

**Recovery and Sequestration of CO<sub>2</sub> from Stationary  
Combustion Systems by Photosynthesis of Microalgae**

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## Abstract

Most of the anthropogenic emissions of carbon dioxide result from the combustion of fossil fuels for energy production. Photosynthesis has long been recognized as a means, at least in theory, to sequester anthropogenic carbon dioxide. Aquatic microalgae have been identified as fast growing species whose carbon fixing rates are higher than those of land-based plants by one order of magnitude. Physical Sciences Inc. (PSI), Aquasearch, and the Hawaii Natural Energy Institute at the University of Hawaii are jointly developing technologies for recovery and sequestration of CO<sub>2</sub> from stationary combustion systems by photosynthesis of microalgae. The research is aimed primarily at demonstrating the ability of selected species of microalgae to effectively fix carbon from typical power plant exhaust gases.

This report covers the reporting period 1 April to 30 June 2004 in which PSI, Aquasearch and University of Hawaii conducted their tasks. Based on the work during the previous reporting period, Aquasearch run further, pilot and full scale, carbon sequestration tests with actual propane combustion gases utilizing two different strains of microalgae. Aquasearch continued testing modifications to the coal combustor to allow for longer-term burns. Aquasearch also tested an alternative cell separation technology. University of Hawaii performed experiments at the Mera Pharmaceuticals facility in Kona in mid June to obtain data on the carbon venting rate out of the photobioreactor; gas venting rates were measured with an orifice flow meter and gas samples were collected for GC analysis to determine the carbon content of the vented gases.

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## 1. Introduction

Emissions of carbon dioxide are predicted to increase in this century<sup>1</sup> leading to increased concentrations of carbon dioxide in the atmosphere. While there is still much debate on the effects of increased CO<sub>2</sub> levels on global climate, many scientists agree that the projected increases could have a profound effect on the environment. Most of the anthropogenic emissions of carbon dioxide result from the combustion of fossil fuels for energy production. It is the increased demand for energy, particularly in the developing world, which underlies the projected increase in CO<sub>2</sub> emissions. Meeting this demand without huge increases in CO<sub>2</sub> emissions requires more than merely increasing the efficiency of energy production. Carbon sequestration, capturing and storing carbon emitted from the global energy system, could be a major tool for reducing atmospheric CO<sub>2</sub> emissions from fossil fuel usage.

The costs of removing CO<sub>2</sub> from a conventional coal-fired power plant with flue gas desulfurization were estimated to be in the range of \$35 to \$264 per ton of CO<sub>2</sub>.<sup>2</sup> The cost of power was projected to increase by anywhere from 25 to 130 mills/kWh. DoE's goal is to reduce the cost of carbon sequestration to below \$10/ton of avoided net cost.

Photosynthesis has long been recognized as a means, at least in theory, to sequester anthropogenic carbon dioxide. There has been relatively little research aimed at developing the technology to produce a gaseous combustion effluent that can be used for photosynthetic carbon sequestration. However, the photosynthetic reaction process by plants is too slow to significantly offset the point source emissions of CO<sub>2</sub> within a localized area. Aquatic microalgae have been identified as fast growing species whose carbon fixing rates are higher than those of land-based plants by one order of magnitude.

The Department of Energy has been sponsoring development of large-scale photovoltaic power systems for electricity generation. By this analogy, a large-scale microalgae plantation may be viewed as one form of renewable energy utilization. While the PV array converts solar energy to electricity, the microalgae plant converts CO<sub>2</sub> from fossil combustion systems to stable carbon compounds for sequestration and high commercial value products to offset the carbon sequestration cost. The solar utilization efficiency of some microalgae is ~ 5%, as compared to ~ 0.2% for typical land based plants. Furthermore, a dedicated photobioreactor for growth of microalgae may be optimized for high efficiency utilization of solar energy, comparable to those of some photovoltaic cells. It is logical, therefore, that photosynthetic reaction of microalgae be considered as a mean for recovery and sequestration of CO<sub>2</sub> emitted from fossil fuel combustion systems.

Stationary combustion sources, particularly electric utility plants, represent 35% of the carbon dioxide emissions from end-use of energy in the United States.<sup>1</sup> The proposed process addresses this goal through the production of high value products from carbon dioxide emissions. Microalgae can produce high-value pharmaceuticals, fine chemicals, and commodities. In these markets, microalgal carbon can produce revenues of order \$100,000 per kg C. These markets are currently estimated at >\$5 billion per year, and projected to grow to >\$50 billion per year within the next 10 to 15 years. Revenues can offset carbon sequestration costs.

An ideal methodology for photosynthetic sequestration of anthropogenic carbon dioxide has the following attributes:

1. Highest possible rates of CO<sub>2</sub> uptake
2. Mineralization of CO<sub>2</sub>, resulting in permanently sequestered carbon
3. Revenues from substances of high economic value
4. Use of concentrated, anthropogenic CO<sub>2</sub> before it is allowed to enter the atmosphere.

In this research program, Physical Sciences Inc. (PSI), Aquasearch, and the Hawaii Natural Energy Institute at the University of Hawaii are jointly developing technologies for recovery and sequestration of CO<sub>2</sub> from stationary combustion systems by photosynthesis of microalgae. The research we propose is aimed primarily at quantifying the efficacy of microalgae-based carbon sequestration at industrial scale. Our principal research activities will be focused on demonstrating the ability of selected species of microalgae to effectively fix carbon from typical power plant exhaust gases. Our final results will be used as the basis to evaluate the technical efficacy and associated economic performance of large-scale carbon sequestration facilities.

Our vision of a viable strategy for carbon sequestration based on photosynthetic microalgae is shown conceptually in Figure 1. In this figure, CO<sub>2</sub> from the fossil fuel combustion system and nutrients are added to a photobioreactor where microalgae photosynthetically convert the CO<sub>2</sub> into compounds for high commercial values or mineralized carbon for sequestration. The advantages of the proposed process include the following:

1. High purity CO<sub>2</sub> gas is not required for algae culture. It is possible that flue gas containing 2~5% CO<sub>2</sub> can be fed directly to the photobioreactor. This will simplify CO<sub>2</sub> separation from flue gas significantly.
2. Some combustion products such as NO<sub>x</sub> or SO<sub>x</sub> can be effectively used as nutrients for microalgae. This could simplify flue gas scrubbing for the combustion system.
3. Microalgae culturing yields high value commercial products that could offset the capital and the operation costs of the process. Products of the proposed process are:  
(a) mineralized carbon for stable sequestration; and (b) compounds of high commercial value. By selecting algae species, either one or combination or two can be produced.
4. The proposed process is a renewable cycle with minimal negative impacts on environment.

The research and experimentation we propose will examine and quantify the critical underlying processes. To our knowledge, the research we propose represents a radical departure from the large body of science and engineering in the area of gas separation. We believe the proposed research has significant potential to create scientific and engineering breakthroughs in controlled, high-throughput, photosynthetic carbon sequestration systems.

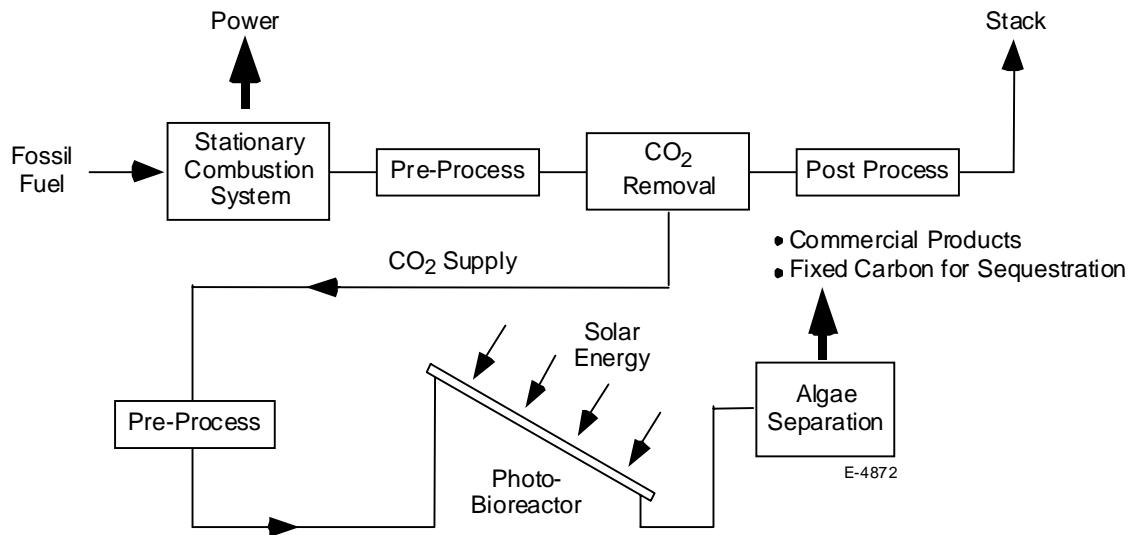


Figure 1. Recovery and sequestration of CO<sub>2</sub> from stationary combustion systems by photo-synthesis of microalgae.

## 2. Executive Summary

This program calls for development of key technologies pertaining to: (1) treatment of effluent gases from the fossil fuel combustion systems; (2) transferring the recovered CO<sub>2</sub> into aquatic media; and (3) converting CO<sub>2</sub> efficiently by photosynthetic reactions to materials to be re-used or sequestered.

Since the inception of the program we have:

- Completed characterization of power plant exhaust gas;
- Identified a number of CO<sub>2</sub> separation processes;
- Analyzed 34 different strains for high value pigments;
- Determined the productivity parameters for over 20 different algae with 5 different simulated flue gases;
- Tested the compatibility of over 20 microalgal species with 5 different simulated flue gases;
- Tested three different strains for carbon sequestration potential into carbonates for long-term storage of carbon;
- Successfully carried out scale up of three microalgal strains to the 2000 liter outdoor photobioreactors;
- Conducted CO<sub>2</sub> mineralization study for Haematococcus in laboratory and in open-pond experiment;

- Installed the diagnostic instrumentation for characterization of coal combustion gas at Aquasearch Inc.;
- Delivered to Aquasearch the PSI coal reactor to be used with the Aquasearch 2000 liter outdoor photobioreactor for direct feeding of coal combustion gas to microalgae;
- Tested the coal reactor and conducted the first pilot scale production run with coal combustion gases and modified the coal combustor to allow for longer-term burns;
- Completed the first full scale production run and conducted the second full scale run at the 25,000 photobioreactor using propane combustion gas utilizing two different strains of microalgae;
- Carried out preliminary work on biomass separation for two microalgal strains grown in 2000 liter outdoor photobioreactors;
- Started to model the costs associated with biomass harvested from different microalgal strains;
- Conducted work on designing key components including: CO<sub>2</sub> removal process; CO<sub>2</sub> injection device; photobioreactor; product algae separation process; and process control devices;
- Developed a photobioreactor design concept for biofixation of CO<sub>2</sub> and photovoltaic power generation.
- Shared the ASPEN model with UH, PSI and Aquasearch for review and discussion;
- UH research staff visited Aquasearch and worked on-site for one week to gather information on the performance of the photobioreactor;
- Photobioreactor data from Aquasearch were analyzed and simple linear relationships for biomass productivity as a function of solar irradiance and CO<sub>2</sub> were developed using multiple regression;
- A review of the technical literature on tubular photobioreactors progressed;
- A literature study progressed to develop the CO<sub>2</sub> flue gas separation subsystem model for both Aspen Plus and Excel models;
- Conducted economic analysis for photobioreactor carbon fixation process; and
- Continued development of economic model to be used in predictions of carbon sequestration cost for a number of scenarios.

