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Chemical Fixation of CO_2 in Coal Combustion Products and Recycling Through Biosystems

Final Technical Report

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ABSTRACT

This Annual Technical Progress Report presents the principle results in enhanced growth of algae using coal combustion products as a catalyst to increase bicarbonate levels in solution. A co-current reactor is present that increases the gas phase to bicarbonate transfer rate by a factor of five to nine. The bicarbonate concentration at a given pH is approximately double that obtained using a control column of similar construction. Algae growth experiments were performed under laboratory conditions to obtain baseline production rates and to perfect experimental methods. The final product of this initial phase in algae production is presented.

Algal growth can be limited by several factors, including the level of bicarbonate available for photosynthesis, the pH of the growth solution, nutrient levels, and the size of the cell population, which determines the available space for additional growth. In order to supply additional CO2 to increase photosynthesis and algal biomass production, fly ash reactor has been demonstrated to increase the available CO2 in solution above the limits that are achievable with dissolved gas alone. The amount of dissolved CO2 can be used to control pH for optimum growth. Periodic harvesting of algae can be used to maintain algae in the exponential, rapid growth phase.

An 800 liter scale up demonstrated that larger scale production is possible. The larger experiment demonstrated that indirect addition of CO2 is feasible and produces significantly less stress on the algal system. With better harvesting methods, nutrient management, and carbon dioxide management, an annual biomass harvest of about 9,000 metric tons per square kilometer (36 MT per acre) appears to be feasible.

To sequester carbon, the algal biomass needs to be placed in a permanent location. If drying is undesirable, the biomass will eventually begin to aerobically decompose. It was demonstrated that algal biomass is a suitable feed to an anaerobic digester to produce methane. The remaining carbonaceous material is essentially bio-inactive and is permanently sequestered.

The feasibility of using algae to convert carbon dioxide to a biomass has been demonstrated. This biomass provides a sustainable means to produce methane, ethanol, and/or bio diesel. The first application of concept demonstrated by the project could be to use algal biomass production to capture carbon dioxide associated with ethanol production.

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1.0 INTRODUCTION

1.1 Conversion of CO_2 to Bicarbonate Using Fly Ash as a Catalyst

The mass transfer of carbon dioxide gas to carbonate solution is the rate-limiting step in producing carbonate solutions. One of the objectives of the "Chemical Fixation of CO2" project was to develop a method to increase the rate of transfer for CO2 using coal combustion products (CCP). The data present here demonstrates that fly ash is able to provide the critical mechanism needed to increase the available CO2 in solution above the limits that are achievable with the dissolved gas alone.

1.2 Algae Growth

Several factors limit algal growth. These include the level of bicarbonate available for photosynthesis, the pH of the growth solution, and the size of the cell population, which determines the available space for additional growth. Increased bicarbonate is demonstrated to increase algal growth beyond what is normally attainable. This was tested with a number of experiments. A number of sampling and analysis issues had to be resolved before reproducible results could be obtained.

Fly ash has been demonstrated to increase the available CO_2 in solution above the limits that are achievable with dissolved gas alone. The additional supply of CO_2 increases photosynthesis and algal biomass production. The amount of dissolved CO_2 can be used to control pH for optimum growth. Periodic harvesting of algae can be used to maintain algae in the exponential phase of growth.

The direct addition of CO2 to the growth media produced a number of problems and artifacts in the algae growth. Some of the problems were due to the aquarium scale of the experiments. To alleviate these problems, a larger scale experiment with indirect CO2 addition was preformed. The larger experiment demonstrated that indirect addition of CO2 is feasible and produces significantly less stress on the algal system.

1.3 Anaerobic Production of Methane

To sequester carbon, the algal biomass needs to be placed in a permanent location. If drying is undesirable, the biomass will eventually begin to aerobically decompose. In order to determine the decomposition characteristics of the cultured algal biomass, a pair of anaerobic digester cells was constructed. These cells were charged alternately with algal biomass and Land O' Lakes milk replacement starter (MRS). Evolved gasses were collected and compared. It was demonstrated that algal biomass is a suitable feed to an anaerobic digester to produce methane. The remaining carbonaceous material is essentially bio-inactive and is permanently sequestered.

2.0 EXPERIMENTAL

2.1 Conversion of CO_2 to Bicarbonate Using Fly Ash as a Catalyst

The mass transfer of carbon dioxide gas to carbonate solution is the rate-limiting step in producing carbonate solutions. A co-current reactor was developed that contained fly ash and was compared to a similar reactor containing 5-mm glass beads.

The reactor (Figure 1) consisted of a transparent PVC column (3.8 cm (1.5") diameter x 18 cm (7") long) with fitting on each end to introduce liquid and gas and to collect the overflow liquid and gas. Lean liquid was introduced at the bottom along with a controlled flow of CO_2. Water flow was controlled with a constant displacement pump. The setup for the experimental control also included a transparent PVC column (3.8 cm (1.5") diameter x 18 cm (7") long). In the control the column was packed with 5-mm glass beads. The CO_2 gas was introduced into the re-circulated salt water solution prior to column inlet.

The test setup consisted of a similar column packed with fly ash. Gas flow was adjusted so that all the CO_2 was reacted in the reactor column. In this experiment, gas flow was electronically controlled to about 3 cc/min with a 50 sccm/min Tylan FC260 mass flow controller (four equal streams were produced with a total flow of 12 sccm). The gas stream was split into four segments using 0.013 mm (0.0005") PEEK capillary tubes approximately 12.7 cm (5") long. The flow rates through each of the four tubes were individually checked using a bubble flow meter and matched to less than one percent.

The glass bead control was tested under the same conditions. In this and the previous test, the actual flow was monitored with a bubble flow meter.

In all the tests, inorganic carbon (IC) analyses were performed on samples taken from an open container in which the solution was being re-circulated. Sample vials were filled to the top and capped with zero head space.

2.2 Micro Algae Culture

Initially, three species of micro algae were obtained as disc cultures (MICRO ALGAE DISKS®, Florida Aqua Farms Inc., Dade City, FL) and prepared according to manufacturer's instructions. Isochrysis, Tetraselmis and Nannochloropsis were cultured in 1 L glass jars and then transferred to 5 gallon glass carboys. An artificial seawater medium was used (Instant Ocean and de-ionized water, prepared according to product labeling). Cultures were aerated with air stones and placed under grow lights. The carboy cultures were used as stock for cultures used in algae growth experiments. For experiments, normally four to eight liters of the carboy stock culture were added to a five gallon aquarium and brought to 16 liters final volume with artificial seawater.

In the months following the initial growth experiments, the three stock cultures commingled and Tetraselmis began to predominate. Tetraselmis was the predominant species in laboratory cultures.

Figure 1. CO_2 Reactors

2.3 Stock Culture Maintenance

Cultures were diluted on a regular basis to maintain an active cell population. Nutrients (Kent Marine Pro-Culture F/2 Nutrient Solutions Parts A & B, obtained from Aquatic Ecosystems, Apopka, FL) were added weekly according to manufacturer instructions, and fresh de ionized water was added to aquariums to make up for evaporative losses. In the final 200 gallon experiment, it was necessary to add nutrient twice a week.

2.4 Microscopic Evaluation and Enumeration of Cells

During the experiments, aquariums were sampled regularly to check for contamination and enumeration of cells. Algae cells were counted under 100 x magnification using a hemocytometer, according to the method described in Plankton Culture Manual, (Hoff and Snell, ISBN: 09662960-0-1, Florida Aqua Farms).

2.5 Algae Growth—Screening

Three aquaria (19 liter (5 gal), 800 cm2 top surface area), each containing a different species of phytoplankton (isochrysis, nannochloropsis, and tetraselmis) were used (Figure 2). Four liters of liquid culture from the previous experiment was used and diluted with 12 liters of Instant Ocean (mixed according to package instructions). Four liters of liquid culture was also retained and filtered to ascertain biomass content.

Carbon dioxide gas was bubbled into the aquaria each morning. The pH was monitored to keep the pH above the low (pH = 6) levels seen in previous experiments. The low pH apparently shocked the algae and prevented growth until the pH was high enough. Dissolved oxygen, pH, chlorophyll, salinity, specific conductance, ORP, and temperature were monitored by unattended programmable sondes (YSI Incorporated, Model 6820, Yellow Springs, Ohio), and daily measurements were taken with a hand-held sonde to check the data. Biomass samples were taken of the water column twice daily (morning and afternoon). Prior to each sampling, the liquid culture was stirred to distribute settled biomass. Water column sampling used a 22 mm ID glass tube, approximately 25 cm long. A number four rubber stopper on the end of an 8 mm glass rod, approximately 60 cm long was used to seal the end of the sample tube. Sampling was accomplished by placing the stopper rod on the bottom of the aquarium and slowly lowering the sampling tube over the rod down through the water column. The lower end was sealed with the stopper and the sample removed.

These samples were vacuum filtered through a tared 0.4µ filter to collect the algal biomass. Sample sizes for filtering were between 25 and 50 mL. Larger samples could not be easily filtered. Filters were dried in a 65ºC oven and placed in a desiccator prior to obtaining a constant weight. Samples were taken for inorganic carbon analysis before and after CO_2 addition and in the afternoons to determine how much IC was depleted in the course of a day. Sampling was performed over four consecutive days.

The three aquaria were exposed to artificial sunlight produced by grow lights with photosynthetically active radiation of 130 W/m^2 (600 $\mu E/m^2/sec$). This is approximately a third of solar light available on a clear day. The lights were operated on a simulated day of

14 hours on (6:00 a.m.—8:00 p.m.) and 10 hours off (8:00 p.m.—6:00 a.m.). The experiment was conducted during four consecutive days.

2.6 Algae Growth—Biomass Optimization

In order to assess the effect of CO_2 additions and subsequent pH changes on algal growth, a CO_2/pH control system was implemented (Figure 3). The control system maintained the desired pH in each aquarium by monitoring pH levels, and opening and closing CO_2 supply valves as needed to increase and decrease the pH. A pH controller in each aquarium monitored the pH level. When no CO_2 was being supplied to the aquarium, the pH increased due to depletion of CO_2 in solution from algal photosynthesis. When the pH reached the desired upper limit, the CO_2 feed valve was opened, supplying CO_2 to the reactor water stream, which was continually circulated from the aquarium, through the CO_2 reactor, and back into the aquarium. When the pH in the aquarium decreased to the lower limit, the CO_2 supply to the water stream was discontinued. A set of experiments was conducted to determine if the pH control system was functioning properly, and to determine optimum pH for the culture of marine phytoplankton. The pH levels were controlled in 0.2 increments for experiments 1 through 4 (Table 1). In all these experiments, the sides of the aquaria were covered with cardboard to exclude light from the sides.

Experiment 1

Aquariums were prepared using carboy stock solutions as described above in section 2.2, "Micro Algae Culture", and the pH levels were controlled as described above. Due to a data logging error in the data collection program, pH data was not available for this experiment.

For this experiment, two liters were harvested each day from the 16 liter volume in each aquarium. Two 200 mL aliquots were taken from the 2 liter sample and centrifuged at 10,000 rpm for 10 min. The resulting pellets were re suspended with de ionized water and centrifuged once more at 10,000 rpm. The pellets were combined and quantitatively transferred to a tared aluminum weighing pan and dried. In addition to algae, the pellets contained fly ash that had washed out of the column into the aquarium, so the sample was then ashed to a constant weight to determine the percent biomass, or algae, of the total pellet weight. The remainder of the 2 liter sample (~1600 mL) was vacuum-filtered through tared 24 cm Whatman #3 paper, and the filter papers were dried in an oven to a constant weight. The water from the centrifugation and filtering procedures was recovered and returned to the respective aquariums, in order to maintain the proper volumes.

