The earliest work compared digestion of domestic wastewater sludge and green microalgal biomass, *Scenedesmus* and *Chlorella*, harvested from wastewater ponds (Golueke et al. 1957). They found that these algae could yield as much as 0.25-0.50 L CH₄/g VS input at an 11-day retention time when incubated at 35-50°C. (Methane yield is typically expressed as liters of methane produced per gram of volatile solids introduced into a digester.) The lower value was 32% less than the yield from the wastewater sludge. In addition, the maximum VS destruction was about 45% for the algae, compared to 60% for the wastewater sludge. They suggested that the relatively low digestability and thus yield of microalgal biomass was the result of cell walls resisting bacterial degradation, but being more readily digested by bacteria at the higher temperature. Later laboratory studies with waste-grown algae essentially

confirmed the results of Golueke et al. (Uziel et al. 1978, Eisenberg et al. 1979), and the relatively low yield was reproduced at fullscale at the City of Sunnyvale, California wastewater treatment plant years later (EOA-Bracewell Engineering 1988). Digestion of the cyanobacterium *Spirulina maxima* again gave similar yield results (Samson and LeDuy 1983).

Cell wall disruption is a strategy for increasing digestion. Chen and Oswald (1998) evaluated thermochemical pretreatment of green microalgae biomass, also harvested from wastewater ponds, finding that methane production rates increased by one third when the biomass was pretreated at 100°C for 8 hours at a solids concentration of 3.7%. However, they did not consider the energy balance of the process.

As mentioned above, inhibitory ammonia concentrations might also be a cause of low methane yields from algae digestion (Parkin and Owen 1986). Algae biomass typically has a high protein content (40-50%; C:N ratio $\approx 6:1$), which contributes to high total ammonia concentrations in the sludge. Co-digestion with high-carbon, low-nitrogen substrates has potential for diminishing any ammonia toxicity and also increasing the biogas production per unit volume of digester tank. Methane yield and productivity were doubled when equal masses of wastewater sludge and *Spirulina* biomass were co-digested (Samson and LeDuy 1983). Similarly, Yen (2004) and Yen and Brune (2007) added waste paper (50% w/w) to aquacultural microalgal sludge to adjust the C:N ratio to around 20-25:1 which, in turn, doubled the methane production rate from 0.6 L/L day to 1.2 L/L day at 35°C and with a hydraulic retention time of 10 days.

The present research initiative strives to present new data on co-digestion with organic wastes. The focus of the project is to identify the essential information required for full-scale implementation of algae co-digestion at wastewater treatment plants, including the optimal conditions to maximize the methane yield, the volumetric methane productivity, and net energy production. The first phase of the overall research project includes characterization of different organic wastes, as well as laboratory-scale batch experiments at CDM and semi-continuous experiments at Cal Poly. Co-substrates used in experiments thus far are soybean oil (to mimic waste grease), glycerin (a biodiesel production byproduct), and primary wastewater sludge (not covered in this paper). These preliminary tests will determine which waste streams are most beneficial to use as a co-digestion feedstock.

Materials and Methods

Two rounds of algae digestion batch experiments have been completed thus far. The first round focused on two primary variables: amount of algae per a given amount of inoculum, and the presence of soybean oil as a codigestion feedstock. The second round sought to further refine the optimal algae loading, and examined biodiesel glycerin (the primary byproduct of biodiesel production) as a codigestion feedstock.

The method was the same for each round. All conditions were run in triplicate, and six different conditions were tested per round (for a total of 18 experimental bottles per round). The 260-mL serum bottles were incubated on a shaker table/water bath at 120 rpm and 30°C. The contents for the six different experimental conditions are shown in Table 1. After adding the amounts of each component shown in Table 1 to each bottle, the bottles were capped, sparged with nitrogen gas, and placed in the shaker table. Gas production was measured daily by inserting a needle attached to a frictionless syringe through the septum and allowing the headspace to equilibrate with atmospheric pressure. The compositions of the headspaces were analyzed by gas chromatograph with a flame ionization detector (GC-FID) near the end of the experiment.

EXPERIMENTAL PLAN				
Bottle Number	Inoculum (mL)	Algae (mL)	Soybean Oil (mL)	
1 – 3	90			
4 - 6	90	9		
7 – 9	90	18		
10 - 12	90	9	0.5	
13 – 15	90	18	0.5	
16 – 18	90		0.5	

Table 1. Components of Round 1 Experiments.