In Table 1, current status of each work scope is summarized.

Table 1. Current Status of Each Work Scope

Tasks	Title	% Complete	Milestone/Status Description
Task 1.0	Supply of CO <sub>2</sub> from Power Plant Flue Gas	85%	Overall status for Tasks 1.1 through 1.3
Task 1.1	Power Plant Exhaust Characterization	100%	Most of pertinent exhaust gases were analyzed
Task 1.2	Selection of CO <sub>2</sub> Separation and Clean-up Technologies	95%	MEA method identified. Direct injection of exhaust gas into water may be an option.
Task 1.3	Carbon Dissolution Method	75%	Analytical study completed. Direct exhaust gas injection may be studied per our Task 3 outcome.
Task 2.0	Selection of Microalgae	100%	Selection of 6 species out of initial 20
Subtask 2.1	Characterization of Physiology, Metabolism and Requirements of Microalgae	100%	Test compatibility of 20 species with 5 flue gases
Subtask 2.2	Achievable Photosynthetic Rates	100%	Productivity parameters of 20 species with 5 flue gases
Task 3.0	Optimization and Demonstration of Industrial Scale Photobioreactor	30%	Demonstrate viability of CO <sub>2</sub> with algae at industrial scale
Subtask 3.1	Pilot Evaluation	35%	Evaluation at 2000 L pilot scale. Experimental work with coal reactor started
Subtask 3.2	Full Scale Production Runs	35%	Evaluation at 24,000 L industrial scale with propane combustion gas.
Subtask 3.3	Algae Separation and Final Product	55%	Evaluation of biomass separation
Task 4.0	Carbon Sequestration System Design	50%	Incorporating new system concept
Task 4.1	Component Design and Development	50%	New concept being incorporated
Task 4.2	System Integration and Simulation Analysis	50%	Analyses of new system concept to be made
Task 5.0	Economic Analysis	15%	Economic analysis of commercial microalgal CO <sub>2</sub> sequestration
Task 5.1	Gas Separation Process	85%	Direct exhaust gas injection option to be assessed
Subtask 5.2	Photobioreactor Carbon Fixation Process	15%	Economic analysis of photobioreactor CO <sub>2</sub> fixation
Subtask 5.3	Product Processing	5%	Economic analysis of product processing

The work discussed in this report covers the reporting period from 1 April 2004 to 30 June 2004.

### 3. Experimental

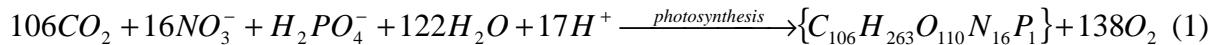
#### 3.1 Task 3: Optimization and Demonstration of Industrial Scale Photobioreactor

##### Carbon Sequestration into Mineral Carbonates

Although not a specific separate subtask, the sequestration of carbon into mineral carbonates is an integral part of our objectives. Carbon sequestered into relatively stable compounds such as carbonates would generate a long-lived and easy-to-store form of sequestered carbon. In previous reports (QR #4), we demonstrated that microalgal cultures can modify the chemistry of the culture medium sufficiently to induce the precipitation of carbonates at small scale. We have now started to scale up those observations to full-scale photobioreactors.

In our previous work, at bench-top scale, we made the argument that as the pH of a culture increases caused by photosynthetic CO<sub>2</sub> uptake, the proportion of CO<sub>3</sub><sup>2-</sup> in the medium increases. The increased availability of CO<sub>3</sub><sup>2-</sup> in the medium increases the probability that it would react with Ca<sup>2+</sup> ions to form CaCO<sub>3</sub>, which represents a stable form of carbon useful for long-term sequestration of CO<sub>2</sub>. Furthermore, the concentration of CO<sub>3</sub><sup>2-</sup> can also be increased without a change in pH if the total alkalinity of the medium increases. In our previous reports, we reported our first attempts to model the changes in alkalinity in the medium that results from the cells photosynthetic and growth activities.

Photosynthetic uptake of CO<sub>2</sub> produces changes in the pH of the medium but does not change the alkalinity *per se*. However, other growth processes, such as the uptake of NO<sub>3</sub><sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> do (Eq. (1)). The stoichiometry of photosynthesis-based cellular growth indicates that for every 106 moles of CO<sub>2</sub> taken up 16 moles of NO<sub>3</sub><sup>-</sup> and 1 mole H<sub>2</sub>PO<sub>4</sub><sup>-</sup> are taken up. At the same time, 17 moles of H<sup>+</sup> are taken up from the medium which results in an equivalent increase in alkalinity.



Based on Eq. (1) we modeled the expected change in alkalinity caused by photosynthetic growth equivalent to 1 mM of carbon and estimated the resulting changes in nutrient concentrations (N, P) as well as in inorganic carbon species. We then extended that analysis to estimate the changes expected in a long-term microalgal culture assuming reasonable growth rates as obtained from our experimental cultures. Finally, we compared the modeled results with those obtained from an actual culture of *Haematococcus pluvialis* at commercial scale (25,000 liters).

In this quarter, we have continued the analysis presented in QR#14 to include data obtained from outdoor photobioreactor cultures (pilot and full scale) growing two more microalgal strains (AQ0012, a locally isolated Cyanobacterial strain, and AQ0073, *Botryococcus braunii*). The cultures were grown as per our standard operating procedures. The culture's pH was controlled (7.4-7.6) by direct injections of CO<sub>2</sub> or propane combustion gases into the medium. Every morning, pH and alkalinity determinations were conducted on samples from the photobioreactor (PBR) cultures as described in previous Quarterly Reports. From the pH and alkalinity values, the concentrations of the different dissolved inorganic carbon species in the medium were calculated as described previously.

### 3.2 Subtask 3.1: Pilot Evaluation of Coal Combustion Gases

During this quarter we have continued to work with the coal reactor. Specifically we have carried out design modifications that will allow us longer burn times needed to support microalgal culture growth. The custom-built coal combustor (Figure 2) is utilized to burn bituminous coal from the Upper Freeport Mine. A vacuum pump is used to transfer the gases from the combustor to the PBR. Because of continuing technical problems (see Results and Discussion section) no growth experiments with coal combustion gases were carried out this quarter.



Figure 2. Custom built coal reactor used to generate flue gases used in microalgal carbon capture experiments.

### 3.3 Subtask 3.2: Full Scale Production Runs

The goal of our final set of experiments is to optimize gas delivery systems for photobioreactor performance at present commercial scale. These experiments are conducted in Mera Growth Modules (MGM), the commercial PBRs on which current economic models are based. Flue gas is supplied by a slipstream from the existing propane combustor to the commercial scale bioreactors. The composition of the flue gas can be modified as needed by the addition of more CO<sub>2</sub> and acid gases in order to simulate the flue gas compositions determined in Task 1 if needed.

Based on the results of Task 1.3, we will optimize the gas injection system for maximum dissolution of CO<sub>2</sub>. We will conduct experiments in the 25,000-L MGM using propane combustion product flue gas supplied by the system developed and using only the 5-6 species of

microalgae selected for large-scale experiments. Each species will be run at this scale for 6-10 weeks, allowing for optimization.

This quarter we have conducted two large scale experiment with strains AQ0012 (a locally isolated Cyanobacterial strain) and AQ0073 (*Botryococcus braunii*). Cultures were grown in our commercial scale MGM photobioreactors at 7.5 pH. The cultures were initially grown using pure CO<sub>2</sub> and, after a few days, propane combustion gases were used. Gas additions, whether pure CO<sub>2</sub> or stack gases, were added to the PBR cultures on demand, i.e., when the pH of the cultures indicated lowering of the concentration of CO<sub>2</sub> in the medium.

Data was collected daily on the concentration of cells in the cultures to estimate growth rate and carbon capture, the fluorescence yield of the cultures (as described earlier) and the pH and alkalinity of the cultures' medium to estimate the concentration of CO<sub>2</sub>, HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>=</sup> and total dissolved inorganic carbon (DIC). The pH of the cultures was continuously monitored by our computerized monitoring and control system. Changes in pH were used to estimate the rate of carbon assimilation by the microalgal cells as described above. Problems with our data acquisition system limited the amount of useful data available.

#### 3.4 Subtask 3.3: Algae Separation and Final Product

Algae separation from the growth medium represents a significant fraction of the costs associated with microalgal biomass processing. So far, we have considered the use of centrifuges because of its high efficiency. However, centrifugation is relatively costly, in capital costs (centrifuges at several hundred thousand dollars each would be necessary for even a small operation) and running costs (high electricity usage and associated CO<sub>2</sub> production). In this quarter, we have investigated the use of passive lamellar settlers as an alternative. Lamellar settlers are an existing technology used in the separation of solids from, e.g., waste waters. Their use in microalgal biotechnology is nearly non-existing because the specific density of most microalgae is too close to that of the medium in which they grow. However, we feel that this technology can be successfully applied to specific microalgal products. Specifically, cells of *Haematococcus pluvialis* cells become significantly heavier following physiological stress. Thus, we have tested whether lamellar settling can be useful in harvesting *H. pluvialis* cells.

A lamellar settler (L/S) consists of a container with vertical walls. Inside the container, a series of sheets (the lamellae-plural- or lamella-singular) are stacked up at some angle off the horizontal (about 10°-40°). The operating principle of a L/S is that it accelerates gravity settling by shortening the distance over which the particles need to travel before hitting a surface. An example is shown in Figure 3.

To test this concept we have built a simple unit consisting of a clear PVC box (0.10 x 0.08 x 103 cm; WxHxL). Essentially, this is a one-lamella lamellar settler (Figure 4). Calculations based on the design constrains and the settling velocity of *H. pluvialis*, we estimated that this unit should be able to harvest 100% of the cells at a through put of 0.5 liter/minute. To measure the harvest efficiency of the model lamellar settler, we estimated the biomass concentration of the culture fed into the unit by measuring its fluorescence and comparing it with the fluorescence of the culture at the outflow of the unit.