Figure 2. Typical Algae Tank at Beginning of an Experiment

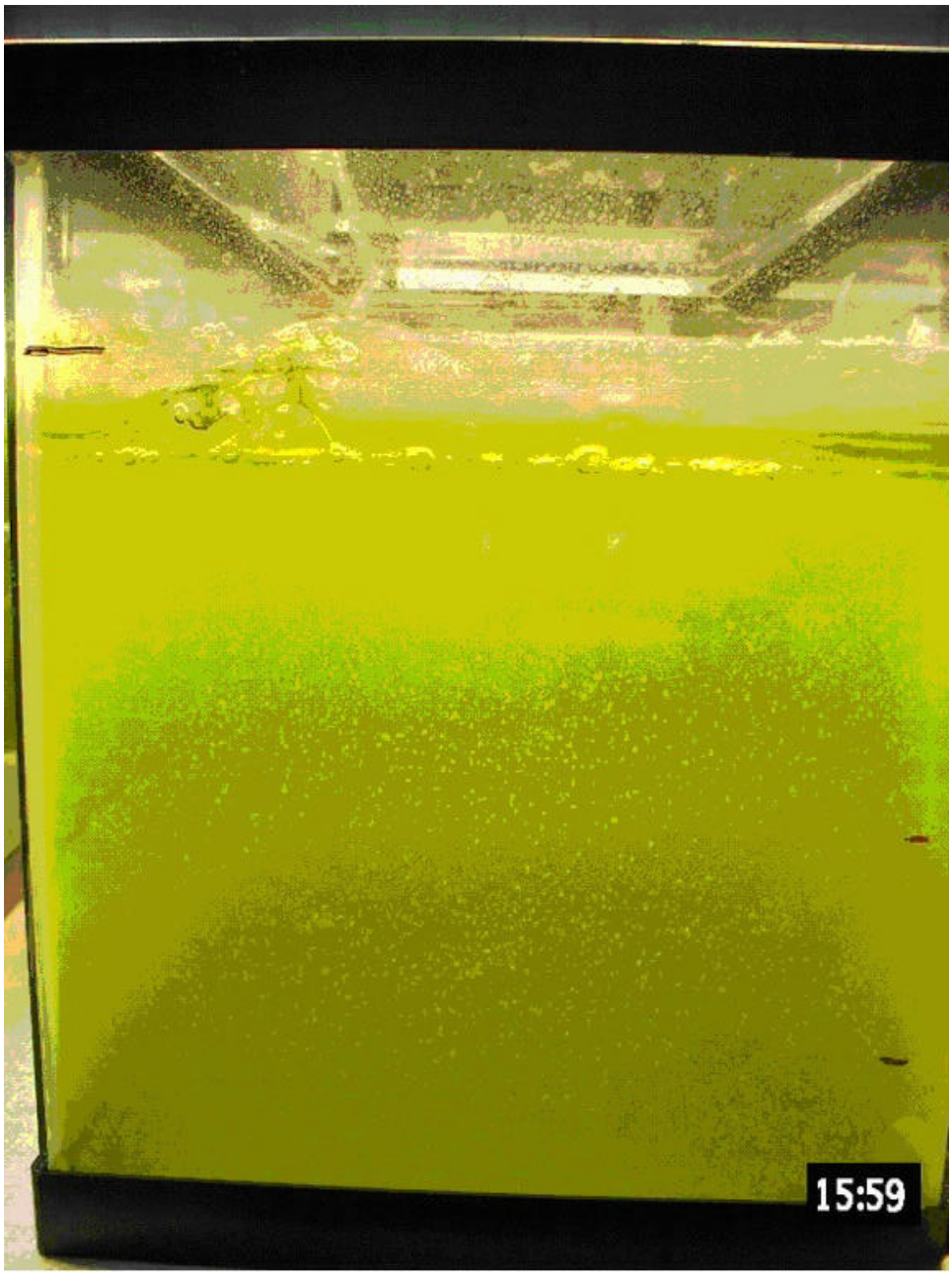


Figure 3. Algal Bio-system pH Control System

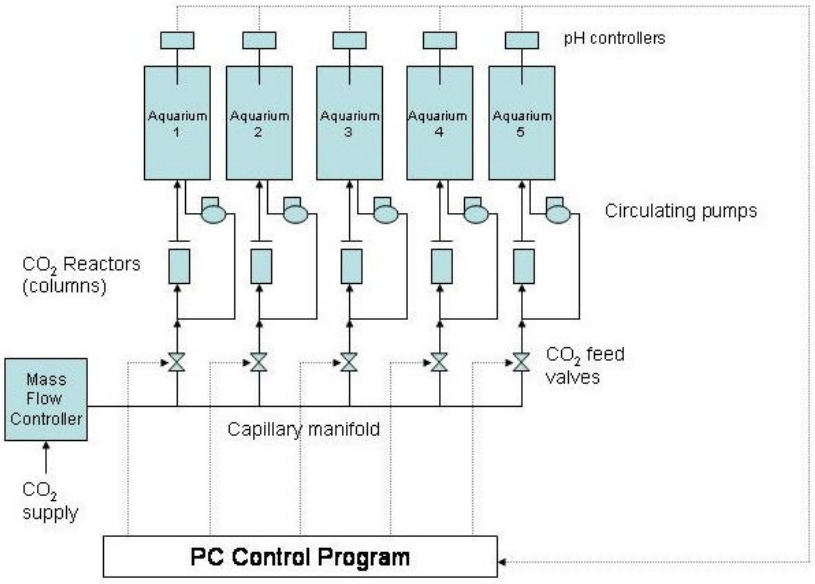


Table 1. pH treatment ranges for experiments 1-4

pH 7.8-8.0
pH 7.6-7.8
pH 7.2-7.4
pH 7.0-7.2

To obtain an estimation of total biomass in each aquarium, the biomass of the two 200 mL aliquots plus the biomass of the filtered 1600 mL fraction were combined, with the filtered fraction being corrected for ash using the ash content of that day's centrifuged pan sample. The biomass of this 2 L sample was then used to estimate the biomass of the total 16 L volume in the aquarium.

Experiment 2

Based on the falling cell populations encountered after repeated harvesting during experiment 1, experiment 2 was designed to track cell population trends during CO_2 introduction without the influence of harvesting. Aquarium preparation and pH level control were the same as in experiment 1, but no algal biomass was harvested for this experiment.

Experiment 3

After observing the appearance of a film of algal biomass on the surface of the aquariums during the main growth phase in experiments 1 and 2, the harvesting technique was modified not to remove a specific volume of algal suspension, but to periodically "skim" off this film and determine its biomass.

The pH was controlled by CO_2 addition to the algal biosystem, as in previous experiments. Skimmed harvesting samples were collected regularly, then transferred quantitatively to a tared aluminum weigh boat and dried to a constant weight. Samples were then ashed to a constant weight to determine actual biomass content.

Experiment 4

Harvesting technique and CO_2 additions were the same as in experiment 3. A control aquarium without CO_2 addition to the biosystem was included in this experiment. At the completion of the experiment, all the algae from each aquarium were harvested by vacuum filtration to determine total biomass for each treatment.

Experiment 5

Harvesting technique and CO_2 additions were the same as in experiments 3 and 4. Expanded pH ranges were used in this experiment (Table 2).

Table 2. pH treatment ranges for experiment 5

pH 9.0-9.5
pH 8.5-9.0
pH 8.0-8.5
pH 7.5-8.0

2.7 Algae Growth—800 Liter Scale up

A number of problems arose in earlier experiments due to the scale of the experiments and the method to add carbonation to the growth cell. The principle scale problem was the inability to reliably control liquid and gas flows at the low rates required by the experiments. The carbonation problem was due to passing the growth medium through the circulation pumps. The 4’ x 8’ x 1’ growth cell was constructed from ½” exterior plywood attached to a 4” x 4” frame and legs. See Figures 3 thru 6. The cell was elevated 3’ above the floor. The inside was lined with pond liner. Bulkhead interfaces (Figure 4) at each end were fabricated from 3" ID x 4" OD PVC Floor Drains. A 12” length of 3” PVC pipe extending to the inside was cemented in each of the floor drains. The end section of the 1 ½” inlet and outlet manifolds were passed through 3” PVC pipe and interfaced to the 3” pipe with 3” x 1 ½” flexible reducing couplings.

The CO_2 was supplied by diffusion from a low pH feed system. The surface pH in the growth cell was controlled in range of about 8.4 to 8.6 by the addition of CO_2. A control/monitor computer was used to control the overall process. For surface pH of greater than 8.4, the growth cell does not lose CO_2 to the atmosphere. The white cross flow pipes in Figure 4 are the diffusion tubes. They consist of ¾" PVC Schedule 20 pipes in which about one fourth the pipe surface area has been removed by a ½" router. The pipe is then covered with a Dacron sleeve (Donated by Zens Industrial Knit Products, P. O. Box 12504, Milwaukee, WI 53212-0404). There is no direct mixing of the low pH solution with the higher pH growth medium. This avoided the pH shock and damage to algae experienced in earlier experiments. Each of the diffusion tubes is approximately 36" (cut to fit) long with a 30" active zone. Thirteen diffusion tubes were attached to a 1 ½" PVC inlet and outlet manifolds with 1 ½" x ¾" PVC reducing tees.

Circulating solution is pumped from a reservoir to a pair of fly ash catalyzed reactors in which the CO_2 is added. The pH of the CO_2 rich circulating solution input to the diffusion tubes is controlled between 6 and 6.4 so as to be in equilibrium with a 100% CO_2 atmosphere. This avoids loss to the atmosphere from within the circulation loop. The output of the reactors is fed to each end of the input manifold.

Sensors for pH were placed in the two inlet and outlet streams. A pH sensor was also placed in the center of the tank to measure the surface pH. . Dissolved oxygen, pH, chlorophyll, salinity, specific conductance, ORP, and temperature were monitored by an unattended programmable sonde that was place about the center of the tank lengthwise and about 18" from the edge. The sonde sensors were approximately 3" from the bottom of the tank. Inlet, outlet, and surface pH probes were Cole Palmer catalog number U-27001-70. The probes were interfaced to the control/logging computer through Oakton Alpha 100 pH/ORP controllers (Model WD 35100-10).

The growth cell was filled to a depth of 10" with artificial seawater medium (Instant Ocean) prepared according to label instructions with de chlorinated tap water. The depth was controlled by adjusting the output manifold to overflow any excess. The diffusion array reservoir tank (a 30 gallon plastic trash can) was filled to just activate (about 20 gallons) a float switch in the reservoir. The float switch controlled a pump in 50 gallon tank of de chlorinated water. The float switch activated a 30 minute time delay relay to prevent rapid cycling of the make up pump. Make up water was added to compensate for evaporation whenever the float switch indicated a low level. Nutrients (Kent Marine Pro-Culture F/2 Nutrient Solutions Parts A & B, obtained from Aquatic Ecosystems, Apopka, FL) were added according to manufacturer instructions. The tank was the inoculated with 32 liters of nannochloropsis culture, and 16 liters of tetraselmis culture. Each of the cultures had been growing in greenhouse condition with air bubbling for about a month.

Throughout most of the experiment, harvesting was accomplished by pumping about 30 gallons per hour into each of two continuous centrifuges. The pumps were pond recirculation pumps and were placed at the reservoir end of the growth cell. The centrifuges were programmed to operate for a fixed time each day by a programmable

timer. The effluent from the centrifuges was returned to the growth cell on the control end (opposite pumps) of the growth cell. The centrifuges were mounted on platforms at two of the corners of the growth cell.

Harvested material was dried in a 150 °C drying oven to constant weight. A one gram aliquot was then ashed at 600 °C to determine the biomass fraction.

Figure 4. Algae Growth Cell—800 Liter Scale up

Figure 5. Algae Growth Cell—Bulkhead Interface

Figure 6. Algae Growth Cell—Reservoir End

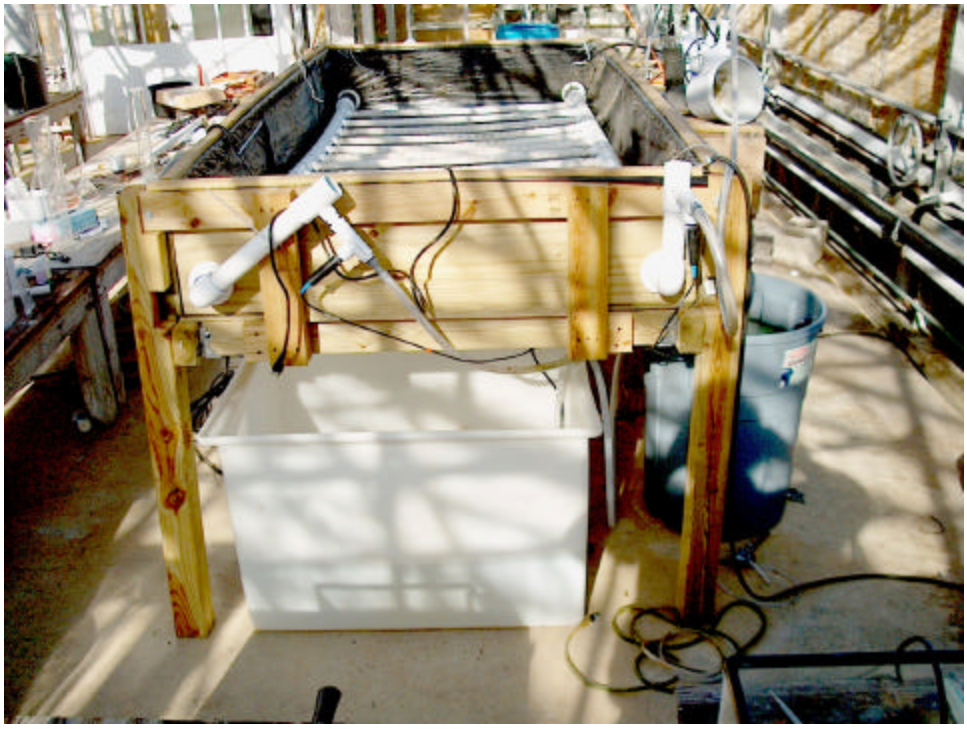


Figure 7. Algae Growth Cell—Controller End

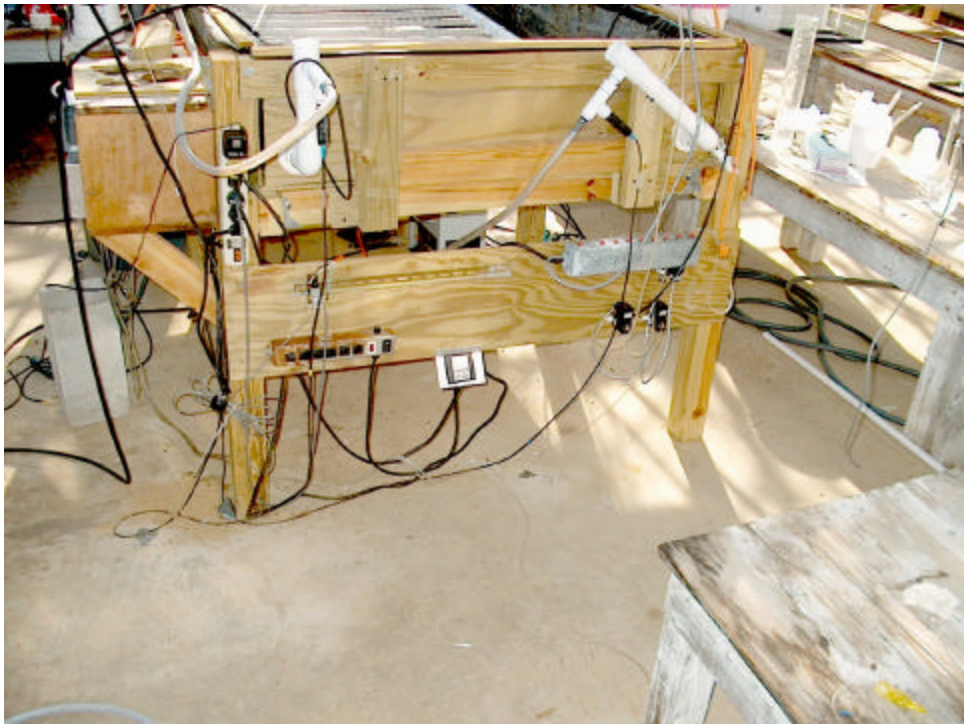


Figure 8. Harvesting Centrifuge (Shown without cover)

2.8 Anaerobic Production of Methane

Digesters

Two digesters were fabricated from 10 liter Pyrex vessels approximately 46 cm high and 19 cm in diameter (Figure 9). The digesters were fitted with rubber stoppers with 4 holes to allow for gas collection, feeding, effluent collection and temperature measurement. The exit tube for gas collection extended just below the bottom of the stopper and was connected to a 3.78 liter Nalgene gas collection bottle in a water bath using Tygon tubing (Figure 10). The water in the gas collection bottle and the water bath containing the gas collection was maintained at a pH of approximately 2.5 by the addition of citric acid to minimize carbon dioxide absorption. The tubes for feed addition and effluent collection extended approximately half way and all the way to the bottom of the digester, respectively. The fourth hole in each stopper was fitted with a stainless tube which was closed at one end and extended approximately 15 cm into the digester liquid. A Type K thermocouple was placed in each of the stainless steel tubes to monitor digester temperature. An additional Type K thermocouple was used to monitor the temperature of the water bath containing the digesters.