The inoculum for Round 1 was a mixture of digester effluents from two different digesters. One digester was a full-scale municipal anaerobic digester at the King County South Plant in Renton, WA. The second was from a lab-scale digester at Cal Poly being fed algae. The two digester seeds were mixed in equal proportions. This mixed inoculum was tested for both volatile solids (VS) and chemical oxygen demand (COD). The VS of the inoculum was 2.2%, and the COD was 50 g/L. The algae used in these experiments were 12% VS, and had a COD level of 250 g/L. The soybean oil used was store-bought, and was 100% VS, and 1800 g/L COD.

The second round sought to refine the maximum loading of algae to the digester bottles. Since in the first round the bottles that received 18 mL of algae performed better than those that only received 9 mL, the second round increased the algae added to 36 mL per bottle. Also, because we wanted to perform experiments using a codigestion feedstock that may be available to wastewater treatment plants, we examined biodiesel glycerin, the primary byproduct of biodiesel production. The experimental conditions for the serum bottles in Round 2 can be seen in Table 2.

Table 2. Components of Round 2 Experiments

EXPERIMENTAL PLAN				
Bottle Number	Inoculum (mL)	Algae (mL)	Glycerin (mL)	
1 – 3	90			
4 - 6	90	18		
7 – 9	90	36		
10 - 12	90	18	0.082	
13 - 15	90	36	0.082	
16 – 18	90		0.082	

Results and Discussion

Round 1 - Soybean Oil

The results of this round of experiments can be seen in Figure 1. It is obvious from this graph there is a substantial amount of acclimation occurring. The two conditions that contained oil were impeded in their biogas production for two weeks, before they increased their biogas production rate dramatically. After 4 weeks of the experiment, they had well surpassed the conditions without oil. These results show promise for the typically difficult-to-digest algae biomass in anaerobic digesters.



Figure 1. Biogas production from digestion of algae (Round 1 experiments).

Near the end of the experiment, headspace gas samples from each bottle were analyzed for their methane content. Table 3 shows the total biogas produced after 28 days, the percent methane calculated for the biogas produced, and the volume of methane produced for each set of bottles. The highest values, both in terms of biogas production and methane content, were bottles 10-12 and bottles 13-15, which were the two conditions that received both algae and soybean oil. Inoculum with algae alone, and with oil alone, had lower methane percentages in the headspace.

Table 3. Methane Results for the Round 1 Experimen	its
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Bottle Number	Total Biogas after 28 days (mL)	%CH4	CH4 (mL)
1 – 3	480	58%	279
4 - 6	852	59%	498
7 – 9	1294	61%	787
10-12	1419	69%	974
13 – 15	1794	66%	1178
16 - 18	550	48%	266

Round 2 - Biodiesel Glycerin

The results for Round 2 are shown in Figure 2, and they are significantly different from Round 1. The first thing to notice is that for the first 3 weeks of the experiment, the bottles with 18 mL of algae outperformed the bottles with 36 mL of algae. This implies that there is some inhibition from the excess algae. The second thing to notice is that the glycerin did not have as profound an effect on the biogas production as the oil did. This is likely due to the fact that less glycerin was added (on a COD basis) than the oil. However, it may also be due to some inhibitory effect, such as high sodium or sulfur (both of which are characteristics of waste biodiesel glycerin). Although it is difficult to draw many significant conclusions about how to enact algae digestion at full-scale, this preliminary work does suggest that it may be possible for further research to optimize the process.



Table 2. Biogas production from digestion of algae (Round 2 experiments).

Bottle Number	Total Biogas after 28 days (mL)	Final pH Value
1-3	372	7.76
4-6	929	7.76
7 – 9	1205	7.67
10-12	1013	7.81
13 – 15	1173	7.56
16 - 18	402	7.82

Table 4. Methane and pH Results for the Round 2 Experiments

Conclusion

These experiments show that it is possible to digest algae in anaerobic digesters. The addition of a high-strength, high-carbon waste may balance the high-nitrogen nature of the waste-grown algae. The batch experiments show that acclimation does occur, with significant increases in biogas production rate occurring multiple weeks into the tests. Further experiments are underway to help identify the issues, and benefits, of implementing algae co-digestion at full-scale wastewater treatment plant.

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