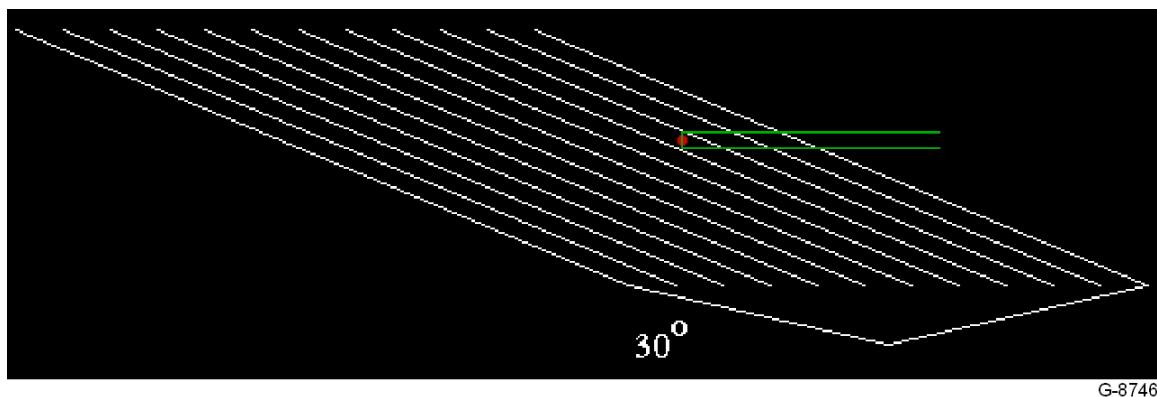


Figure 3. Diagram of a lamellar settler with lamellae at 30° (from <http://www.rpi.edu/dept/chem-eng/Biotech-Environ/SEDIMENT/lamel.html>).

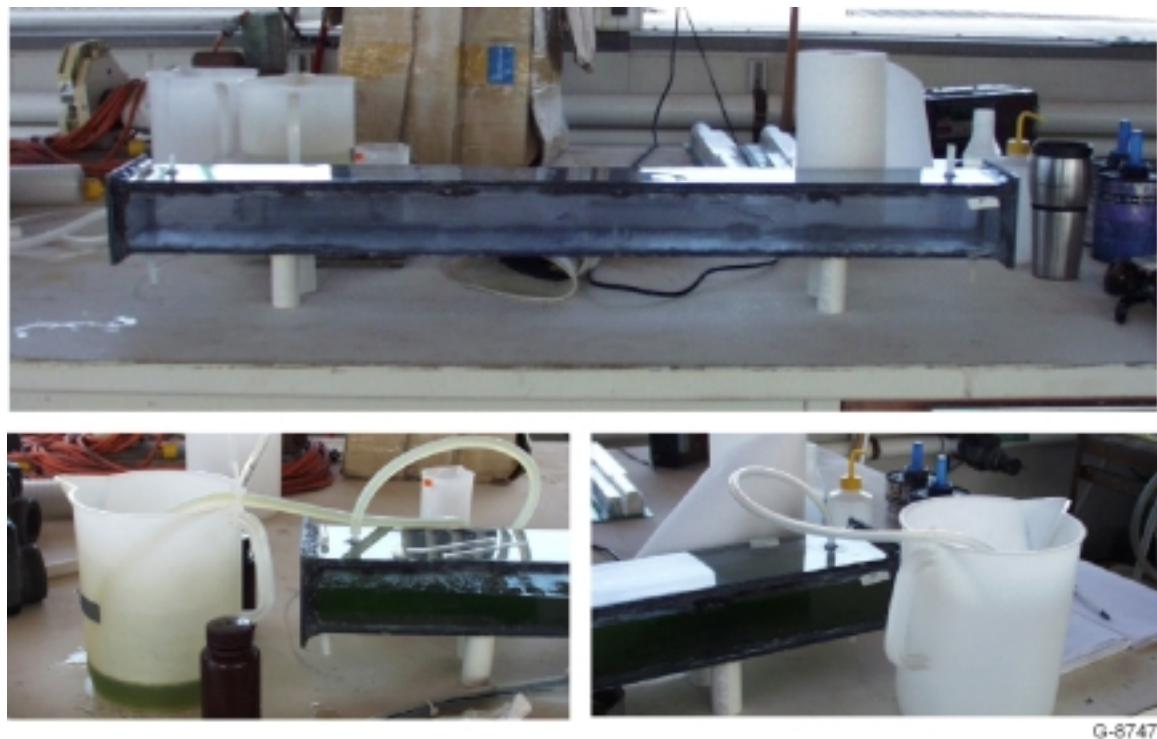


Figure 4. Model lamellar settle (one-lamella) and inlet and outlet details.

## 4. Results and Discussion

Work accomplished in this reporting period is summarized according to the task structure of the program.

### 4.1 Task 1: Supply of CO<sub>2</sub> from Power Plant Gas to Photobioreactor

Most of the work within the two subtasks (Task 1.1: Power Plant Exhaust Characterization and Task 1.2: Selection of CO<sub>2</sub> Separation and Cleanup Technologies) has been conducted during the previous reporting periods. No additional activity was made during the present reporting period.

### 4.2 Task 2: Selection of Microalgae

Almost all work in this task was completed in the previous reporting periods. We have conducted additional work for Task 2.2: Achievable Photosynthetic Rates, High Value Product Potential and Sequestration of Carbon into Carbonates.

### 4.3 Task 3: Optimization and Demonstration of Industrial Scale Photobioreactor

The goal for this phase of our research program is to optimize carbon sequestration, high value component production and CO<sub>2</sub> mineralization utilizing microalgal cultures at a commercially significant scale. This is being done in two phases. First, we are conduct a pilot evaluation using 2,000 liter enclosed PBRs (pilot scale MGM, Task 3.1) and actual coal combustion gases as the carbon source for the microalgal cultures. Second, we are conducting full scale production runs using 25,000 liter enclosed PBRs (full scale MGM, Task 3.2) and actual combustion gases from a propane burner as the carbon source for the algal cultures. Concurrently, research into the appropriate technologies for harvesting and processing the produced biomass will be conducted (Task 3.3). At the same time we are investigating the scale up of carbon sequestration into relatively stable compounds such as carbonates which would generate a long-lived and easy-to-store form of sequestered carbon.

#### Carbon Sequestration into Mineral Carbonates

In our previous quarterly report (QR#14) we showed that as the microalgal cultures grow and take up NO<sub>3</sub><sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> from the medium, both the alkalinity and concentration of dissolved inorganic carbon increase in the medium. This direct effect of photosynthesis-driven growth constitutes carbon sequestration into dissolved inorganic carbon (DIC). During this quarter we have attempted to extend our observations to cultures of strain AQ0012 (a locally isolated Cyanobacterial strain) and AQ0073 (*Botryococcus braunii*). The culture of AQ0073, however, did not grow when transferred to a outdoor photobioreactor, thus no data for this strain is yet available. The culture of strain AQ0012 grew for only a few days before a leak developed in the photobioreactor and contaminant organisms (including other microalgae) were introduced. Still, our results show that as the culture grew, the concentration of dissolved inorganic carbon in the medium increased (Figure 5).

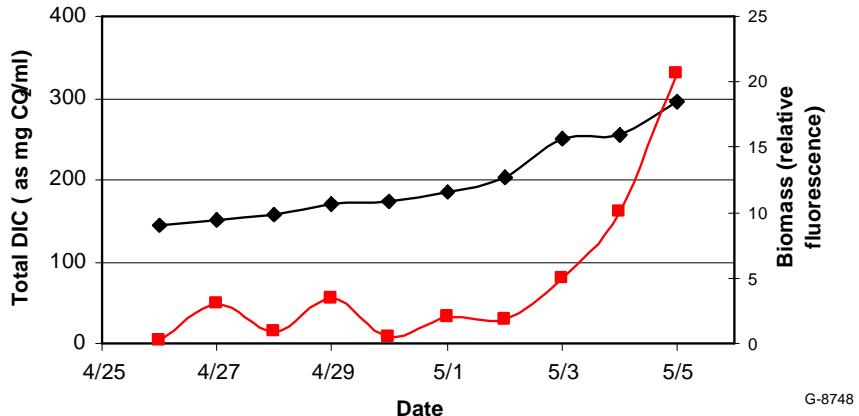


Figure 5. Total dissolved inorganic carbon measured in the medium of a microalgal culture. The figure panel shows the increase in total DIC for a culture of AQ0012 (black diamonds), a locally cyanobacterial strain as the cells grew and photosynthetized. Red squares are the fluorescence-based biomass estimates.

We had previously shown that increases in culture medium alkalinity and DIC could be used to drive reactions resulting in the calcification of dissolved inorganic carbon (QR#4). We plan to test this process at commercial scale in upcoming experiments.

#### 4.4 Subtask 3.1: Pilot Evaluation of Coal Combustion Gases

As indicated in the 14<sup>th</sup> Quarterly Report, a number of technical problems associated with the coal combustor have significantly delayed progress in this part of the research program. During this quarter, further modifications to the coal combustor have been attempted.

While we apparently have solved all the coal feeding problems, we must still overcome the problem of blockage at the reactor exit. During the last quarter, and after discussions with Joe Morency, a new reactor exit and ash can were designed. The new design consisted of removing the ceramic constrictor, enlarging the reactor exit pipe to the same size as the alumina retort and enlarging the ash can in order to accept the enlarged exit pipe.

During this quarter, we have received the newly built parts and installed them on the coal reactor. Figure 6 shows a photograph of the new exit pipe and ashcan assembly constructed for the coal combustor. The larger diameter of the pipe has allowed us to eliminate the recurring blockage from the reactor's exit with slag and ash by eliminating the ceramic restrictor at the bottom of the reactor and matching the diameter of the combustion chamber's retort (Figure 7). Figure 8 shows the inside of the new ashcan following several hours of coal burning. The larger size ashcan will also allow us to conduct longer duration burns before accumulation of ash forces us to shut down the combustor for maintenance. However, because of the longer duration runs we run the risk of fouling up the inlet diffuser at the top of the combustion chamber (see Figure 9).



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Figure 6. Photograph of the new exit pipe and ashcan assembly constructed for the coal combustor. The larger diameter of the pipe has allowed us to eliminate the recurring blockage from the reactor's exit with slag and ash.



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Figure 7. Top end of the new pipe and ashcan assembly. The diameter of the pipe matches the inner diameter of the combustion chamber's retort thus eliminating restrictions at the exit of the combustion chamber.



Figure 8. Inside view of the new ashcan. Its larger capacity permits us to carry out longer duration coal burns.



Figure 9. Photograph of the diffuser at the top of the combustion chamber showing accumulation of ash and unburned coal powder.

Following installation of the new parts, a test burn was conducted on May 27<sup>th</sup>. The test burn lasted for a few hours and it appeared to work perfectly. Figure 10 shows the measured gas concentrations in the combustion exhaust (stack 1). We obtained CO<sub>2</sub> concentrations of about 2% and SO<sub>x</sub> and NO<sub>x</sub> concentrations in the 200-250 ppm range.