The digesters were placed in a 46 cm by 80 cm by 36 cm Nalgene water bath fitted with a Haake D3 heater/temperature controller/circulator set at 35C. The water bath was placed on top of two magnetic stirrers (one for each digester) for mixing of the digester contents using 5 cm by 1 cm stir bars.

Digester Inoculation

The inoculum for the digesters was obtained from an anaerobic digester treating aquaculture (fish) waste at TVA's Constructed Wetlands Research Facility in Muscle Shoals, Alabama. Approximately 30 liters of digester effluent was collected in two 20 liter carboys and the solids were allowed to settle overnight. The majority of the clear supernatant was decanted from each carboy and the remaining solids (approximately 5 liters) were pooled together. Two liters of the digester solids were placed in each of the two Pyrex digesters and brought to a volume of 9.5 liters with tap water. Thus each Pyrex digester had a headspace of approximately 500 ml.

The Pyrex digesters were then purged for 3 hours with nitrogen gas to remove residual oxygen and the digester liquid was allowed to come to 35C in the water bath while being stirred with the magnetic stirrers.

Digester Feed

Feed for the digesters was either algae or Land O' Lakes milk replacement starter (MRS). The MRS has been used in previous wetlands research as a nutrient rich readily degradable carbon source and was selected for this study to provide comparative

information on methane production between the unknown algal feedstock and the MRS feedstock containing significant amounts of easily metabolized sugars and protein.

Chemical oxygen demand (COD) of the MRS and algae suspension was used to determine the amount of feed necessary to provide the desired feed rate. Methane production reported in this study was normalized to g/l of COD or Biochemical Oxygen Demand (BOD) added as MRS or algae. COD was measured using the Hach COD digestion procedure with glucose as a standard and BOD was determined using standard procedures

The COD and BOD of a 1g/L MRS suspension were 1379 and 839 mg/L, respectively. Similarly, the COD and BOD of the algae suspension were 28,600 and 18,900 mg/L, respectively. The volume of algae suspension fed was adjusted to equal the amount of COD or BOD added as MRS so that both digesters were receiving the same amount of feed.

The MRS feed was prepared by adding the desired amount of MRS to water and dissolving the MRS. The algal feed was prepared from algae harvested during one of TVA's algae production tests. The collected algae were filamentous and heterogeneous in composition. To provide a homogenous feed, the raw algae were processed in a Waring blender for approximately 45 seconds to produce a thick, homogenous suspension suitable for digester feed. A part of the algae suspension was refrigerated for near-term use and the remainder was frozen for use in the latter stages of the study.

Before feeding the digesters the magnetic stirrers were turned off to allow digester solids to settle. Digester feeding was accomplished by clamping off the gas collection tube and opening the digester feed and effluent collection ports. Feed was added using a 60 ml plastic syringe which attached to the feed port. As the feed was added, effluent was forced from the digester and collected for subsequent pH and COD analysis. Feeding rates were increased as needed based on digester stability and apparent gas production. The volume of either MRS or algae suspension added at each feeding was initially 100 ml and increased to 200 ml at the end of the study. For the 9.5 liter liquid volume of each digester, this translates to a range in hydraulic retention time of between 95 and 48 days.

Effluent pH was measured at each feeding and then the effluents from each week of feeding were pooled for COD analysis.

To help ensure that the digesters operated on a comparable basis and to minimize any potential toxic effects from either feed, the feed for the digesters was switched, generally every two weeks throughout the course of the study. For example, Digester 1 would receive algae for two weeks while Digester 2 received MRS. After the two week period Digester 1 would be fed MRS and Digester 2 would be fed algae.

Digester Start-up

After temperature equilibration, both digesters were fed MRS for two weeks to ensure that the digesters performed similarly with the same feed. During this two week period an average of 267 ml and 441 ml of methane were produced by digesters based on one gram of fed COD and BOD, respectively. In subsequent weeks, the feeding rates of the digesters were gradually increased and the digester feeds were alternated between the two digesters (generally every two weeks) for the duration of the study.

Gas Collection, Sampling and Analyses

Gas from the digesters was collected by the displacement of citric acid acidified water from 3.78 liter Nalgene bottles. The gas-water interface of the bottles were marked daily to provide an indication of the rate of gas production and provide a reference for determining the volume of gas produced.

Gas samples for methane and carbon dioxide analysis were collected weekly by the displacement of acidified water by gas from the gas collection bottles into glass vials fitted with septa.

Two gas samples were taken for each digester during each sampling time. After taking the gas sample the gas collection bottles were refilled with acidified water in preparation the next week's gas sampling.

The glass vials containing the gas samples were then analyzed by gas chromatography. Gas samples were generally analyzed by gas chromatography on the day the samples were collected.

After several weeks of gas analysis it was noted that the composition of the gas from the gas collection bottles had a higher methane content and a lower carbon dioxide content than typically expected for biogas (e.g., 60 to 65 percent methane and 30 to 35 percent carbon dioxide. To address this anomaly (which was caused by carbon dioxide absorption in the acidified water displaced from the gas collection bottles) and gain better information on the composition of gas produced by the digesters, gas samples were also collected from the digester headspace during the latter stages of this study to confirm that the biogas produced actually contained the 60 to 65 percent methane and 40 to 35 percent carbon dioxide that would be expected.

Because of concerns about the gas composition data obtained during the majority of this study, only results for methane production corrected for residual carbon dioxide in the gas samples are presented.

Figure 9. Anaerobic Digesters

Figure 10. Gas Collection from Anaerobic Digesters

3.0 RESULTS AND DISCUSSION

3.1 Conversion of CO_2 to Bicarbonate Using Fly Ash as a Catalyst

Table 3 shows that uptake of CO_2 in the fly ash column is five to nine times the rate in the glass bead column. At 1.5 hours the fly ash column pH was 6.5, while the glass bead column pH was 6.0. This indicates the fly ash has a capacity to buffer the solution. The pH of the fly ash column is more suitable for biological systems than the glass bead column.

Table 3. Glass Beads v. Fly Ash @ 3 cc/min

Time	Glass Beads		Fly Ash	
h:min	IC Conc (ppm)	pH	IC Conc (ppm)	pH
0:00	19.52	10.08	12.25	9.22
0:05	27.11	9.26	55.92	7.78
0:10	33.28	8.72	63.59	7.14
0:15	37.65	7.47	68.55	6.89
0:30	44.68	6.59	84.01	6.61
0:45	50.81	6.34	97.20	6.53
1:00	54.16	6.22	105.60	6.49
1:30	63.73	6.06	128.80	6.48

3.2 Algae Growth- Screening

Table 4 and Figure 11 show the total biomass per aquarium for each of the algae species of phytoplankton (isochrysis, nannochloropsis, and tetraselmis) used in this experiment. The general characteristics of the growth curves are a moderate increase in biomass for two or three days followed by a significant increase on the next day. Afterwards there was a slow decrease in biomass indicating the onset of respiration metabolism for algae near the bottom of the aquaria. The average biomass increase to the maximum for isochrysis was 30 grams/m^2/day, for nannochloropsis was 54 grams/m^2/day, and tetraselmis was 29 grams/m^2/day. The final biomass values obtained in three days are approximately double those obtained in nine days in previous experiments. The previous experiments had only a single addition of carbon dioxide at the beginning.

Figure 12, Figure 13, and Figure 14 show pH and dissolved oxygen along with biomass. Note the sharp increase in pH in the region of maximum growth. This indicates a sharp decrease in bicarbonate level. The dissolved oxygen measurement is an indicator of photosynthetic activity. Note the decrease in dissolved oxygen at the maximum pH values, corresponding to a decrease in photosynthetic activity. Other experiments have indicated very little photosynthetic activity below pH of six.

Table 4. Algae Biomass in Aquarium

Date/Time	Iso	Nanno	Tetra
04/03 13:30	3.36	3.01	2.66
04/03 19:00	2.99	3.73	2.48
04/04 09:00	3.84	4.44	3.09
04/04 16:00	3.74	4.98	4.62
04/05 08:30	6.78	9.50	5.44
04/05 16:00	8.13	7.81	7.26
04/06 09:00	6.02	6.21	5.44
04/06 15:00	5.57	7.07	5.76

Figure 11. Algae Biomass in Aquarium

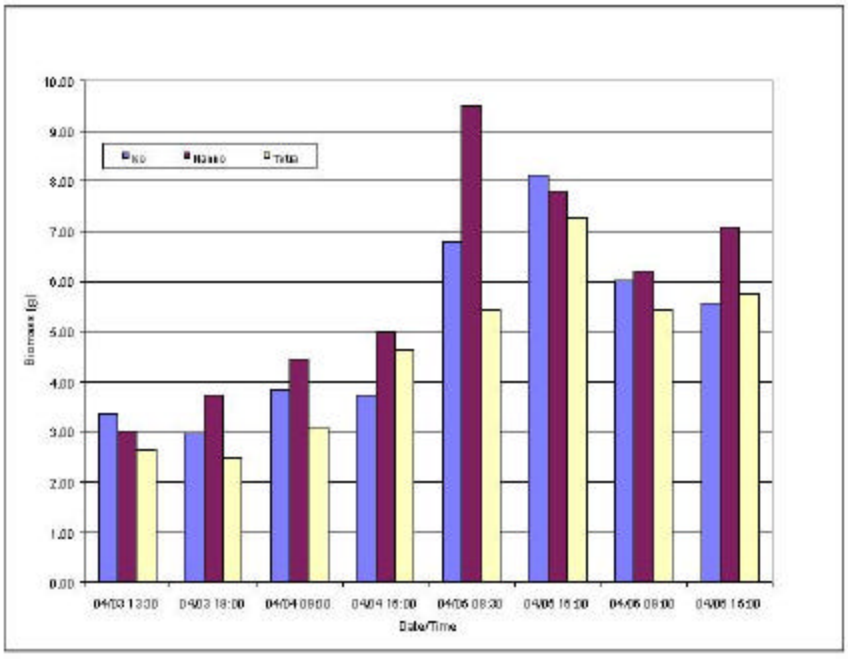


Figure 12. Sonde Data for Isochrysis

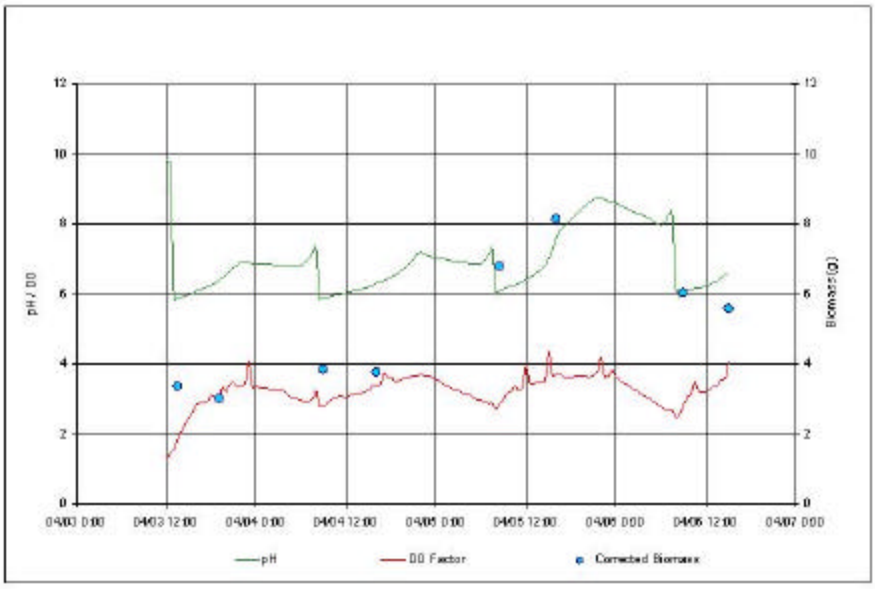


Figure 13. Sonde Data for Nannochloropsis

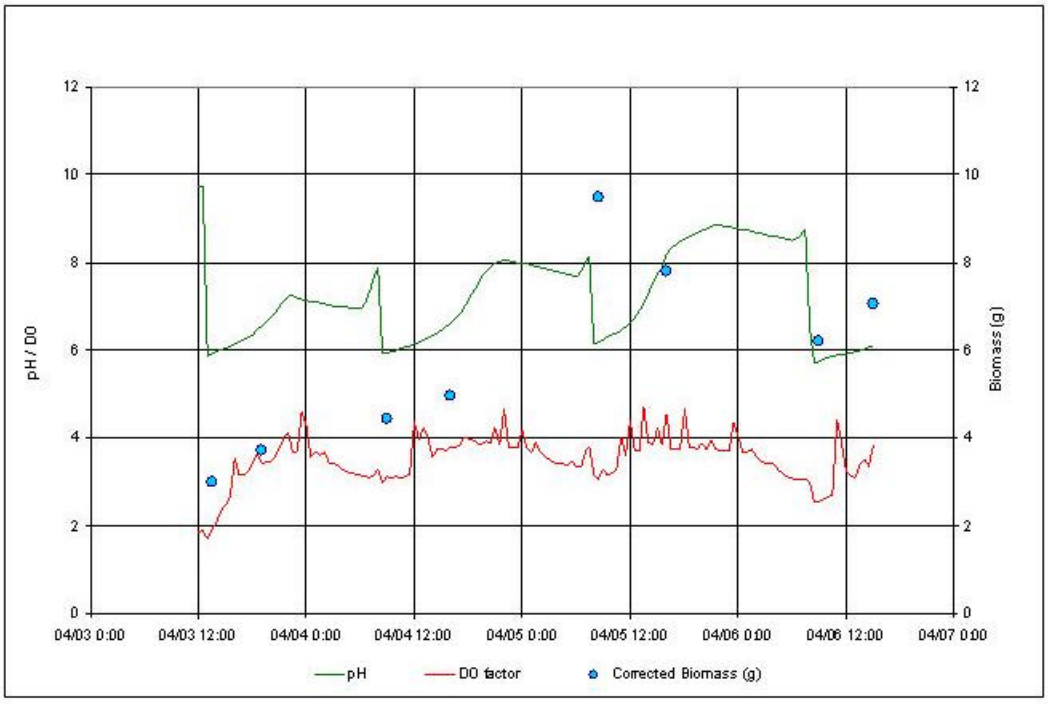
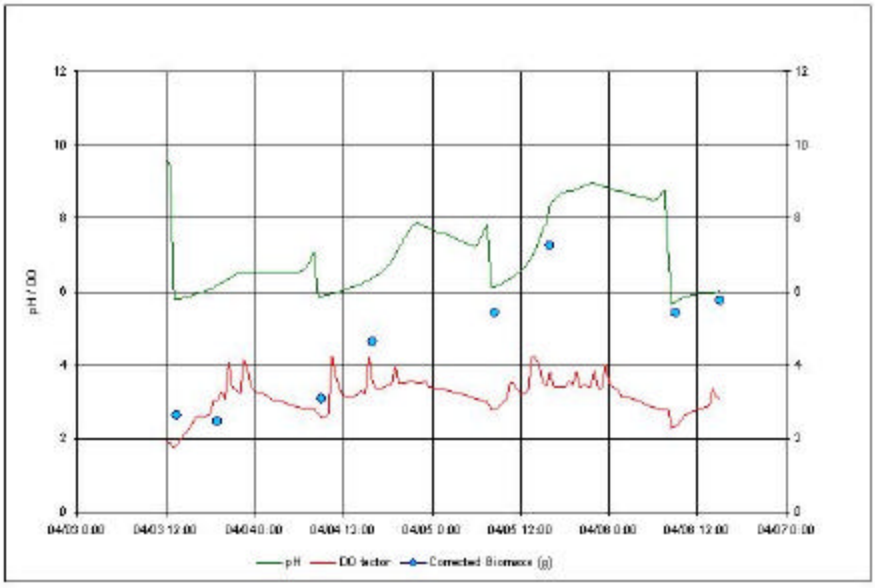