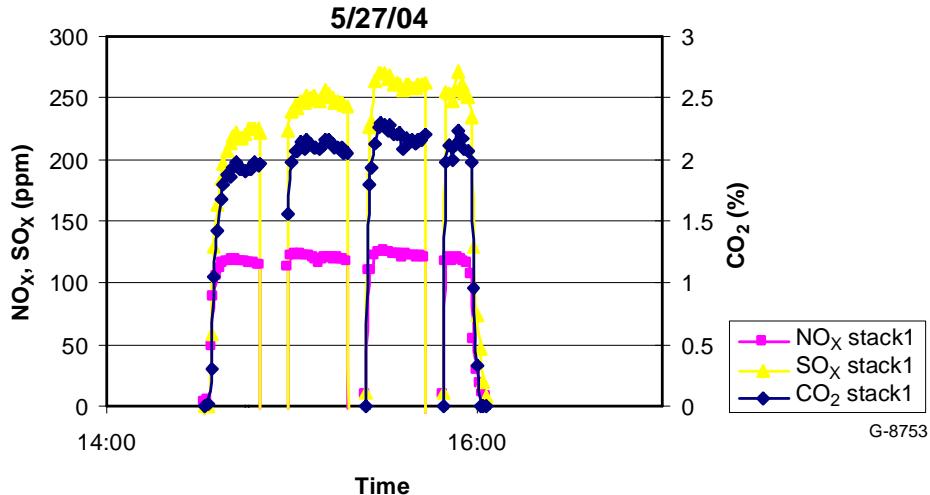


Figure 10. Analysis of the exhaust gas during a coal burn following the installation of the new exit pipe and ashcan assembly.

A second test run was conducted on May 28<sup>th</sup>. After about 2 hours, the measured gas concentrations in stack 1 started to drop and the burn was stopped (Figure 11). It was found that the coal had blocked one of the restrictions in the feeding tube. After cleaning the combustor one more time, a third burn was conducted on June 2<sup>nd</sup>. Shortly after the reactor was started on June 2<sup>nd</sup>, the furnace temperature started to fall and would not rise, decreasing the efficiency of the burn (Figure 12). The reactor was shut down and inspected. The furnace thermocouple and wiring showed signs of wear and the furnace elements did not measure at the proper resistance. A new thermocouple, furnace heating elements and wiring material were ordered from the factory. Unfortunately, these parts were not in stock and had to be manufactured. The manufacturer gave a 6-week lead-time for shipping the parts. These parts are expected to arrive on site the week of July 1<sup>st</sup>.

While we have run into more difficulties with the coal reactor in this quarter, the results obtained so far are very positive. We can now routinely, maintain burns at several hours at a time producing consistent gas concentrations in the reactor's exhaust. So far, we have not found blockage of the new design furnace exit, which was a major problem earlier. We look forward to receiving the newly ordered parts to run our first proper experiments with microalgal cultures.

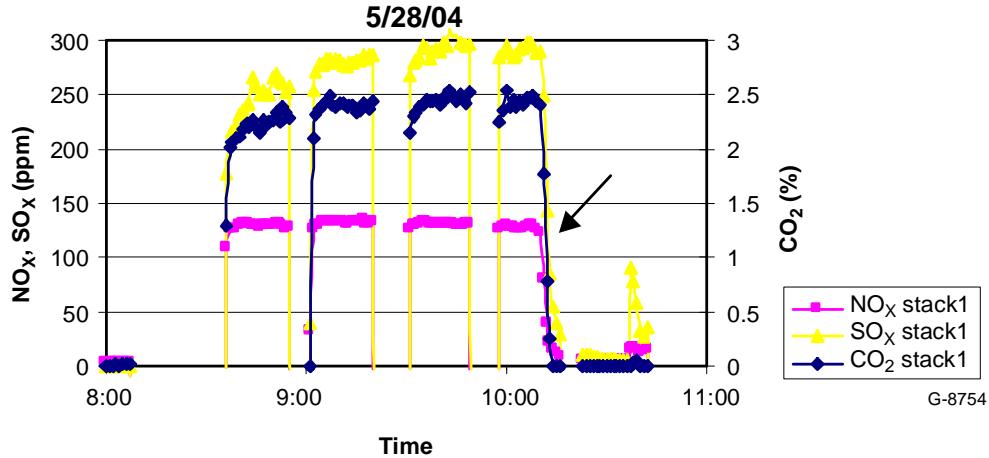


Figure 11. Analysis of the exhaust gas during a coal burn conducted on May 28. The arrow indicates the point in time when the exhaust gas concentrations started to drop, indicating blockage of the coal feeding tube.

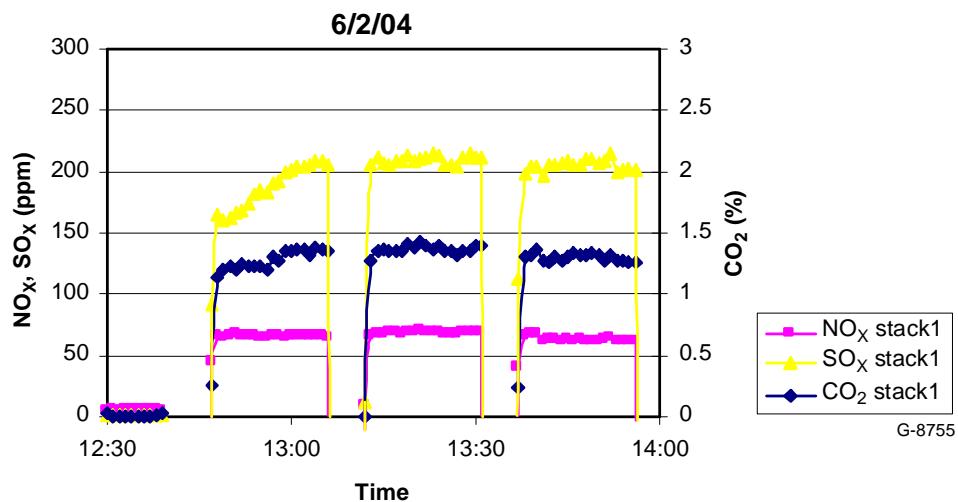


Figure 12. Gas concentrations obtained during a third test burn of the coal reactor conducted on June 2<sup>nd</sup>.

#### 4.5 Subtask 3.2: Full Scale Production Runs

During this quarter we have attempted to culture two more microalgal strains (AQ0012 and AQ0073) at 7.5 pH in full scale PBRs being fed pure CO<sub>2</sub> and propane combustion gases. We were unsuccessful at growing AQ0073. The cells did not grow in the outdoor photobioreactors. We expect to attempt this strain in the near future.

We were more successful with AQ0012, a locally isolated Cyanobacterial strain. Initially we grew AQ0012 in a scale-up photobioreactor of 900 liter capacity using pure CO<sub>2</sub> (Figure 13).

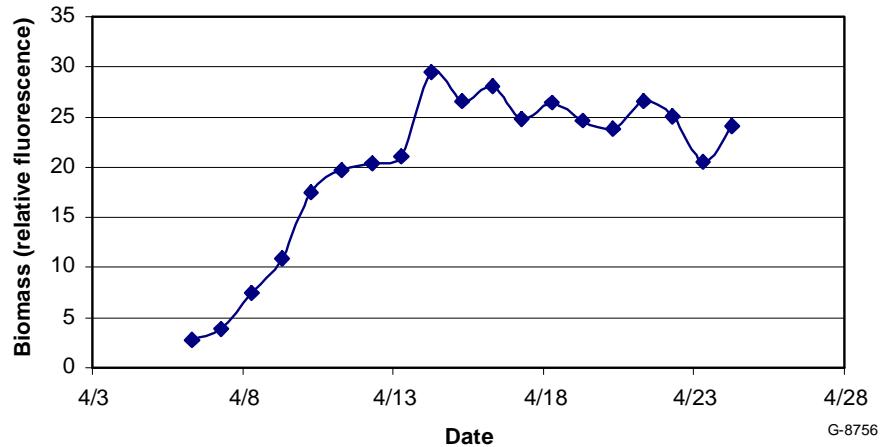


Figure 13. Biomass concentrations achieved in the 900 liter scale-up photobioreactor with a culture of strain AQ0012, a locally isolated Cyanobacterium.

After a 2 ½ week grow out period the culture was transferred to 25,000 liter photobioreactor for CO<sub>2</sub> capture efficiency measurements at full commercial scale. Unfortunately, the photobioreactor's integrity failed and the culture became quickly contaminated and the culture was discarded after 10 days (see Figure 5).

Although the culture was contaminated with other microalgal strains, we went ahead and carried out estimates of CO<sub>2</sub> capture efficiency by the mixed population. The calculated rates of CO<sub>2</sub> disappearance from the medium are shown in Figure 14.

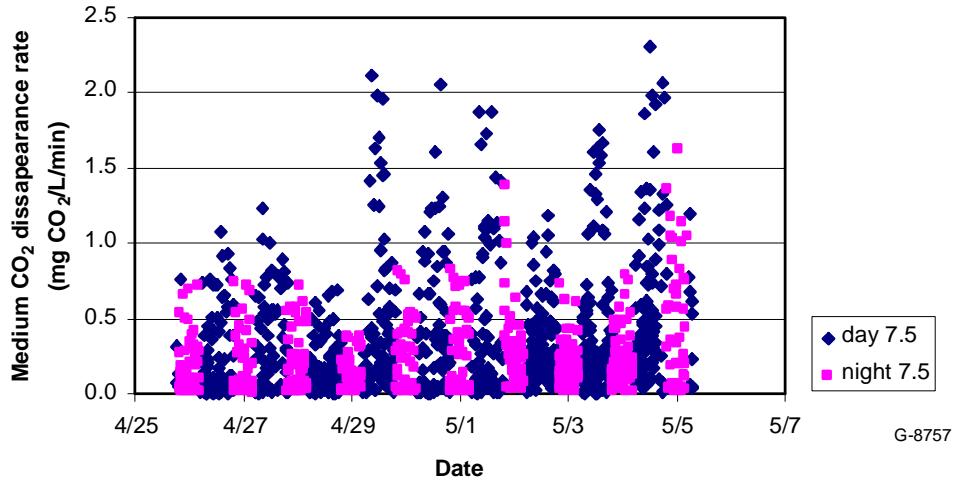


Figure 14. Rates of dissolved inorganic carbon (DIC) disappearance from the medium (photosynthesis and/or degassing) for a culture of strain AQ0012. The different symbols indicate the different conditions under which these data were obtained (night vs. day). The supply of CO<sub>2</sub> to the culture was switched from pure CO<sub>2</sub> to propane combustion gases on May 1<sup>st</sup>.

We have averaged the CO<sub>2</sub> disappearance rate over each day and night period (Figure 15). The data indicate that as the cultures grew older (more biomass in the culture and higher alkalinity, compare with Figure 5), the calculated rates of DIC disappearance increased. This is a direct result of increased dissolved CO<sub>2</sub> concentration in the medium and the resulting rate of CO<sub>2</sub> degassing (see below).

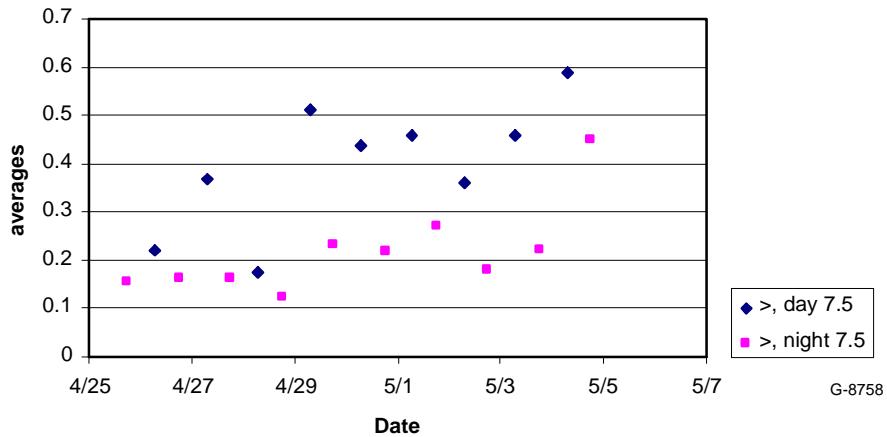


Figure 15. Calculated daily averages of DIC disappearance from the medium (photosynthesis and/or degassing) for a culture of strain AQ0012. The different symbols indicate the different conditions under which these data were obtained (night vs. day). The supply of CO<sub>2</sub> to the culture was switched from pure CO<sub>2</sub> to propane combustion gases on May 1<sup>st</sup>.

Finally, we have considered the effect of CO<sub>2</sub> concentration in the culture medium on CO<sub>2</sub> degassing rate during the night periods (i.e., in the absence of photosynthesis). The results are shown in Figure 16 and corroborate the dependency of degassing of CO<sub>2</sub> from the medium on the concentration of CO<sub>2</sub> in the medium as was reported in previous experiments (QR#12, QR#13 and QR#14). In all cases, and as was the case for the pilot scale experiment (previous reports), more CO<sub>2</sub> is lost from the medium at higher CO<sub>2</sub> concentrations in the medium.

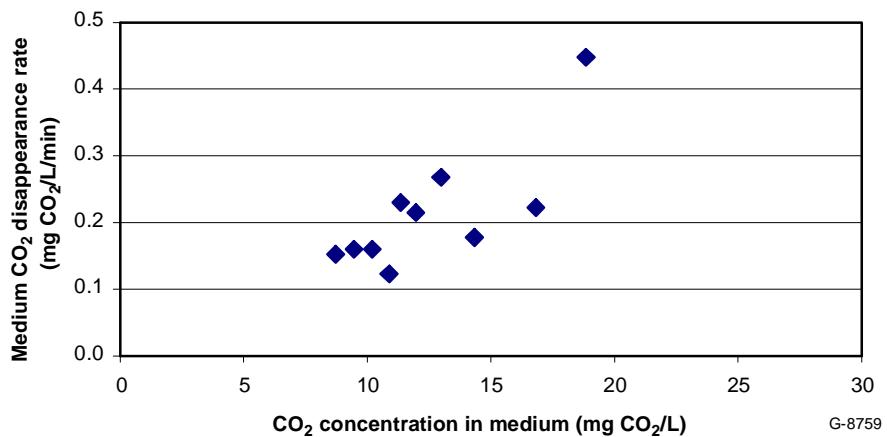


Figure 16. Relationship between CO<sub>2</sub> concentration in the culture medium and night-time rate of dissolved inorganic carbon (DIC) disappearance from the medium (degassing) for a culture of strain AQ0012.

#### 4.6 Subtask 3.3: Algae Separation and Final Product

Our first experiment consisted of using non-stressed *H. pluvialis* cells using the lamellar settler in the horizontal position. These cells were used to obtain data for a worst-case scenario, i.e., cells that are not especially dense and that can swim. The fluorescence-based biomass estimate of the culture fed into the lamellar settler was 420 (relative units) while the outflow was 306. Thus, the biomass harvest efficiency was only 27%.

The next tests were conducted using stressed *H. pluvialis* cells. These cells do not have the ability to swim and have a settling velocity of about 0.5 cm/min. We run the culture through the lamellar settler while placed in the horizontal and at 16° and 30° from the horizontal.

When the lamellar settler was placed horizontally, a maximum of 90% of the biomass was harvested. By placing the settler at 16° and 30° we were able to harvest 96% and 94% of the biomass respectively. The photographs in Figure 17 present views of the inlet and outlet sections of the settler showing the difference in biomass concentration as the settler fills up with culture. Figure 18 consists of two photographs of the bottom of the lamellar settler showing the sedimentation pattern of the cells.

In summary, our tests show that the relatively cheaper lamellar settler technology may be used successfully to harvest microalgal cells but only if the cells are substantially heavier than the growth medium, as is the case for stressed *H. pluvialis* cells.

#### Other Activities

During this quarter, a presentation was made at the Third Annual Conference on Carbon Capture and Sequestration in Alexandria, VA. The presentation was titled “Microalgal removal of CO<sub>2</sub> from flue gases: CO<sub>2</sub> capture from a coal combustor”. The manuscript is included here as Appendix A.

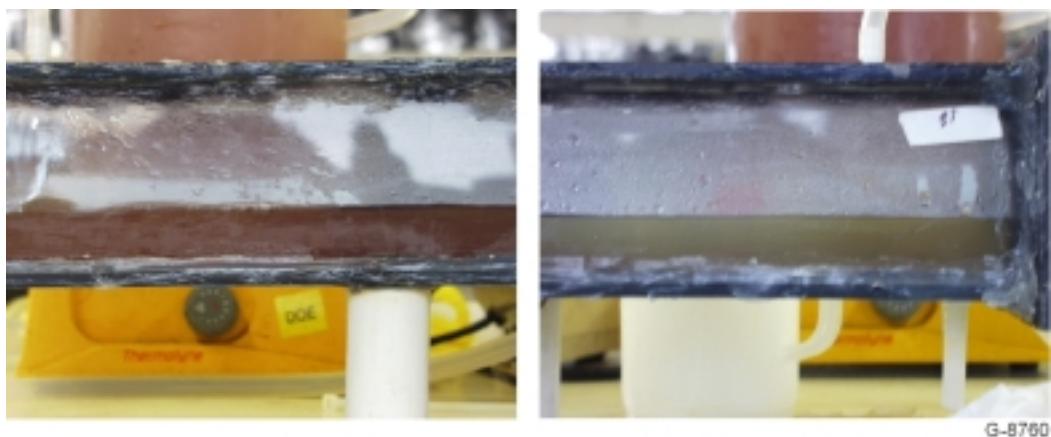


Figure 17. Inlet (left) and outlet (right) sections of the lamellar settler. It can be easily seen that the cells concentration diminishes quickly as the model lamellar settler unit fills up with the microalgal culture.



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Figure 18. Photographs of the bottom of the unit after draining showing the pattern of settled cysts near the inlet (top) and outlet (bottom) ports.

#### 4.7 Task 4.2: System Integration

The integrated process model being developed by UH requires submodels that accurately represent the behavior of key components, notably, the photobioreactor and the CO<sub>2</sub> flue gas separation system.

##### Total Inorganic Carbon Analysis

A description of technical activities conducted by UH during this reporting period is provided below.

##### *Carbon Mass Flow Rate*

As reported previously, the carbon balance relationship for the photobioreactor is:

$$C_{in} - C_{out} = V_l M_C \left( \frac{d[C_{biomass}]}{dt} + \frac{d[DIC]}{dt} \right) + V_g M_C \left( \frac{d[C_{headspace}]}{dt} \right) \quad (2)$$

where C<sub>in</sub> is the mass flow rate of carbon from both CO<sub>2</sub> and air injections into the photobioreactor (g/min), C<sub>out</sub> is the mass flow rate of carbon out of the photobioreactor via venting (g/min), V<sub>l</sub> is the volume of the media (L), M<sub>C</sub> is the atomic weight of carbon (g/mol),

$\frac{d[C_{biomass}]}{dt}$  is the change in concentration of carbon bound in the biomass in the media with respect to time (mol/L/min),  $\frac{d[DIC]}{dt}$  is the change in dissolved inorganic carbon concentration with respect to time (mol/L/min),  $V_g$  is the volume of the headspace in the photobioreactor (L), and  $\frac{d[C_{headspace}]}{dt}$  is the change in carbon concentration in the headspace with respect to time (mol/L/min). Operational data and the %TOC analyses of the microalgae samples discussed in past Quarterly Reports provide most of the information needed for the carbon balance with the exception of the carbon venting term,  $C_{out}$ .  $C_{out}$  can be calculated from the photobioreactor gas venting rate and the concentration of carbon in this gas. Mera Pharmaceuticals does not monitor directly the gas venting rate (which should essentially equal the sum of the air and CO<sub>2</sub> gas flows into the photobioreactor) and the CO<sub>2</sub> concentration in the vented gas falls below the detection limit of their gas analyzer. In order to obtain these data and close the carbon mass balance (to determine sequestration efficiency), measurements were performed by UH during this reporting period.

#### *Orifice Meter*

An orifice meter was selected to measure the gas venting rate from the Mera Pharmaceuticals photobioreactor. A comparison of possible measurement devices was conducted and the orifice meter was determined to be rugged and sufficiently accurate for the present application; it also provided a good compromise between cost and performance. Gas is vented from the photobioreactor through a nominal 3 inch PVC pipe and the orifice meter could be attached to that pipe. Figure 19 presents a photograph of the orifice meter and the connector piece used to attach it to the photobioreactor vent. The orifice meter was fabricated following

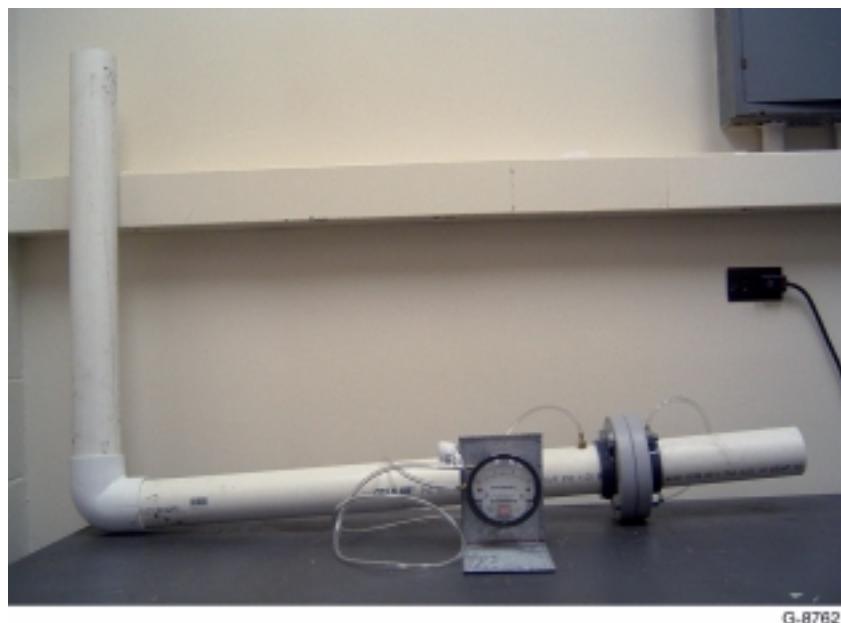


Figure 19. Photograph showing the orifice meter and the connector piece.

standard design practice. It consists of nominal 3 inch PVC pipe and fittings. The ASME sharp edge orifice was machined from Plexiglas plate and is sandwiched between the PVC pipe flanges. Several orifices were fabricated with different diameters to accommodate a range of possible flow rates. The orifice that ended up being used in the tests had an i.d. of 1.2 inches (3.0 cm). Pressure drop across the *vena contracta* taps was monitored with a Magnehelic differential pressure gauge.