Figure 14. Sonde Data for Tetraselmis

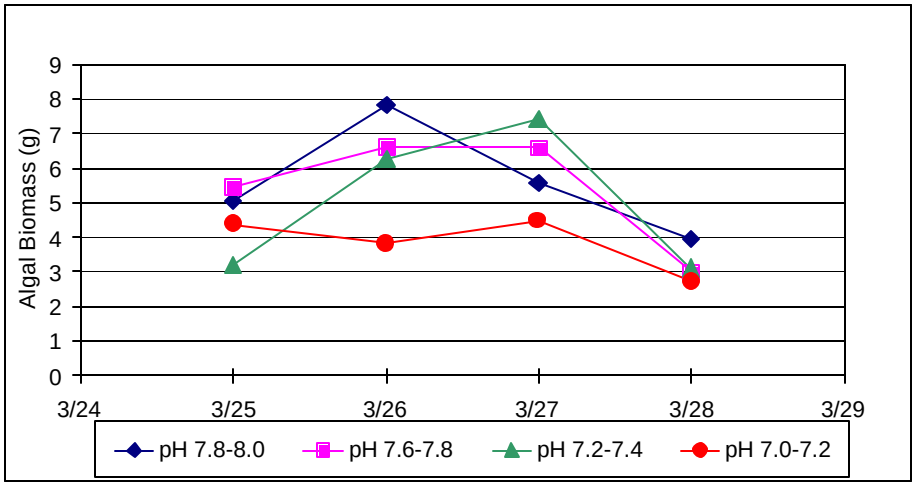


3.3 Algae Growth- Biomass Optimization

Experiment 1

Results from Experiment 1 are present in Figure 15. Total algal biomass in the microcosms during the course of the experiment was similar for all pH treatments except pH 7.0-7.2. For pH 7.0-7.2, the biomass varied between 3.8 and 4.5 g before decreasing to 2.7 g at the final sampling point on 3/28. The remaining pH treatments, however, increased to between 6 and 8 g biomass during this time, before also decreasing to 3 to 4 g at the final sampling point on 3/28, similar to the biomass for the pH 7.0-7.2 treatment. These results indicate that the pH 7.0-7.2 treatment would not provide optimum growth conditions for algae, even though this treatment is receiving the highest amount of CO_2. Apparently the algae cannot take advantage of the high CO_2 provided, due to the reduction in growth from the effect of lower pH.

Figure 15. Experiment 1, Algal Biomass



Experiment 2

The pH monitoring data is given in Figure 16. The pH ranges were controlled by the CO_2 additions. However, the pH ranges were greater than the 0.2 units desired, with ranges of 0.4 to 0.6 pH units, due to the dynamic nature of the system. The biological aspect of the system does not respond to pH control as a conventional chemical system would. Also, difficulties with the control system allowed the pH to go higher than desired for the 7.0-7.2 pH treatment on 4/8 and for the 7.2-7.4 pH treatment from 4/10 to 4/15 before CO_2 additions brought the pH down to the proper level.

Initial cell populations for experiment 2 were approximately 1 x 10^6 cells/mL (Figure 17 through Figure 20). Treatments pH 7.6-7.8 and pH 7.2-7.4 attained the highest cell concentrations of 6.9 x 10^6 and 6.0 x 10^6 cells/mL, respectively, although these high cell counts occurred in only one sampling period. For the remaining sampling points in these treatments and for the other two pH treatments, the highest cells counts normally ranged between 2 x 106 and 3 x 10^6 cells/mL. The pH treatment 7.2-7.4 appeared to be the most beneficial for algal cell growth, with cell counts above 3 x 106 for several sampling points, in addition to the 6.0 x 10^6 cell count discussed above. These higher counts occurred with a relatively high CO_2 feed followed by a period of several low CO_2 feeds,

and the highest cell counts were also observed for pH 7.8-8.0 and pH 7.6-7.8 under these conditions. This suggests that supplying a large amount of CO_2, with little or no CO_2 for a period afterwards, may be effective in enhancing algal cell growth.

Figure 16. Experiment 2, pH

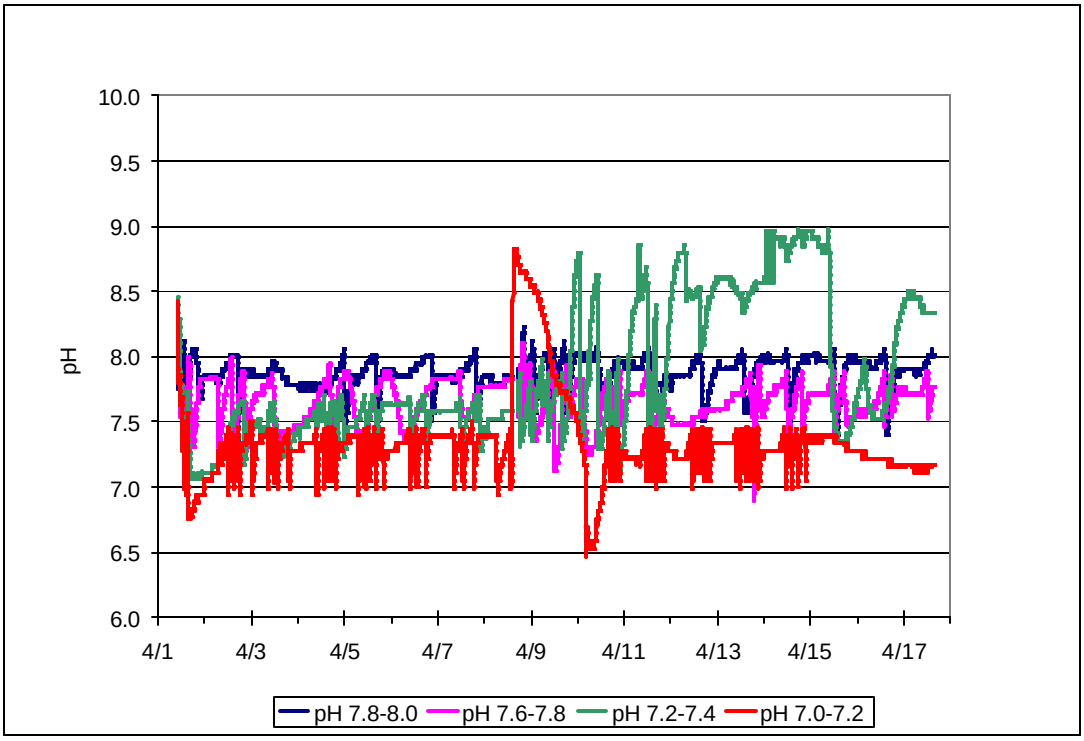


Figure 17. Experiment 2, pH 7.8-8.0

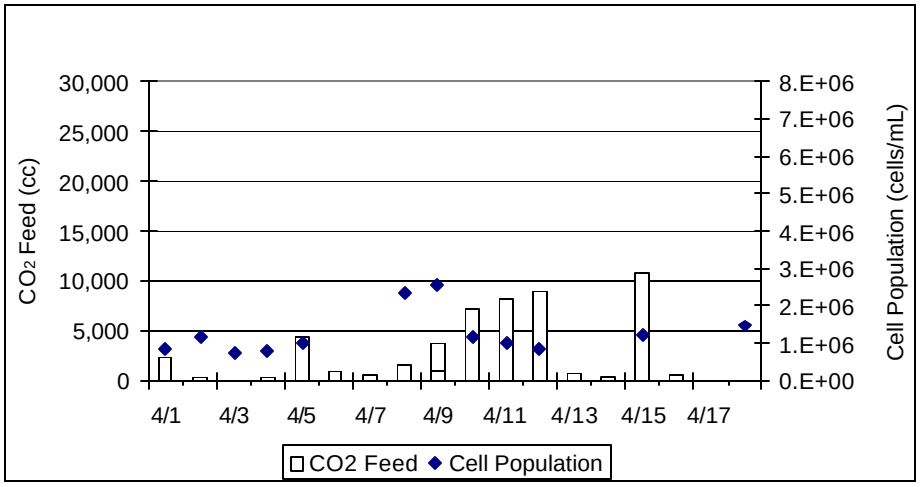


Figure 18. Experiment 2, pH 7.6-7.8

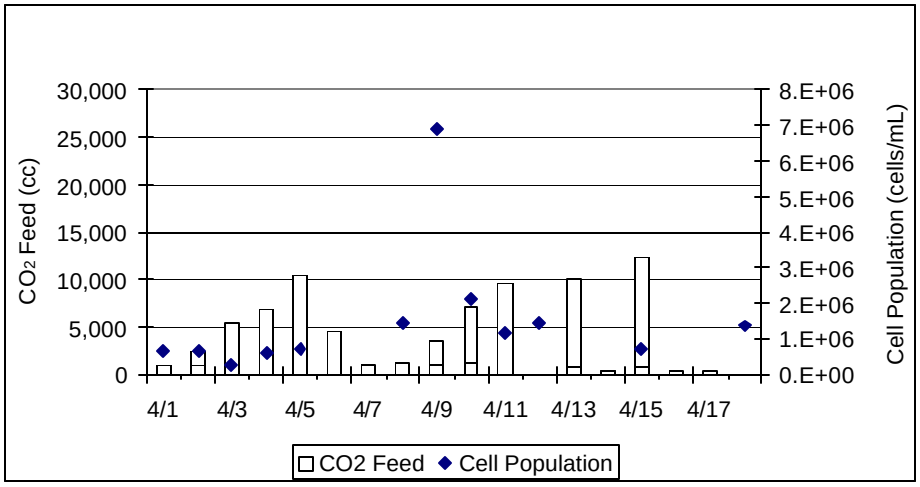


Figure 19. Experiment 2, pH 7.2-7.4

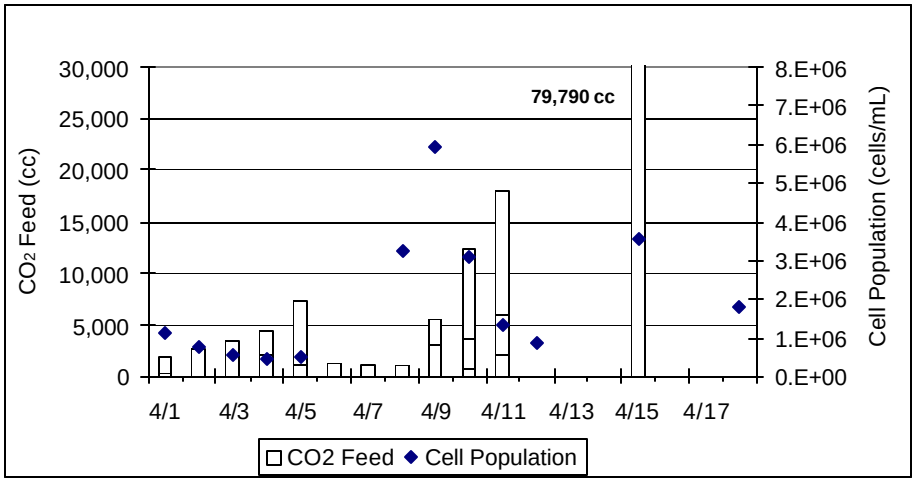
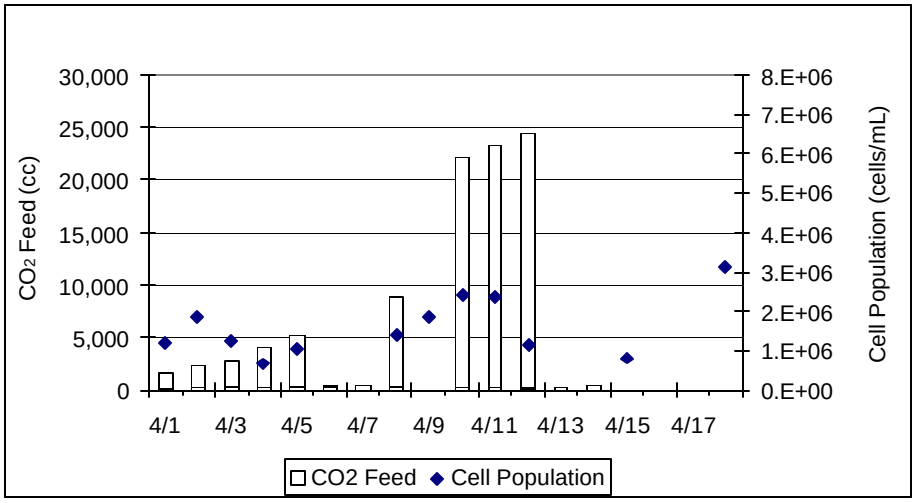


Figure 20. Experiment 2, pH 7.0-7.2



Experiment 3

The pH varied outside the specified ranges, as shown in Figure 21. However, the majority of the time the pH was within the desired range, particularly for the 7.8-8.0 and 7.6-7.8 treatments, as indicated by periods on the plot in which the pH varied very little. The 7.4-7.6 and 7.0-7.2 treatments did not show as many of these stable pH periods, most likely because the addition of more CO_2 to maintain the lower pH levels caused greater fluctuations in pH. The amount of algal biomass skimmed from the surface of the water is given in Figure 22. No pH treatment showed a consistent advantage over the others in enhancing biomass growth. The total biomass skimmed over the course of the experiment was also similar for the pH treatments (Table 5), with pH 7.6-7.8 slightly higher than the other treatments.

Figure 21. Experiment 3, pH

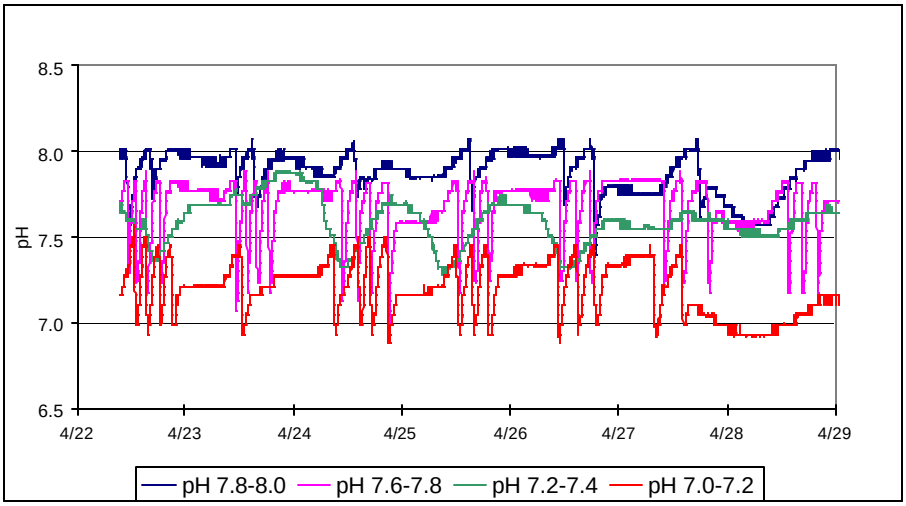


Figure 22. Experiment 3, Algal Biomass (Skimming Harvest)

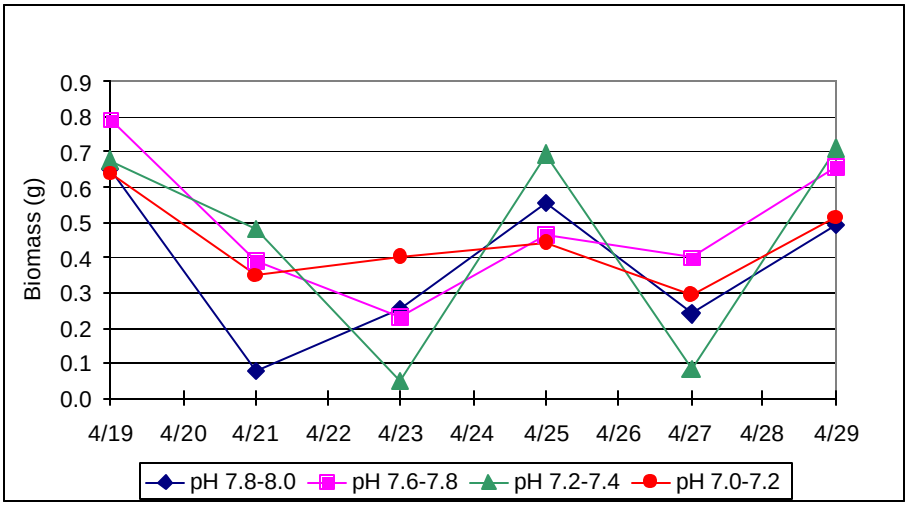


Table 5. Total biomass skimmed from water surface in experiment 3

pH Treatment	Total Skimmed Biomass (g)
7.0 - 7.2	2.64
7.2 - 7.4	2.70
7.6 - 7.8	2.94
7.8 – 8.0	2.27

Experiment 4

For the pH 7.2-7.4 treatment, initially the system was not provided with CO_2 due to a pump malfunction, which caused the pH to increase to 8.8 (Figure 23). A large amount of CO_2 was then put into the system, which brought the pH down to the desired range, and very little CO_2 was added after this to maintain the pH range.

After the large addition of CO_2 in the pH 7.2-7.4 treatment, cell counts increased steadily to a maximum of 2.2 x 10^6 cells/mL at the final measurement on 5/10, which was the highest cell population observed for the treatments (Figure 24 to Figure 28). In addition, the total biomass harvested from the pH 7.2-7.4 treatment was 50% higher than the next

highest biomass total (Table 6). Aquariums were skimmed only two times during the experiment, so the skimmed biomass has been included with the total biomass reported. These results suggested that allowing the algae to grow over a large pH range may be an effective method to increase biomass yield, similar to the results observed in experiment 2. This could be accomplished by adding a relatively large amount of CO_2 that would decrease the pH by 0.5 to 1.0 units, followed by a period during which the reduction of CO_2/HCO^3 in solution due to algal photosynthesis would cause an increase back to the original pH, followed by another CO_2 addition. The subsequent experiment 5 was designed to address this concept.

Figure 23. Experiment 4, pH

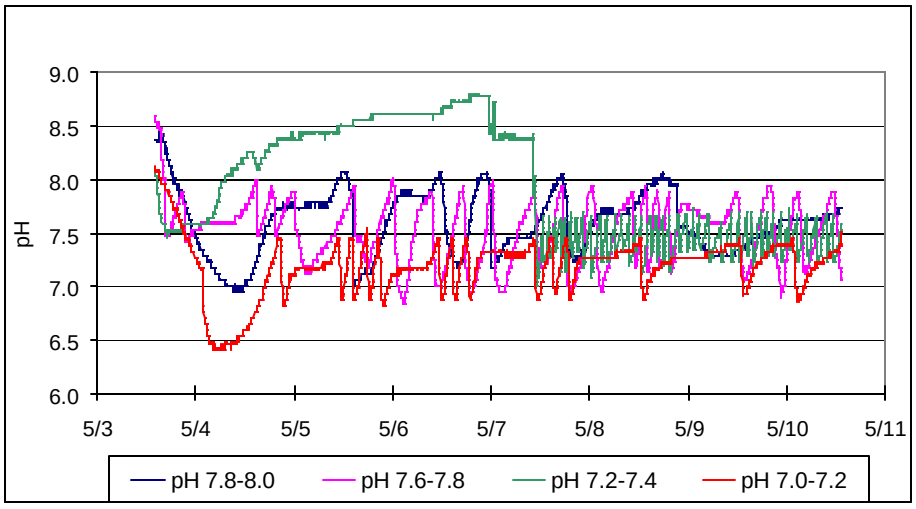


Figure 24. Experiment 4, pH 7.8-8.0

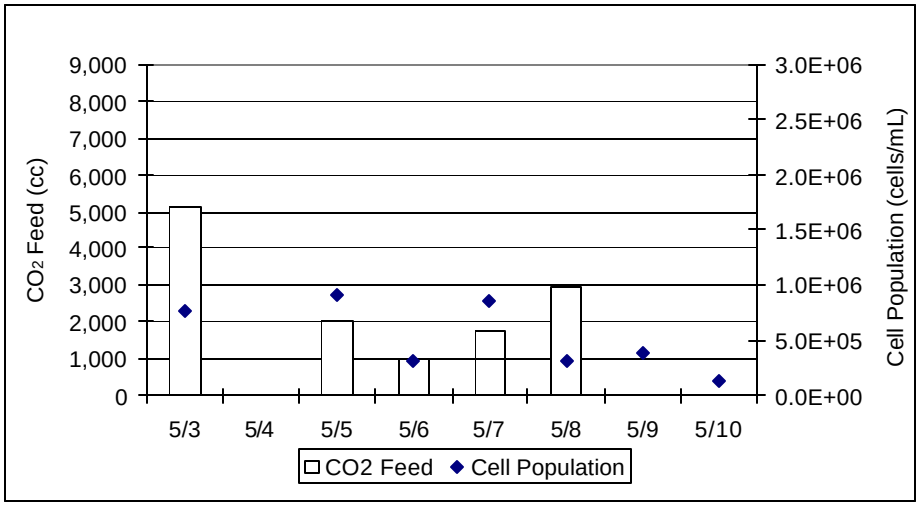


Figure 25. Experiment 4, pH 7.6-7.8

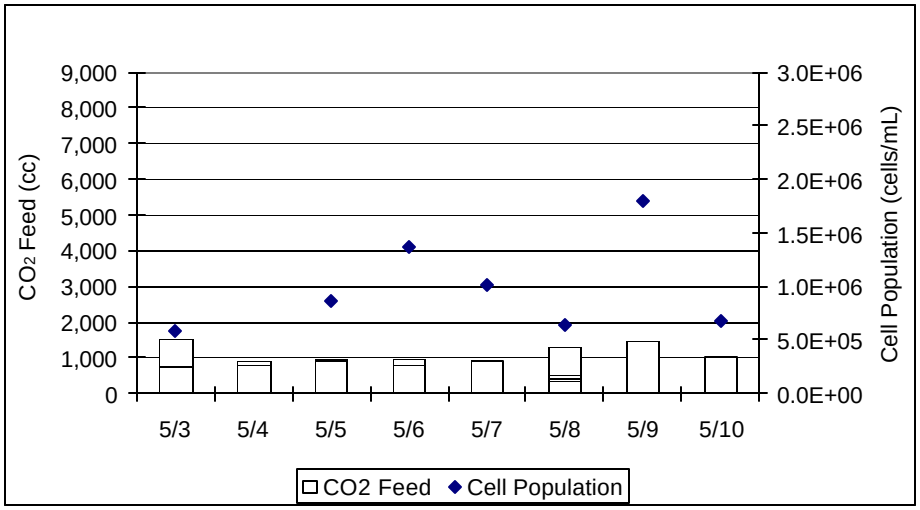


Figure 26. Experiment 4, pH 7.2-7.4

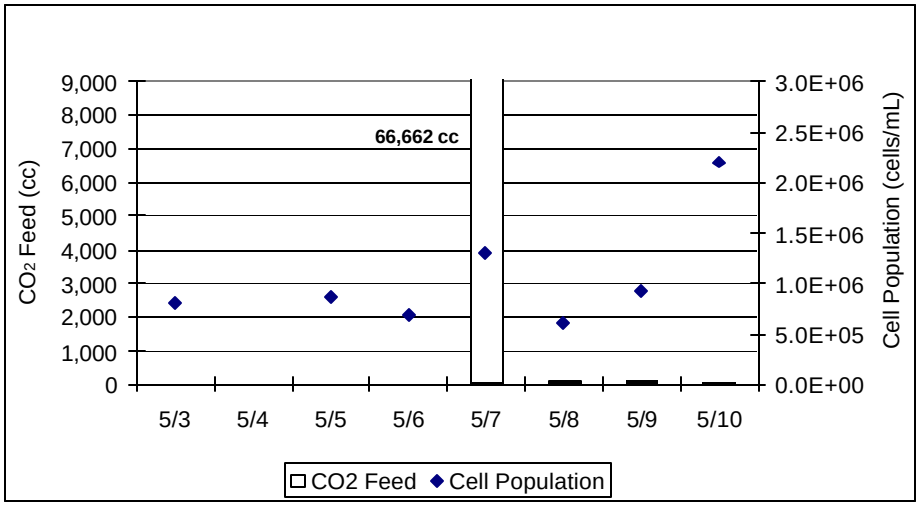


Figure 27. Experiment 4, pH 7.0-7.2

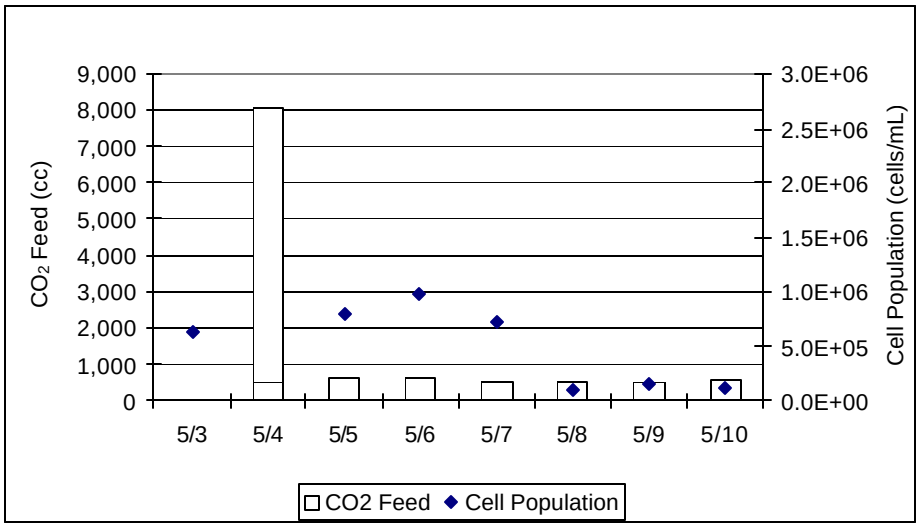


Figure 28. Experiment 4, Control Cell Population

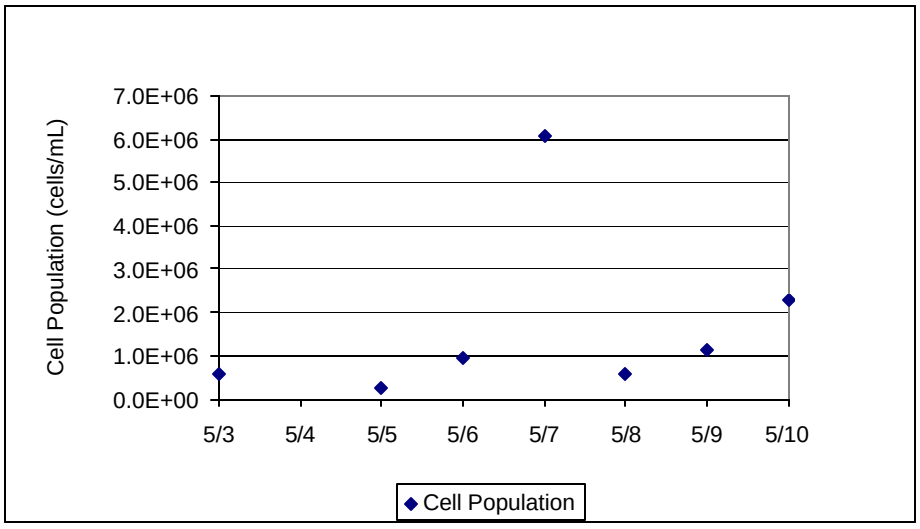


Table 6. Total biomass for pH treatments in experiment 4

pH Treatment	Total Biomass Harvested* (g)
7.8-8.0	7.52
7.6-7.8	8.31
7.2-7.4	14.80
7.0-7.2	9.98
Control	8.21

* total biomass refers to the total of daily skimming harvests plus the amount of biomass material filtered out of the aquarium after experiment completion.