### *Gas Sampling and Analysis*

The orifice meter was used to measure gas venting rate. In order to determine  $C_{out}$ , the concentration of carbon in that gas must be known. Since a number of gas chromatographs are available at the University of Hawai‘i, it was decided to collect gas samples and bring them to Honolulu for analysis.

Tygon tubing was inserted into the vent downstream of the orifice and samples were extracted with a vacuum pump and stored in 1 liter teflon sampling bags. An inline filter removed any carryover liquid water. Figure 20 shows the simple gas sampling system used in the experiments.



Figure 20. Photograph of the gas sampling system.

The graduate research assistant (GRA), Mr. Simon Tsang, performed experiments to measure photobioreactor vent flow rate and collected vent gas samples at the Mera Pharmaceuticals facility in Kona on 16 June 2004. Figure 21 is a photograph of the orifice meter and gas sampling system installed at the end of the downward-facing vent tube from the photobioreactor.



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Figure 21. Photograph showing the gas sampling system and the orifice meter attached to the photobioreactor vent at the Mera Pharmaceuticals facility.

During the experiments, the automated CO<sub>2</sub> injection system was turned off so that the start time and duration of the CO<sub>2</sub> injections could be manually adjusted. Tests were performed where CO<sub>2</sub> was injected continuously into the photobioreactor for 21 minute periods. The amount of pure CO<sub>2</sub> injected was monitored and recorded. Vent gas samples and differential pressure readings (i.e., vent gas flow rates) were taken before, during, and after the injections. The gas samples were brought back to UH for GC analysis using a Shimadzu Model 14A gas chromatograph equipped with a FID and TCD. Results of these experiments will be provided in the next Quarterly Report and applied to the model development.

## 5. Conclusion and Future Plans

### 5.1 Task 3: Optimization and Demonstration of Industrial Scale Photobioreactor

In this quarter, we have continued preparations for our pilot scale photobioreactor experiments where we will use combustion gases from coal to produce microalgal biomass and sequester carbon and we have run full scale propane combustion experiments with two more microalgal strains. Specifically we have:

- Extended our observations that microalgal photosynthetic CO<sub>2</sub> capture does not only results in assimilation of organic carbon but also increases the concentration of inorganic carbon in the medium using one more microalgal strains,

- Carried out modifications on the coal combustor which allow us to conduct extended coal combusting runs, and
- Extended our observations of carbon capture by microalgae from actual propane combustion gases to one more previously untested strains at commercial scale.

Within the next quarter we expect to

- Start the first full experimental runs with microalgal cultures fed coal combustion gases.
- Continue propane-fed, full scale, photobioreactor experiments with further strains of microalgae.
- Test modifications to our large scale photobioreactors that are expected to enhance the dissolution of gases into the culture medium.

## 5.2 Task 5: Economical Analysis

In this quarter we have not advanced in the development of an economic model for industrial scale algae facilities. However, over the next quarters we expect to

- Continue development of the economic model to be used in predictions of carbon sequestration cost for a number of different scenarios.
- Incorporate productivity parameters for the different microalgal strains as determined during Tasks 2 and 3 of this project.
- Continue large scale centrifugation and separation experiments that will test our cost predictions based on our centrifugation cost models presented in previous quarterly reports.

## 6. **References**

1. U.S. Department of Energy, Energy Information Agency, *Emissions of Greenhouse Gases in the United States 1996*, DOE/EIA-0573(96), October 1997.
2. IEA (International Energy Agency), *Carbon Dioxide Capture from Power Stations*, 1998. [available at <http://www.ieagreen.org.uk>]

## APPENDIX A

### Microalgal removal of CO<sub>2</sub> from flue gases: CO<sub>2</sub> capture from a coal combustor

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Manuscript presented at the Third Annual Conference on Carbon Capture and Sequestration

Alexandria VA, May 2-6, 2004.

### Introduction

Emissions of carbon dioxide are predicted to increase this century (US DOE, 1997) leading to increased concentrations of carbon dioxide in the atmosphere. While there is still much debate on the effects of increased CO<sub>2</sub> levels on global climate, many scientists agree that the projected increases could have a profound effect on the environment. A large fraction of the anthropogenic emissions of carbon dioxide result from the combustion of fossil fuels for energy production (e.g., Kadam, 2002). It is the increased demand for energy, particularly in the developing world, which underlies the projected increase in CO<sub>2</sub> emissions. Meeting this demand without huge increases in CO<sub>2</sub> emissions will require more than merely increasing the efficiency of energy production. Carbon sequestration, capturing and storing carbon emitted from the global energy system, could be a major tool for reducing atmospheric CO<sub>2</sub> emissions from fossil fuel usage.

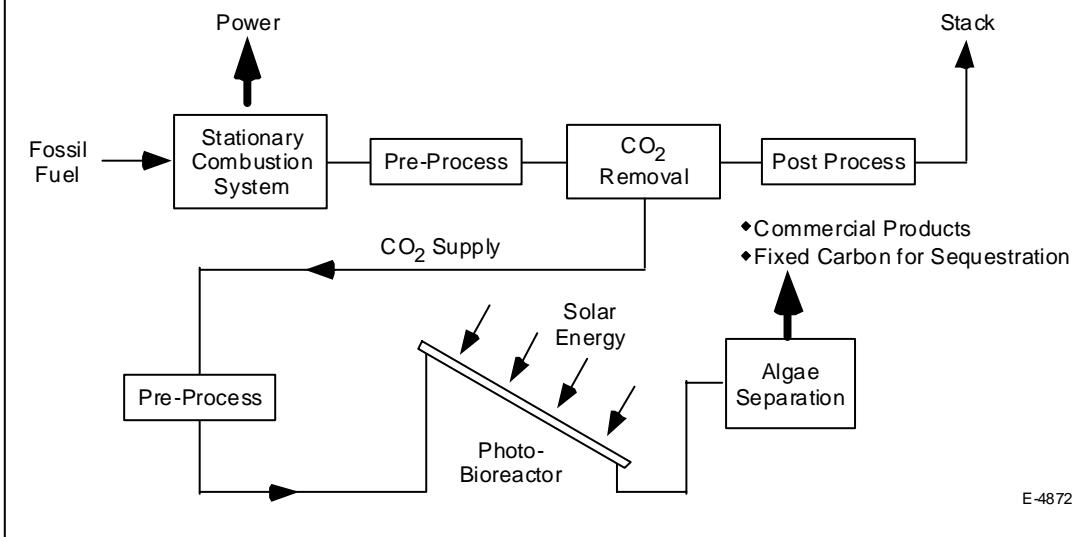
While chemical and physical means exist to capture CO<sub>2</sub> from smoke stack emissions, the cost of utilizing these technologies would result in a significant increase in the cost of power (IEA, 1998). For example, the cost of removing CO<sub>2</sub> from a conventional coal-fired power plant with flue gas desulfurization was estimated to be in the range of \$35 to \$264 per ton of CO<sub>2</sub>. The cost of power was projected to increase by anywhere from 25 to 130 mills/kWh. DOE's goal is to reduce the cost of carbon sequestration to below \$10 /ton of avoided net cost.

Photosynthesis has long been recognized as a means, at least in theory, to capture anthropogenic carbon dioxide. Photosynthesis is the original process that created the fixed carbon present in today's fossil fuels. Aquatic microalgae are among the fastest growing photosynthetic organisms, having carbon fixation rates an order of magnitude higher than those of land plants. Microalgae utilize CO<sub>2</sub> as one of their main building blocks and we propose that algal photosynthesis may be a viable option for anthropogenic CO<sub>2</sub> capture and sequestration. While microalgal culturing is expensive, microalgae can also produce a variety of high value compounds that can be used to generate revenues (Borowitzka, 1995; Olaizola 2003a). Those revenues could pay for the cost of carbon capture and sequestration. Microalgal photosynthesis can also result in the precipitation of calcium carbonate, a potentially long-term sink of carbon (Mazzone et al., 2002)

Our vision of a viable strategy for carbon sequestration based on photosynthetic microalgae is shown conceptually in Figure 1. In this figure, CO<sub>2</sub> from the fossil fuel combustion system and nutrients are added to a photobioreactor where microalgae utilize sunlight to photosynthetically convert the CO<sub>2</sub> into compounds of high commercial values or mineralized carbon for sequestration. The advantages of using a microalgal-based system are that

- High purity CO<sub>2</sub> gas is not required for algal culture. Flue gas containing varying amounts of CO<sub>2</sub> can be fed directly to the microalgal culture. This will simplify CO<sub>2</sub> separation from flue gas significantly.
- Some combustion products such as NO<sub>x</sub> or SO<sub>x</sub> can be effectively used as nutrients for microalgae. This could simplify flue gas scrubbing for the combustion system.
- Microalgae culturing may yield high value commercial products. Sale of these high value products can offset the capital and the operation costs of the process.
- The envisioned process is a renewable cycle with minimal negative impacts on environment.

Figure 1. A simple concept for a microalgal-based carbon capture scheme. High value products obtained from the microalgal biomass would offset the cost of CO<sub>2</sub> removal.



The concept of using microalgae to ameliorate CO<sub>2</sub> emissions from stationary combustion sources is not new (Kadam, 1997; Oswald and Golueke, 1968; Sheehan, et al., 1998). A number of studies have been carried out to determine the ability of microalgae to withstand the high CO<sub>2</sub> concentrations present in flue gas (Hanagata et al., 1992; Yun et al., 1997) as well as the potentially toxic accompanying SO<sub>x</sub> and NO<sub>x</sub> gases (Lee et al., 2002; Negoro et al., 1991). Thus, a number of efforts were carried out to isolate microalgal strains that are especially adept to this application such as those by the RITE program (Murakami and Ikenouchi, 1997) and others (Chang and Yang, 2003; Maeda et al., 1995; Sung et al., 1999).

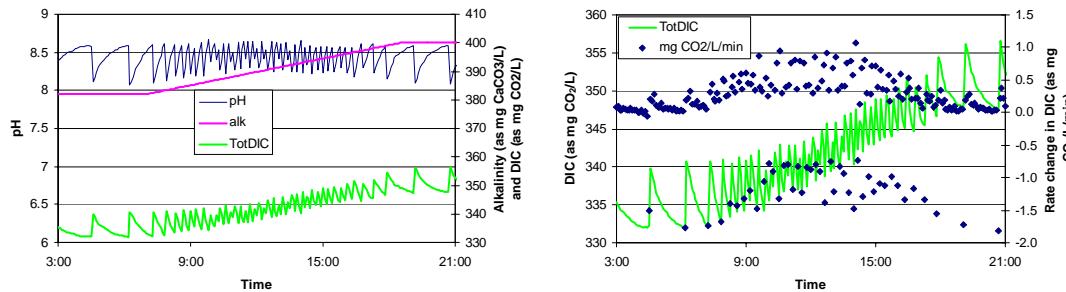
We are working towards developing technologies for recovery and sequestration of CO<sub>2</sub> from stationary combustion systems by microalgal photosynthesis. Specifically, our aims are to quantify the efficacy of microalgae-based carbon sequestration at industrial scale and determine under which conditions carbon capture and sequestration by microalgal photosynthesis is economically attractive when compared with other means of carbon capture and sequestration. We are focusing our efforts on demonstrating the ability of selected species of microalgae to effectively fix carbon from typical power plant exhaust gases.

Here, we report on experiments conducted to estimate the effects of medium pH and flue gas composition (e.g., coal and propane combustion gases and other simulated gas mixtures) on the microalgal CO<sub>2</sub> capture efficiency. The results indicate that, medium pH is a key determinant of CO<sub>2</sub> capture efficiency while the effect of flue gas composition is negligible.

## Methods

The experiments reported here were designed to test the carbon capture efficiency of microalgal cultures from the growth medium under several different culture conditions. Specifically, we compared the rate of photosynthetic carbon uptake versus the amount of carbon lost from the medium by degassing. This was done by measuring the changes in dissolved inorganic carbon (DIC) content of the culture medium, estimated from pH and alkalinity measurements (e.g., Eaton et al., 1995), over time (Figure 2). Estimates of DIC disappearance from the medium in the dark were assumed to be caused by degassing. By comparing the rates of DIC disappearance from the medium in the light versus dark, we estimated the rate of DIC disappearance caused by photosynthetic carbon uptake.

Figure 2. Calculate DIC concentration in a microalgal culture from pH and alkalinity measurements (left panel). The changes in DIC over time were used to estimate the rate of carbon disappearance from the medium (right panel).



The microalgal strains used for these experiments were selected from the Mera Pharmaceuticals Culture Collection (Olaizola, 2003b). The cultures were initially grown in computer controlled 3.3 liter chemostats (Figure 3) for pH and gas composition experiments at laboratory scale. For the first set of experiments, the chemostats were maintained at 3 different pH levels (6.5, 7.5 and 8.5, see Olaizola, 2003b for details) by injections of 100% CO<sub>2</sub> in response to increases in pH. The chemostats were kept at 25°C and on a 14:10 L:D cycle (fluorescent, 120  $\mu\text{E m}^{-2} \text{s}^{-1}$ ). The pH of the culture was constantly monitored and adjusted by a custom monitoring and control system designed and built in-house. For a second set of experiments, the pH of the chemostats was kept at 7.5 by injecting different mixtures of gases designed to mimic the flue gas composition that would be produced by combusting different fuels in different types of combustors (Table 1).

Experiments were also carried out under outdoor conditions in large tubular photobioreactors (Olaizola 2000, Figure 4). In these experiments, the photobioreactors (PBR) were maintained at 7.5 pH. This was accomplished by on-demand injections of 100% CO<sub>2</sub> or injections of flue gases produced by an actual coal combustor (Figure 5) in the case of 2,000 liter PBR or by a propane combustor (a commercial water heater) in the case of 25,000 liter PBR. For the large scale experiments, we used *Haematococcus pluvialis*, a green microalga (Chlorophyta) known to produce astaxanthin, a high value carotenoid pigment.

Figure 3. 3.3 liter chemostat used for laboratory scale experiments.

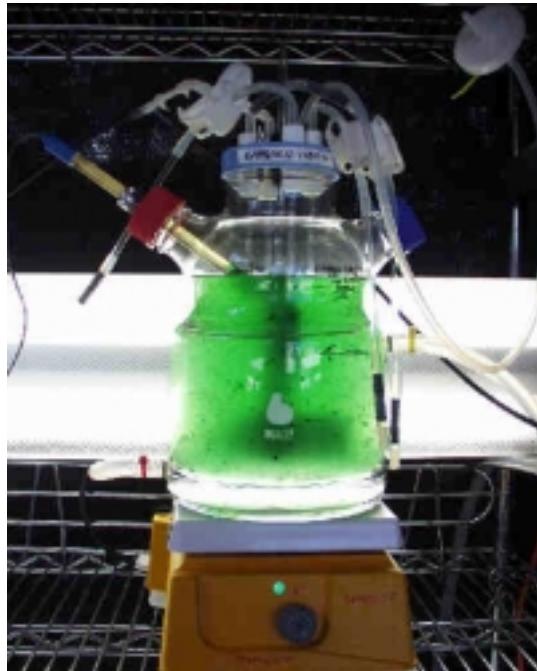


Table 1. Composition of gas mixtures used in the simulated flue gas experiments according to the combusted material. A sixth treatment was 100% CO<sub>2</sub>.

Fuel Type	A. Bituminous Coal	B. Sub-bituminous Coal	C. Natural Gas	D. Natural Gas	E. Fuel Oil
Gas (wt)	Utility boilers			Gas Turb Comb	Diesel
CO <sub>2</sub> (%)	18.1	24.0	13.1	5.7	6.2
O <sub>2</sub> (%)	6.6	7.0	7.6	15.9	17.0
N <sub>2</sub> (%)	71.9	68.1	79.3	78.4	76.7
SO <sub>2</sub> (ppm)	3504.0	929.7	0.0	0.0	113.1
NO (ppm)	328.5	174.3	95.1	22.1	169.7
NO <sub>2</sub> (ppm)	125.9	66.8	36.5	8.5	65.0

Figure 4. The 25,000 liter MGM photobioreactor.



Figure 5. The custom built coal reactor used to provide actual flue gases to the cultures in the photobioreactors.



For these experiments we used a gas analyzer consisting of a IMR400 gas dryer and a IMR5000 analyzer to measure the concentration of  $\text{NO}_x$ ,  $\text{SO}_x$  and  $\text{CO}_2$  in the gas stream from the coal and propane combustors before and after the gas was introduced into the photobioreactor. From these values, we have estimated the relative capture efficiency of the microalgal culture for these gases. The gas analyzer was programmed to alternate between analyzing gases from the combustor smoke stack for a period of 20 minutes, switch to a purge period for five minutes, switch to the photobioreactor exhaust for 30 minutes and again to a five minute purge period. Then, the cycle repeated itself.

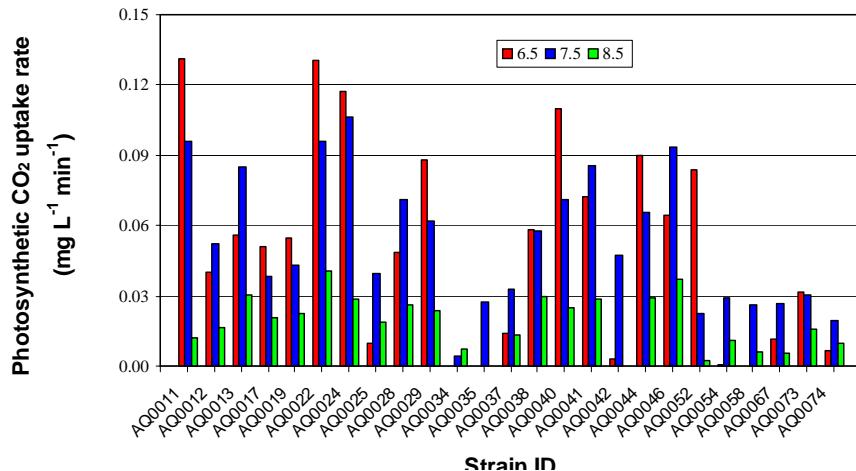
## Results

### *Achieved $\text{CO}_2$ rates at laboratory scale. Effects of pH.*

We used the changes in DIC in the cultures to estimate the relative importance of pathways that affect the concentration of DIC in the culture medium under different pH conditions. First, we considered the rate of DIC loss from the medium measured during the dark periods, for all strains, at three different pH levels. This “dark” rate represents net losses of DIC from the medium (degassing – respiration). The individual dark rate values measured for each strain ranged from less than 0.01 to 0.03, 0.02 to 0.08, and 0.20 to 0.49 at pH 8.5, 7.5 and 6.5 respectively. Thus, at lower culture pH the DIC loss rates from the medium are, on average, much larger than at higher medium pH.

Second, we considered the rates of DIC loss during the light periods. These values represent the net loss of DIC from the medium (degassing + photosynthesis – respiration). We assume that, barring large changes in respiration between dark and light periods, the difference between the “light” and “dark” rates correspond to net photosynthesis. The results are summarized in Figure 6. The highest net photosynthetic rate was  $0.13 \text{ mg CO}_2 \text{ l}^{-1} \text{ min}^{-1}$ .

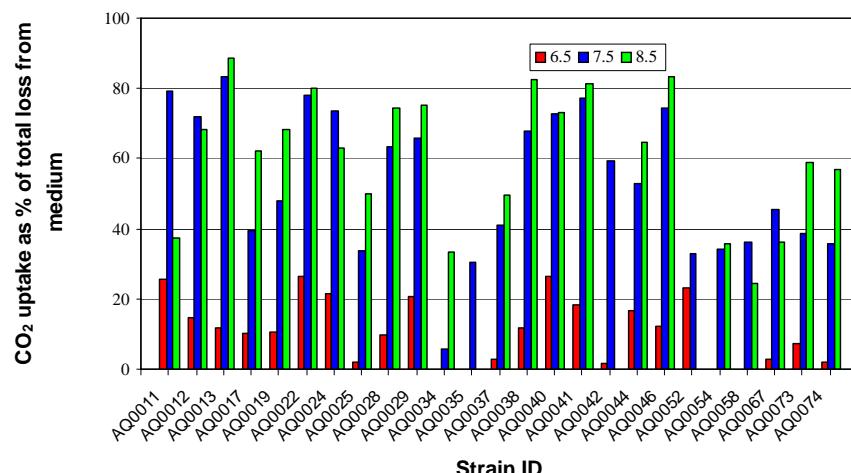
Figure 6. Net photosynthetic rates measured for 25 strains at three pH conditions. The microalgal strains are identified by their collection number (AQ00XX).