Experiment 5

The pH controller/monitor data showed some difficulties with maintaining the proper pH ranges for the treatments (Figure 29). The pH 7.5-8.0 treatment maintained its range; however, the pH levels for 8.0-8.5 and 8.5-9.0 treatments were similar, with both ranging between a pH of 8.0 to 9.0. The pH 9.0-9.5 treatment did not reach its desired pH level, but stayed very consistently between pH 8.5 and 9.0. Only a small amount of CO_2 was added late in the experiment on and after 5/31 for this treatment, indicating that algal photosynthesis could not raise the pH above 9.0.

Cell populations were similar for the four pH treatments, with no treatment showing a consistent enhancement in cell numbers over the others (Figure 30 to Figure 34). The pH 8.0-8.5 treatment had the highest total biomass of the four treatments, but was lower than the control biomass (Table 7). Algal cells in the control aquarium were not passed through a fly ash column and pump, and higher biomass in the control may have been due to the absence of the mechanical buffeting experienced by cells in the pH treatments. Comparison of the total biomass for the pH 9.0-9.5 treatment, in which very little CO_2 was added but the algal cells were circulated through the pump and reactor column, with the control biomass shows that the control algal culture produced approximately two times the biomass as the 9.0-9.5 treatment, and this difference may be due to the mechanical buffeting of the algal cells. Subsequent experiments will address methods to minimize or eliminate this problem.

Figure 29. Experiment 5, pH

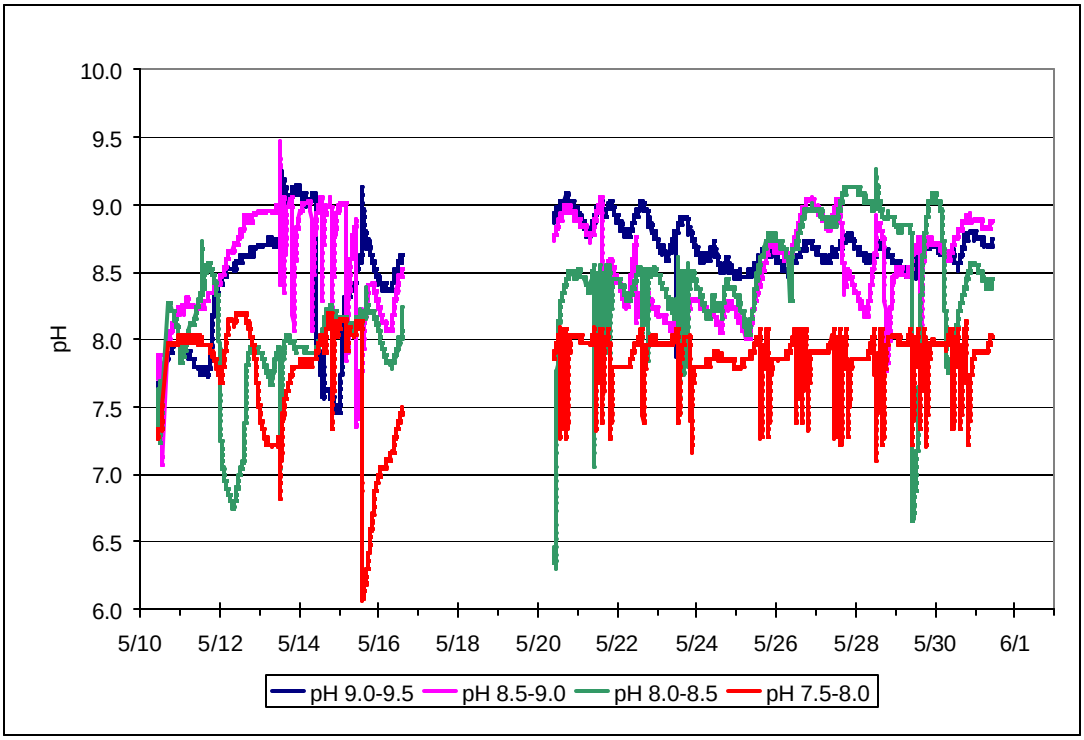


Figure 30. Experiment 5, pH 9.0-9.5

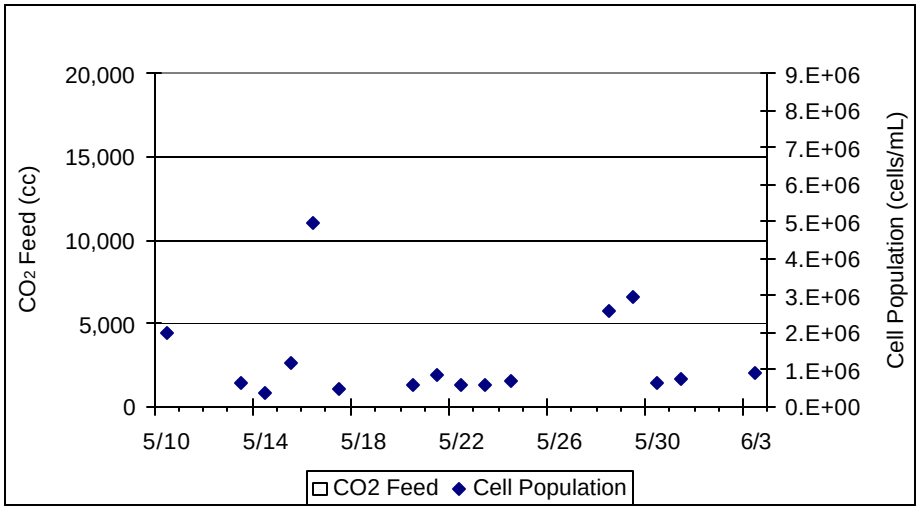


Figure 31. Experiment 5, pH 8.5-9.0

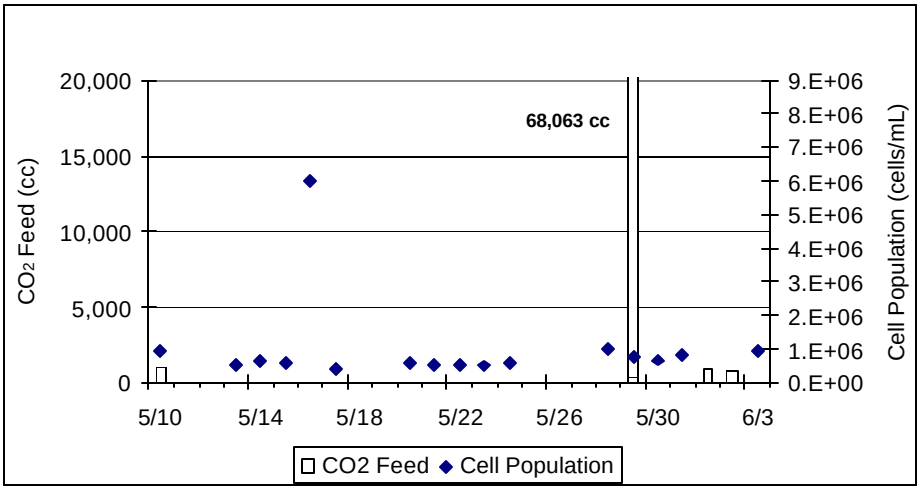


Figure 32. Experiment 5, pH 8.0-8.5

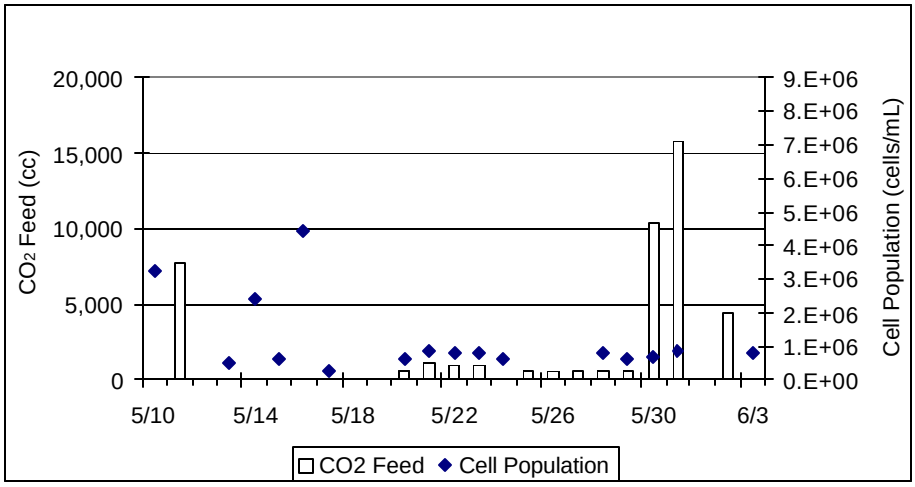


Figure 33. Experiment 5, pH 7.5-8.0

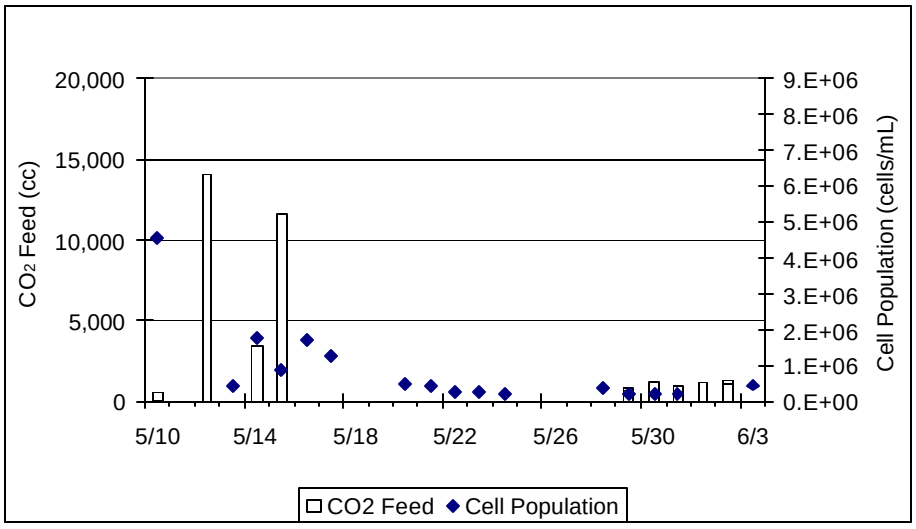


Figure 34. Experiment 5, Control Cell Population

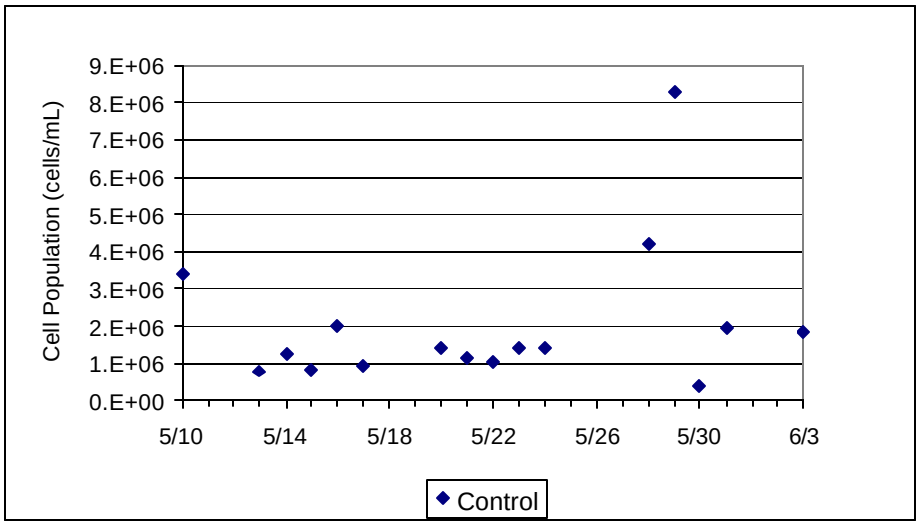


Table 7. Total biomass harvested from aquariums for experiment 5

pH Treatment	Total Biomass (g)
9.0-9.5	6.89
8.5-9.0	9.54
8.0-8.5	11.35
7.5-8.0	7.65
Control	13.75

3.4 Algae Growth- 800 Liter Scale Up

Prior to filling the growth cell with simulate seawater, the cell was filled with tape water and all the plumbing and circulation components checked for flow. At the end of the flow check, a ½ ounce bottle of food coloring was added to the circulation stream at the two inlet ports on the cell. The colored dye was observed to flow evenly from all the diffusion tubes. After about 4 hours, the coloring had reached equilibrium.

The growth tank and reservoir were than filled with simulate seawater and carbon dioxide addition begun. The tank reached an equilibrium pH of about 7 when run overnight.