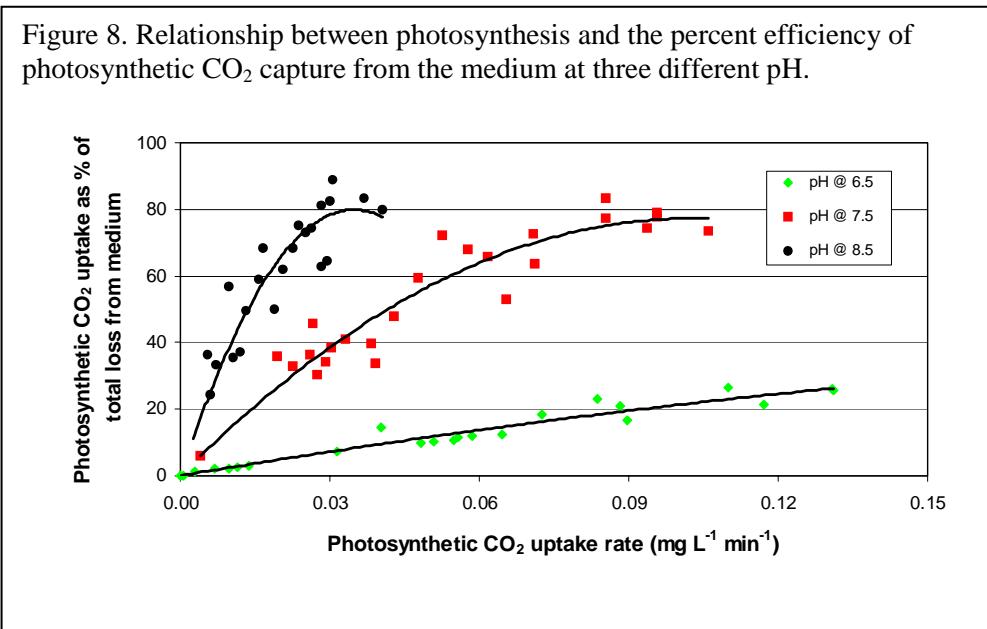
#### Achieved CO<sub>2</sub> capture efficiency at laboratory scale. Effects of pH.

We then calculated the efficiency with which microalgae captured CO<sub>2</sub> from the medium by normalizing the calculated photosynthetic rates (above) to the “light” rates and multiplying the number by 100 (%). That number is the percentage of DIC lost from the medium caused by photosynthesis. The results indicate that, on average, the efficiency of photosynthetic CO<sub>2</sub> capture is higher at higher medium pH values, i.e., the probability for CO<sub>2</sub> to be lost from the medium back to the gas phase is less at high pH (Figure 7), although there is substantial variability from strain to strain.

Figure 7. Percent efficiency of photosynthetic CO<sub>2</sub> capture from the medium at three different pH.



Finally, we consider the relationship between photosynthetic rates and CO<sub>2</sub> capture efficiency. Figure 8 shows three different relationships between calculated photosynthetic rates and the efficiency of photosynthetic CO<sub>2</sub> capture. It is clear that the efficiency of photosynthetic CO<sub>2</sub> capture is, first, dependent on the actual photosynthetic rates accomplished by the cultures (the three different lines in the figure) but, two, also dependent on the pH of the culture (i.e., the difference between the three lines).

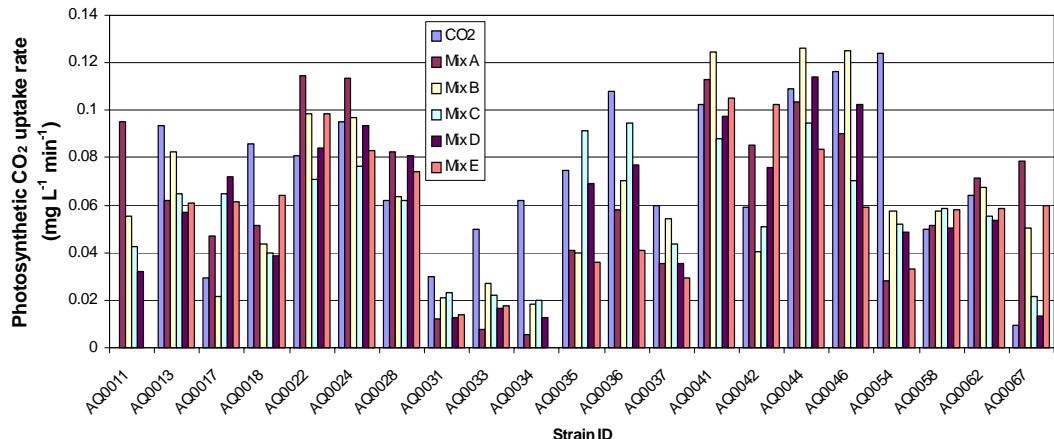


#### *Achieved CO<sub>2</sub> rates at laboratory scale. Effects of gas composition.*

We used the same approach as described for the pH experiments (above) to analyze the data from the flue gas experiments. If we consider the rate of DIC loss from the medium measured during the dark periods for all strains grown with 100% CO<sub>2</sub> and the five experimental gas mixtures we find virtually no differences. The values ranged between 0.033-0.131, 0.035-0.097, 0.029-0.127, 0.037-0.123, 0.035-0.114, and 0.033-0.098 mg CO<sub>2</sub> l<sup>-1</sup> min<sup>-1</sup> for 100% CO<sub>2</sub> and gas mixes A, B, C, D, and E respectively (Table 1).

The rates of DIC loss during the light periods represent the net loss of DIC from the medium (degassing + photosynthesis – respiration). We again assume that, barring large changes in respiration between dark and light periods, the difference between the “light” and “dark” rates correspond to net photosynthesis. The photosynthetic values thus obtained are summarized in Figure 9 and they indicate large differences among strains.

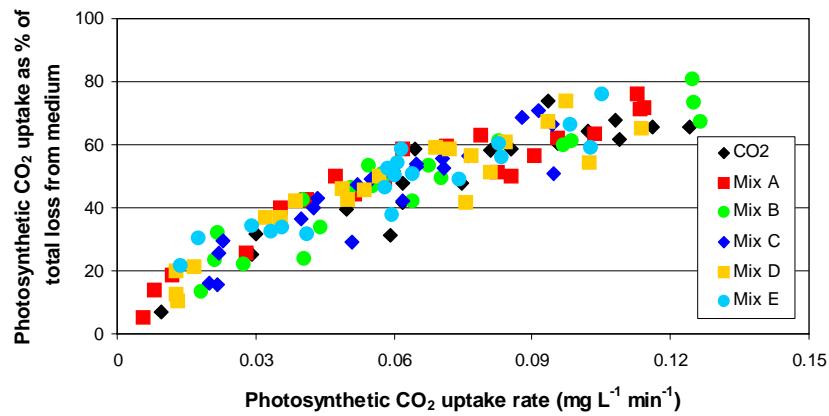
Figure 9. Net photosynthetic rates for 21 microalgal strains exposed to 100% CO<sub>2</sub> or one of the five gas mixtures (Table 1).



#### *Achieved CO<sub>2</sub> capture efficiency at laboratory scale. Effects of gas composition.*

Finally, we also consider the relationship between photosynthetic rates and CO<sub>2</sub> capture efficiency for the cultures grown under 100% CO<sub>2</sub> and the five gas mixtures. For this set of experiments, the relationships between photosynthetic rate and CO<sub>2</sub> capture efficiency are indistinguishable for the 5 gas mixtures and the 100% CO<sub>2</sub> treatment (Figure 10).

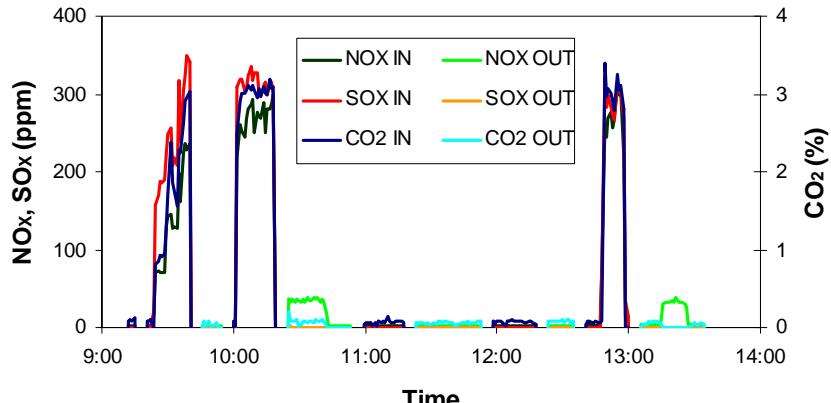
Figure 10. Relationship between photosynthesis and the percent efficiency of photosynthetic CO<sub>2</sub> capture from the medium for cultures exposed to 100% CO<sub>2</sub> or one of the five gas mixtures (Table 1).



### Achieved CO<sub>2</sub> capture rates at pilot and industrial scale.

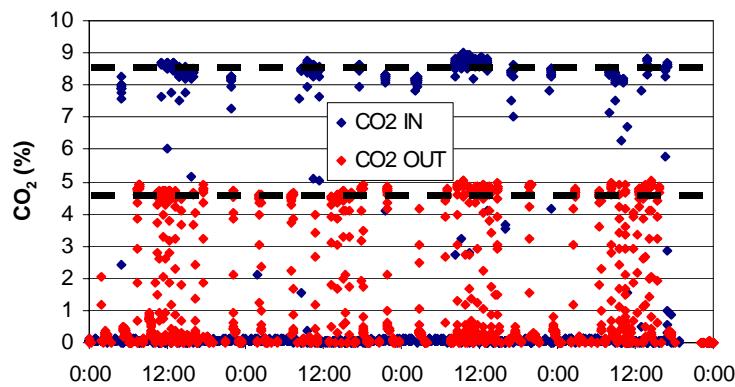
Typical composition of coal combustion flue gases, before and after entering the pilot scale PBR (2,000 liter) microalgal photobioreactor, are shown in Figure 11. On average, our mass calculations indicate that the microalgal culture was able to capture nearly 70% of the available CO<sub>2</sub> when the culture was maintained at pH 7.5.

Figure 11. Gas analysis of coal combustion gases before (IN) and after (OUT) passage through the pilot scale photobioreactor.



Typical CO<sub>2</sub> composition of propane combustion flue gases, before and after entering the full scale PBR (25,000 liter) microalgal photobioreactor, are shown in Figure 12. On average, our mass calculations indicate that the microalgal culture was able to capture about 45% of the available CO<sub>2</sub> when the culture was maintained at pH 7.5.

Figure 12. Concentration of CO<sub>2</sub> in the gas stream supplied from the propane combustor into the photobioreactor (IN) and in the gas stream leaving the photobioreactor (OUT) for a 4-day period.



## **Summary**

In this report we show that

- Microalgae are able to capture anthropogenic CO<sub>2</sub> from a wide variety of simulated flue gases and from actual coal and propane combustion gases,
- Microalgae are able to capture anthropogenic CO<sub>2</sub> under a wide variety of pH and gas concentrations
- The efficiency of CO<sub>2</sub> capture by microalgae is directly dependent on the pH of the culture but is not affected by differences in gas composition,
- The process is scalable to industrially significant scales.

## **Future Work**

We are now continuing our work on carbon capture and sequestration by microalgae using actual flue gases from the coal and propane combustors. Among other things, we will test whether significant changes in capture efficiency are realized when the culture conditions (such as pH) change at industrial scale. Such results will have a significant impact, for example, on the design of a microalgal facility designed to remove CO<sub>2</sub> from the flue gases produced by an actual stationary combustion system such as a power plant.

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