The growth rate of the algae is indicated by the early rise in chlorophyll after the starter cultures were added to the growth cell (Figure 35, 6/9 thru 6/13). The increase and decrease of chlorophyll percent full scale are reverse correlated with solar activity (Figure 36). The decrease in chlorophyll at the bottom of tank (where the sonde sensor is located) with increase sun light is caused by the algae floating to the top. As photosynthesis proceeds, a small oxygen bubble attaches to the algae cell and causes it to float. Thus the maxima (Figure 37) in the chlorophyll readings just before sunup are an estimate of the relative algae population. Note that a chlorophyll percent full scale of 160 is the maximum reading from the sonde chlorophyll sensor.

The pH gradient from bottom to surface is considerably less than expected (Figure 35), indicating the algae consume bicarbonate near the bottom at a rate greater than diffusion from the diffusion tubes. The result of this deficiency was that throughout most of the experiment, the algae growth was bicarbonate limited. Near the end, carbon dioxide was manually added by bubbling directly into the growth cell.

Previous experiments had indicated that excessive nutrient would be detrimental to algae growth. We were therefore reluctant to arbitrarily add nutrient. As a result, there were several population crashes due to lack of nutrient. These are noted on Figure 35. Other population crashes were due to failure in the carbon dioxide addition system that resulted in pH excursions above 9.

The growth cell temperature did not differ significantly from the ambient temperature in the greenhouse (Figure 38). Near the end of the experiment, auxiliary cooling was added to the growth cell. This significantly improved the stability of the culture.

Harvesting extracted growth medium from the top one inch of the cell in an attempt to extract the floating algae. This did not function well, since most of the algae were actually on the surface and the harvesting pumps did not extract significant surface material (Figure 39). The high chlorophyll reading near the experiment were caused by the surface layer of floating algae being so dense that very little light reached the bottom of the growth cell. During this period, almost all the photoactive zone was within about 6 inches of the surface.

Figure 35. Chlorophyll and pH

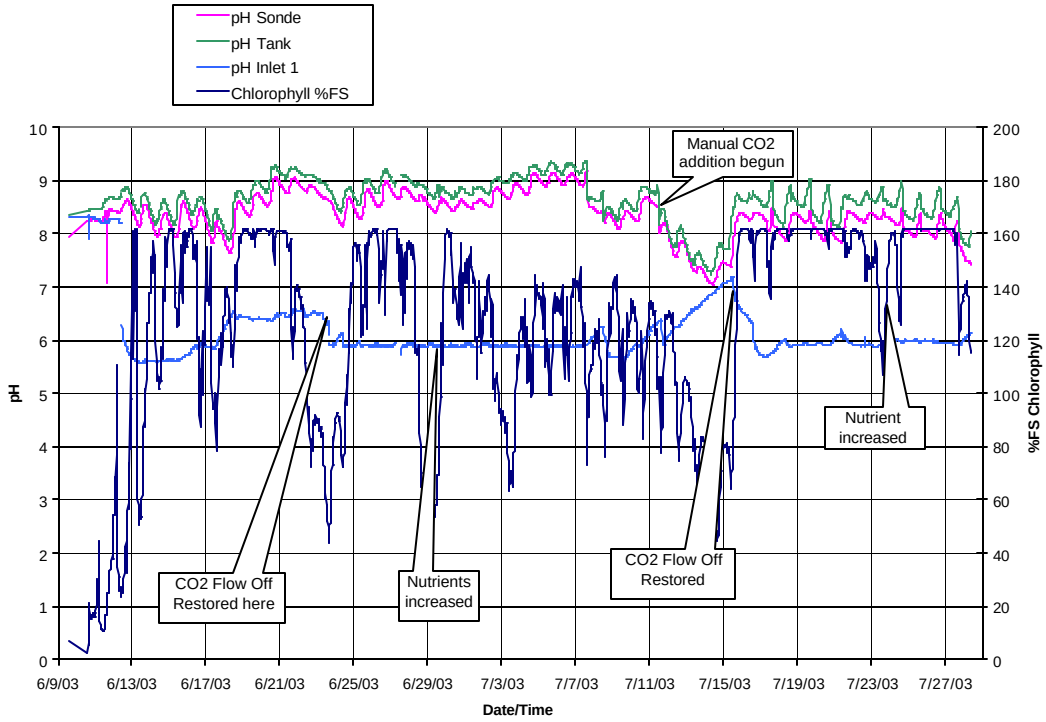


Figure 36. Solar Panel Output and Chlorophyll Enlarged

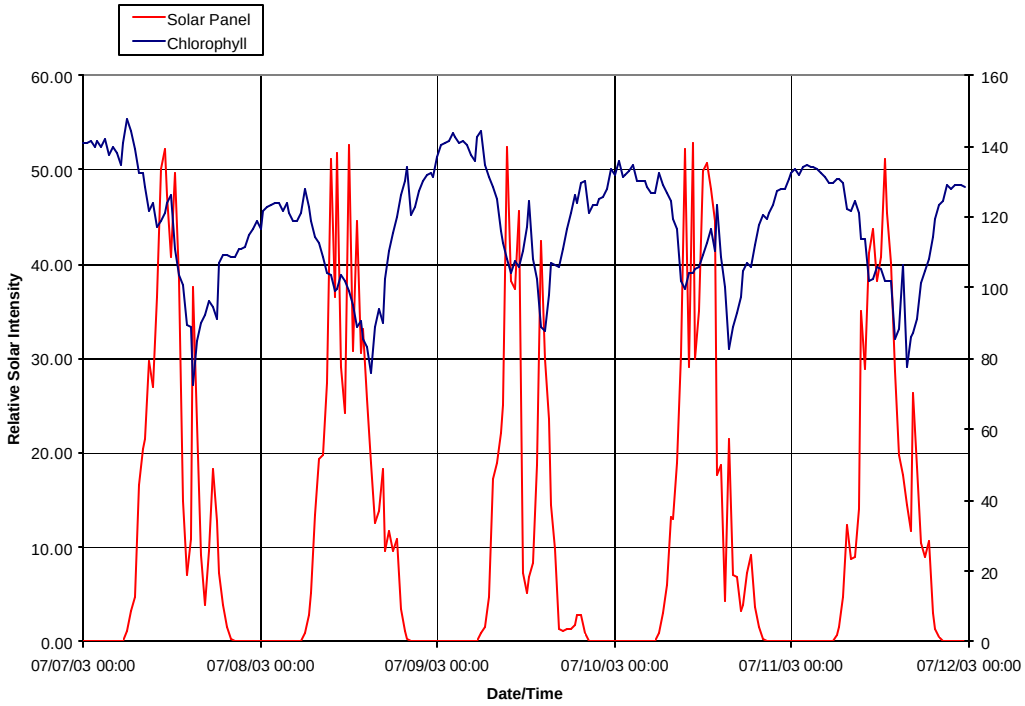


Figure 37. Chlorophyll Maxima and %FS

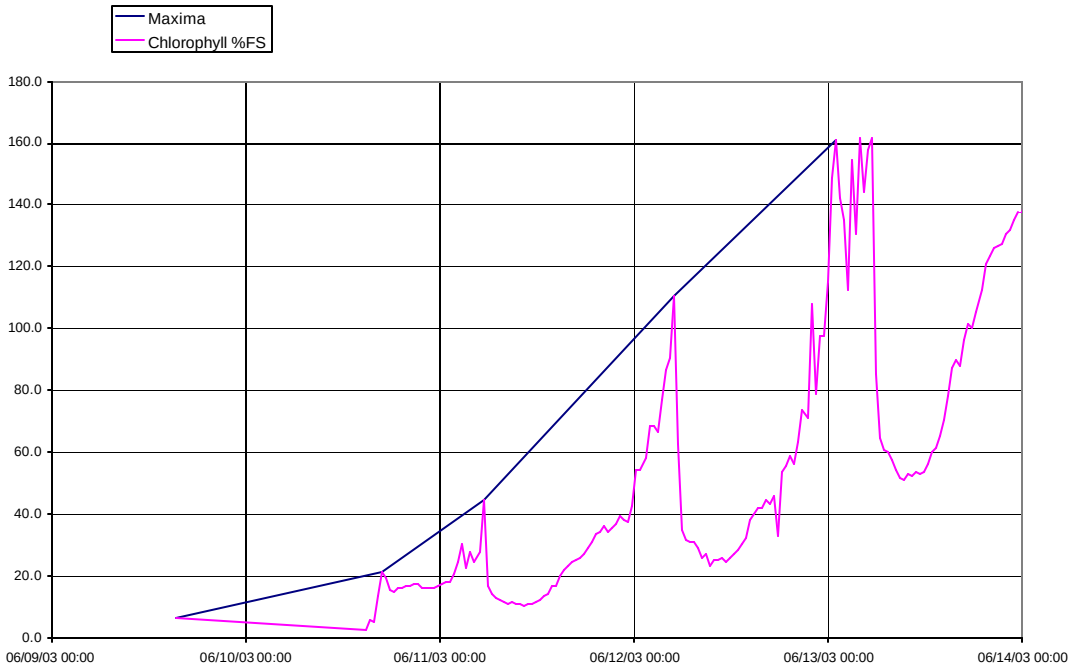


Figure 38. Sonde Temperature and Chlorophyll

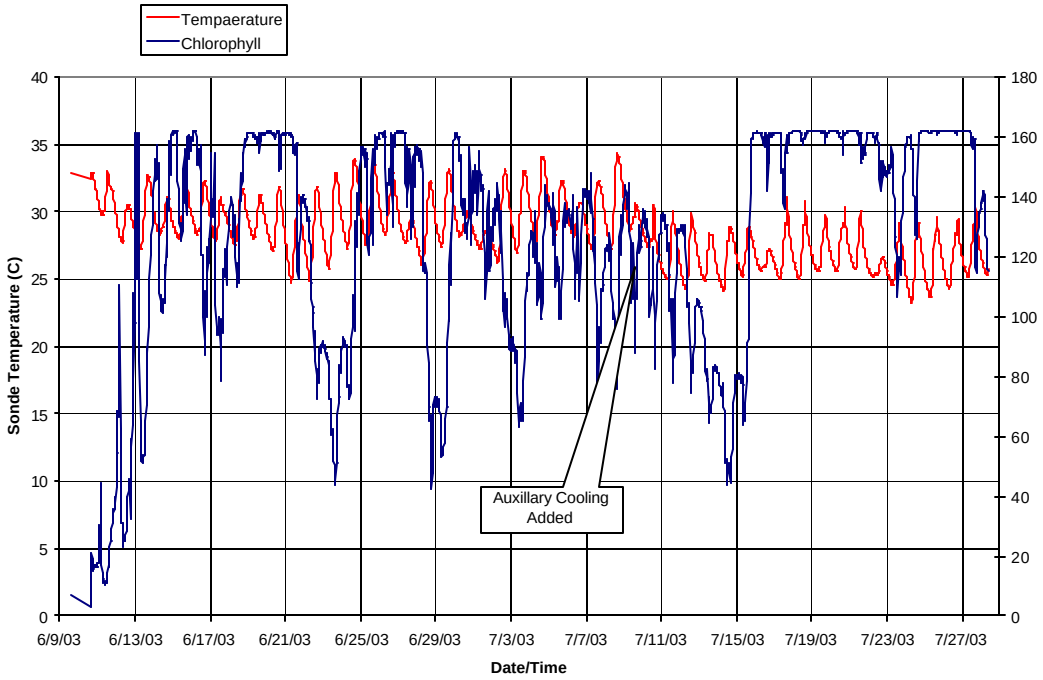
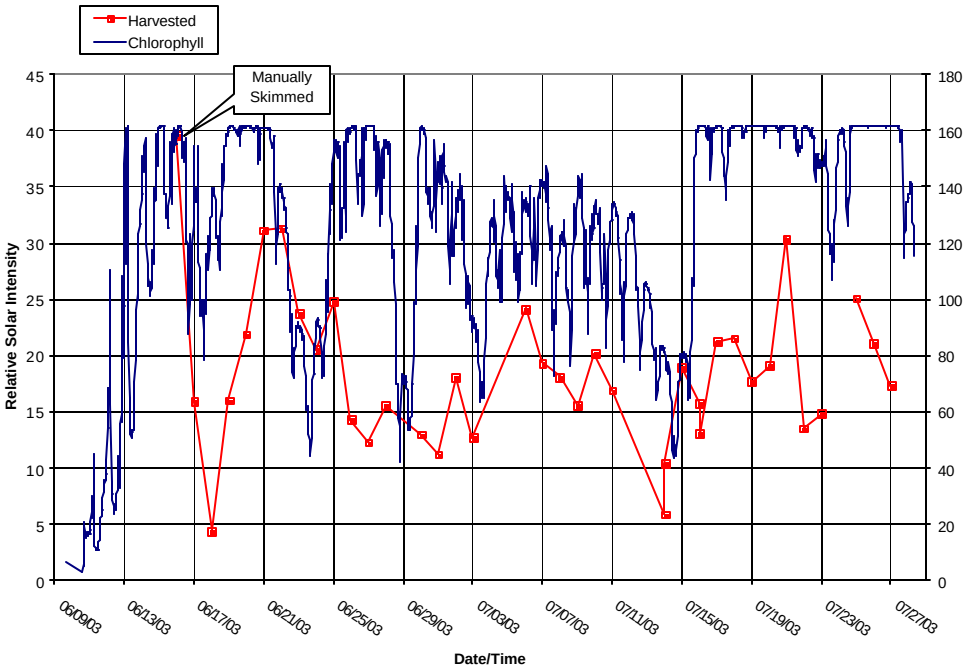


Figure 39. Biomass per Liter Collected and Chlorophyll



Harvest data is shown in Table 8. The efficiency of harvesting apparently decreased when we were down to only one centrifuge. This was probably due to the centrifuge rotor containing more material than with two centrifuges.

The maximum harvest was 24 grams. This corresponds to a harvest of 8 metric tons per square kilometer per day or an annual biomass harvest of about 3,000 metric tons per square kilometer.

Table 8. Harvest Weight Data

Dish #	Date	Centrifuge Run Time	Number Centrifuge	Volume Harvested (L)	Final Dry Biomass (g)	Biomass per Liter Harvested (mg/L)	Comments
1	06/16/2003 Mon	2	2	456	18.1	40	13th-15th
2	06/17/2003 Tue	2	2	456	7.2	16	
3	06/18/2003 Wed	2	2	456	2.0	4	
4	06/19/2003 Thu	2	2	456	7.3	16	
5	06/20/2003 Fri	2	2	456	10.0	22	
6	06/21/2003 Sat	2	2	456	14.2	31	
7	06/22/2003 Sun	2	2	456	14.3	31	
8	06/23/2003 Mon	1	2	228	5.4	24	
9	06/24/2003 Tue	2	2	456	9.4	21	
10	06/25/2003 Wed	2	2	456	11.3	25	
11	06/26/2003 Thu	4	2	912	13.0	14	
12	06/27/2003 Fri	4	2	912	11.2	12	
13	06/28/2003 Sat	4	2	912	14.2	16	
14	06/30/2003 Mon	4	2	912	11.8	13	
15	07/01/2003 Tue	4	2	912	10.2	11	
16	07/02/2003 Wed	4	2	912	16.4	18	
17	07/03/2003 Thu	2	2	456	5.8	13	Only 1 Centrifuge ran full time
18	07/06/2003 Sun	6	1	684	16.5	24	
19	07/07/2003 Mon	3	2	684	13.2	19	
20	07/08/2003 Tue	3	2	684	12.4	18	
21	07/09/2003 Wed	3	2	684	10.6	16	
22	07/10/2003 Thu	3	2	684	13.8	20	
23	07/11/2003 Fri	3	2	684	11.6	17	
24	07/14/2003 Mon	3	2	684	4.0	6	
25	07/14/2003 Mon	3	1	342	3.6	10	NOTE: 1 centrif. in service
26	07/15/2003 Tue	3	1	342	6.5	19	NOTE: 1 centrif. in service
27	07/16/2003 Wed	3	1	342	5.4	16	NOTE: 1 centrif. in service
28	07/16/2003 Wed	3	1	342	4.5	13	NOTE: 1 centrif. in service
29	07/17/2003 Thu	6.5	1	741	15.7	21	NOTE: 1 centrif. in service
30	07/18/2003 Fri	7	1	798	17.2	22	NOTE: 1 centrif. in service
31	07/19/2003 Sat	7	1	798	14.1	18	NOTE: 1 centrif. in service
32	07/20/2003 Sun	7	1	798	15.3	19	NOTE: 1 centrif. in service
33	07/21/2003 Mon	7	1	798	24.2	30	NOTE: 1 centrif. in service
34	07/22/2003 Tue	7	1	798	10.8	14	NOTE: 1 centrif. in service
35	07/23/2003 Wed	7	1	798	11.9	15	NOTE: 1 centrif. in service
36	07/24/2003 Thu	unknown	1		2.3		centrifuge failed during run
37	07/25/2003 Fri	7	1	798	20.0	25	NOTE: 1 centrif. in service
38	07/26/2003 Sat	7	1	798	16.8	21	NOTE: 1 centrif. in service
39	07/27/2003 Sun	7	1	798	13.8	17	NOTE: 1 centrif. in service
40	07/28/2003 Mon	Empty Tank			28.0		Drain tank
41	07/28/2003 Mon	Rinse Tank			36.9		Rinse tank with tap water
41A	07/28/2003 Mon				3.1		Algae from 2 cross tubes + 4 "Ts" + 4 connectors
41B	07/28/2003 Mon				6.3		Algae from 1.274 sq ft on bottom of tank
41C	07/29/2003 Tue	Rinse Tank			18.9		Rinse tank with tap water
41D	07/29/2003 Tue	Rinse Tank			9.6		Rinse tank with tap water
41E	07/29/2003 Tue	Rinse Tank			9.6		Rinse tank with tap water
41F	07/29/2003 Tue	Rinse Tank			7.6		Rinse tank with tap water
41G	07/30/2003 Wed	Rinse Tank			3.9		Rinse tank with tap water

3.5 Anaerobic Production of Methane

Table 9 summarizes the feeding information, pH, methane production and effluent COD data collected from the digesters during this study.

The pH of the digesters remained in the desirable range of 6 to 7 or higher during the entire course of the study. The gradual increase in feeding rate likely prevented overloading the digesters during the early stages of the project. Over feeding could have resulted in increased acid production, the lowering of digester pH and the reduction in methane

production. The stable or slightly increasing pH seen during the later feeding periods with higher feeding rates suggests that the digesters could have maintained suitable pH levels at even higher feeding rates.

Methane production from both algae and MRS was higher based on BOD than COD. For the algae and MRS the ratio of COD to BOD was 1.51 and 1.64, respectively. This difference indicates that both the algae and MRS likely contained materials that were resistant to breakdown and conversion to methane as measured as COD and not identified as BOD. Whether based on COD or BOD, methane production from the algae was always less than methane production from the MRS. Methane production from the algae averaged 56 percent (a high of 80 percent and a low of 40 percent) of the methane production from the MRS, indicating that the algae could be less or more desirable for methane production than other potential feedstocks.

Effluent COD was generally in the range of 200 to 400 mg/L during the first 11 to 12 weeks of the study whether the feed was algae or MRS. However; even though the pH indicated no sign of digester overloading, in the final weeks of the study the effluent COD increased to between 610 and 802 mg/L. This most likely was the result of recalcitrant material accumulating in the digester from the increased feeding rate coupled with the long hydraulic retentions associated with the two digesters.

In summary, this study showed that methane can be produced from algae produced by the TVA integrated carbon dioxide sequestration system, but that methane production was not as great as from the MRS used as a comparative feedstock. Digester pH remained in the desirable range for anaerobic digestion over the course of the study for both the algae and MRS feeds. Except during the final 4 weeks of the study when feeding rates were the highest, the effluent COD was generally in the range of 200 to 400 mg/L. During the last 4 weeks of the study, the effluent COD increased to the 600 to 800 mg/L range.

Table 9. Feeding Information, pH, Methane Production and Effluent COD

Week	Feed*	pH	g COD fed/digester	g BOD fed/digester	CH4/g COD fed (ml)	CH4/g BOD fed (ml)	Effluent COD (mg/L)
1	MRS	6.62	8.5	5.2	217	356	227
	MRS	6.60	8.5	5.2	264	433	361
2	MRS	6.39	8.5	5.2	295	484	195
	MRS	6.42	8.5	5.2	299	490	376
3	Algae	6.48	4.3	2.8	190	287	360
	MRS	6.41	4.3	2.6	371	608	124
4	Algae	6.69	4.3	2.8	161	243	383
	MRS	6.55	4.3	2.6	290	476	220
5	Algae	6.67	4.3	2.8	134	202	285
	MRS	6.75	4.3	2.6	307	503	243
6	Algae	6.73	4.3	2.8	147	222	347
	MRS	6.72	4.3	2.6	333	546	206
7	Algae	6.88	7.1	4.7	131	148	387
	MRS	6.71	7.1	4.3	194	318	197
8	Algae	6.75	7.1	4.7	116	175	248
	MRS	6.87	7.1	4.3	291	477	409
9	Algae	6.82	7.1	4.7	163	246	315
	MRS	6.73	7.1	4.3	355	582	343
10	Algae	6.84	14.2	9.4	131	198	341
	MRS	6.81	14.2	8.7	168	276	436
11	Algae	7.06	14.2	9.4	133	201	415
	MRS	6.79	14.2	8.7	164	269	460
12	Algae	6.91	14.2	9.4	124	187	409
	MRS	7.06	14.2	8.7	282	462	712
13	Algae	7.09	14.2	9.4	168	254	610
	MRS	6.94	14.2	8.7	280	459	789
14	Algae	7.03	21.3	14.1	129	195	750
	MRS	7.01	14.2	8.7	219	359	732
15	Algae	7.20	21.3	14.1	114	172	802
	MRS	6.91	14.2	8.7	219	359	706

* MRS=Milk Replacement Starter

4.0 CONCLUSION

4.1 Conversion of CO_2 to Bicarbonate Using Fly Ash as a Catalyst

The rate of uptake of CO_2 in a fly ash column is five to nine times the rate of uptake in the control column containing glass beads. At 1.5 hours the fly ash column pH was 6.5, while the glass bead column pH was 5.6. This indicates the fly ash has a capacity to buffer the solution. At a pH of 6.5, the bicarbonate using the fly ash column was double that of the glass beads. The pH and higher bicarbonate levels from the fly ash column are more suitable for biological systems than the glass bead column.

4.2 Algae Growth - Screening

Significant increases in biomass production can be obtained by supplementing the algae growth medium with additional bicarbonate. The annual production of biomass from an algae facility could be in excess of 150 metric tons per hectare (74 metric tons per acre).

4.3 Algae Growth - Biomass Optimization

The amount of CO_2 added to the algal culture solution through the column reactor can be used to control the pH of the growth media. The protocol for CO_2 addition appears to affect the growth rate of the algae as much or more than the pH range used to grow the algae. Results indicate that relatively large additions of CO_2 that decrease the pH by as much as one pH unit, followed by a period of no CO_2 addition in which the pH may then increase as much as one unit, may be more effective for producing biomass than maintaining a narrow pH range of 0.2 or 0.5 units. This also simplifies the control process by reducing the amount of control needed to maintain a narrow pH range. The mechanical buffeting of the algal cells by continuous circulation through the pump and reactor column must also be eliminated, as this appears to significantly affect biomass production.

4.4 Algae Growth — 800 Liter Scale Up

The diffusion array added bicarbonate to the growth cell but was inadequate to achieve the gradients desired. A possible solution would be routing the harvested growth solution to the circulating solution tank. This would cause a pressure gradient that would force bicarbonate rich solution into the growth cell at the bottom.

To maximize the photoactive volume, a means must be developed to remove and harvest the floating algae. This would potentially increase the harvest 3 to 4 fold.

A real time method to determine the algae population needs to be developed. The chlorophyll method appears to work, but needs greater range.

A method to monitor nutrient levels needs to be developed. Several times during the experiment period, the algae population crashed because of lack of nutrients.

Even with problems encountered in 800 liter scale up, it was demonstrated that increases in scale are possible. With better harvesting methods, nutrient management, and carbon dioxide management, the biomass harvest could easily produce 9,000 metric tons per square kilometer.

4.5 Anaerobic Production of Methane

Algal biomass can be used as a feed stock to an anaerobic digester to produce methane. The remaining carbonaceous material is essentially bio-inactive and is permanently sequestered.

4.6 General

The feasibility of using Algae to convert carbon dioxide to a biomass has been demonstrated. This biomass provides a sustainable means to produce methane, ethanol, and/or bio-diesel. The first application of concept demonstrated by the project could be to use algal biomass production in to capture carbon dioxide associated with ethanol production

5.0 REFERENCES

There are no references.

APPENDIX

Conversion of Carbon Dioxide Gas to Carbonate Solution Using Fly Ash as a Catalyst

Conversion of Carbon Dioxide Gas to Carbonate Solution using Fly Ash as a Catalyst

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1. Introduction

The mass transfer rate of carbon dioxide gas to carbonate solution is the rate-limiting step in producing carbonate solutions. One of the objectives of the "Chemical Fixation of CO2" project was to develop method to increase the rate of transfer using coal combustion products (CCP). It was felt that fly ash or scrubber gypsum could provide the critical mechanism needed to increase the available CO2 in solution above the limits that are achievable with the dissolved gas alone.

This would most likely increase algal growth beyond what is normally attainable. Carbon in the algal biomass can then be extracted and converted to hydrogen gas with a gasifier or converted to liquid CO2. An anaerobic digestor in the system may be used to convert the biomass into methane for on-site use in a gas turbine generator. The solid biomass residue from the digestor may be re-cycled as additional fuel stock for the gasifier. The liquid residue from the digestor may be re-cycled to provide nutrients to perpetuate the algal biosystem. The system provides for continued cycling of sequestered carbon within the system.

2. Method and Materials

A co-current reactor was developed that contained fly ash and was compared to a similar reactor containing 5-mm glass beads. Using PEEK capillary tubes and a mass flow controller, a method was developed to deliver a controlled stream of CO2 gas that was introduced at the bottom of the reactor. Water flow was controlled with a constant displacement pump.

The reactor consisted of a transparent PVC column (1.5" dia x 7" long) with fitting on each end to introduce liquid and gas and to collect the overflow liquid and gas. Lean liquid was introduced at the bottom along with a controlled flow of CO_2.

The initial set up for the control included the transparent PVC column (1.5" d x 7" l), packed with 5-mm glass beads, and using a re-circulated salt water solution to which CO_2 gas was introduced prior to column inlet. The gas flow rate was approximately 10 cc/min. It was maintained by adjustment of a needle valve and by observing flow rate of gas using a bubble flow meter.

Next, a similar column packed with fly ash was tested. Gas flow was adjusted so that all the CO2 was reacted in the reactor column. In this experiment, gas flow was electronically controlled to about 3 cc/min with a 50 sccm/min Tylan FC260 mass flow controller (four equal streams were produced with a total flow of 12 sccm). The gas stream was split into four segments using 0.0005 PEEK capillary tubes approximately 5" long. The flow rates through each of the 4 tubes were individually checked using a bubble flow meter and matched to less than 1%.

Finally, the glass bead control was tested under the same conditions. In this and the previous test, the actual flow was monitored with a bubble flow meter.

In all the test inorganic carbon (IC) analysis were performed on samples taken from an open container in which the solution is being re-circulated. Sample vials were filled to the top and capped with zero head space.

2. Conclusions

It is clear, from the table below, that uptake of CO2 in the fly ash column is 5 to 9 times the rate in the glass bead column. At 1.5 hours the fly ash column pH was 6.5?, while the glass bead column pH was 5.6. This indicates the fly ash has a capacity to buffer the solution. The pH of the fly ash column is more suitable for biological systems than the glass bead column.

Glass Beads v. Fly Ash @ 3 cc/min

Time h:min	Glass Bead IC Conc (ppm)	Fly Ash IC Conc (ppm)
0:00	19.52	12.25
0:05	27.11	55.92
0:10	33.28	63.59
0:15	37.65	68.55
0:30	44.68	84.01
0:45	50.81	97.20
1:00	54.16	105.60
1:30	63.73	128.80

The table below further confirms this phenomena. Note that 3 times the gas flow is required to achieve the approximately equal carbonate concentrations.

Fly ash column @3cc/min v. Glass bead column @10cc/min

Time	Fly Ash IC Conc (ppm)	Glass Bead IC Conc (ppm)
0:05	55.92	34.75
0:10	63.59	50.61
0:15	68.55	63.7
0:30	84.01	83.9
1:00	105.6	127.5
1:30	128.8	145.9