

**Recovery and Sequestration of CO₂ 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 CO₂ 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 January to 31 March 2004 in which PSI, Aquasearch and University of Hawaii conducted their tasks. Based on the work during the previous reporting period, Aquasearch run first pilot scale production run with coal combustion gas to microalgae. Aquasearch started the second full scale carbon sequestration tests with propane combustion gases. Aquasearch also conducted modeling work to study the change in alkalinity in the medium resulting from microalgal photosynthesis and growth. University of Hawaii continued effort on system optimization of the CO₂ sequestration system.

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1. Introduction

Emissions of carbon dioxide are predicted to increase in this century¹ leading to increased concentrations of carbon dioxide in the atmosphere. While there is still much debate on the effects of increased CO₂ 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 CO₂ emissions. Meeting this demand without huge increases in CO₂ 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 CO₂ emissions from fossil fuel usage.

The costs of removing CO₂ 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 CO₂.² 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 CO₂ 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 CO₂ 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 CO₂ 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.¹ 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 CO₂ uptake
2. Mineralization of CO₂, resulting in permanently sequestered carbon
3. Revenues from substances of high economic value
4. Use of concentrated, anthropogenic CO₂ 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 CO₂ 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, CO₂ from the fossil fuel combustion system and nutrients are added to a photobioreactor where microalgae photosynthetically convert the CO₂ into compounds for high commercial values or mineralized carbon for sequestration. The advantages of the proposed process include the following:

1. High purity CO₂ gas is not required for algae culture. It is possible that flue gas containing 2~5% CO₂ can be fed directly to the photobioreactor. This will simplify CO₂ separation from flue gas significantly.
2. Some combustion products such as NO_x or SO_x 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.

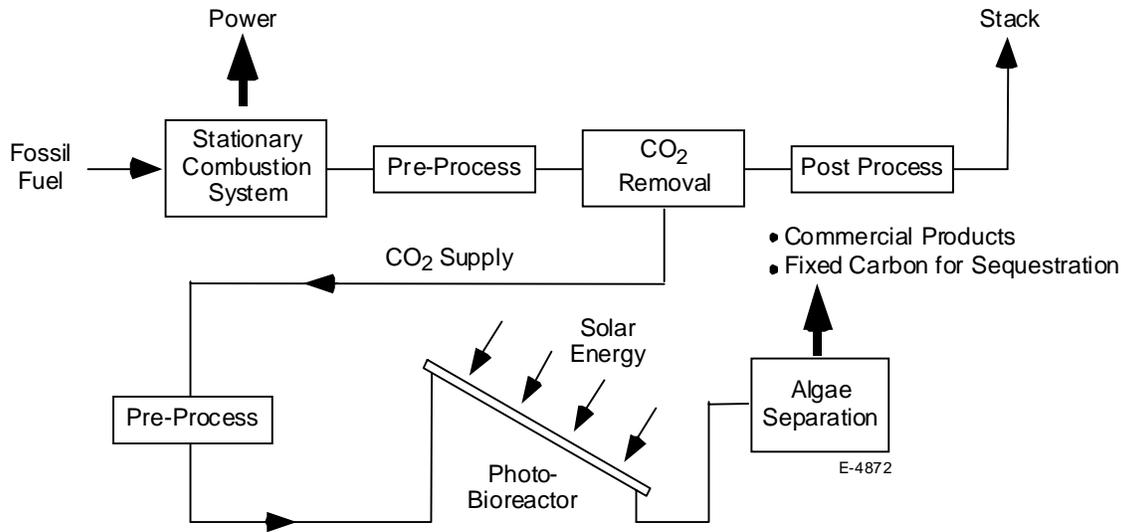


Figure 1. Recovery and sequestration of CO₂ from stationary combustion systems by photosynthesis of microalgae.

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 CO₂ into aquatic media; and (3) converting CO₂ 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 CO₂ 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 CO₂ 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;
- Prepared the coal reactor and conducted the first pilot scale production run with coal combustion gases;
- Completed the first full scale production run and started the second full scale run at the 25,000 liter photobioreactor using propane combustion gas;
- 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: CO₂ removal process; CO₂ injection device; photobioreactor; product algae separation process; and process control devices;
- Developed a photobioreactor design concept for biofixation of CO₂ 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 CO₂ were developed using multiple regression;
- A review of the technical literature on tubular photobioreactors progressed;
- A literature study progressed to develop the CO₂ 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 ₂ 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 ₂ 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	25%	Demonstrate viability of CO ₂ with algae at industrial scale
Subtask 3.1	Pilot Evaluation	30%	Evaluation at 2000 L pilot scale. Experimental work with coal reactor started
Subtask 3.2	Full Scale Production Runs	30%	Evaluation at 24,000 L industrial scale with propane combustion gas.
Subtask 3.3	Algae Separation and Final Product	40%	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 ₂ 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 ₂ fixation
Subtask 5.3	Product Processing	5%	Economic analysis of product processing

The work discussed in this report covers the reporting period from 1 January 2004 to 31 March 2004.

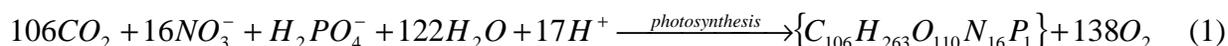
3. Experimental

3.1 Task 2.2: Achievable Photosynthetic Rates, High Value Product Potential and Sequestration of Carbon into Carbonates

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 CO₂ uptake, the proportion of CO₃⁻ in the medium increases. The increased availability of CO₃⁻ in the medium increases the probability that it would react with Ca²⁺ ions to form CaCO₃, which represents a stable form of carbon useful for long-term sequestration of CO₂. Furthermore, the concentration of CO₃⁻ 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 CO₂ 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 NO₃⁻ and H₂PO₄⁻ do (Eq. (1)). The stoichiometry of photosynthesis-based cellular growth indicates that for every 106 moles of CO₂ taken up 16 moles of NO₃⁻ and 1 mole H₂PO₄⁻ are taken up. At the same time, 17 moles of H⁺ 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#13 to include data obtained from outdoor photobioreactor cultures (pilot and full scale) growing two more microalgal strains (AQ0011 and AQ0059). The cultures were grown as per our standard operating procedures. The culture's pH was controlled (7.4-7.6) by direct injections of CO₂ 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 Task 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. A custom built coal combustor shown in Figure 2 was 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 technical problems (see Results and Discussion section) no growth experiments with coal combustion gases were carried out this quarter.



G-6903

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

3.3 Task 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 CO₂ 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 CO₂. 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 five to six 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 AQ0011 and AQ0059. Cultures were grown in our commercial scale MGM PBRs (12,000 and 25,000 liters) at 7.5 pH. The cultures were initially grown using pure CO₂ and, after a few days, propane combustion gases were used. Gas additions, whether pure CO₂ 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 CO₂ in the medium.

Data were 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 CO₂, HCO₃⁻ and CO₃⁼ 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.

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 CO₂ 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 CO₂ 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.

Carbon Sequestration into Mineral Carbonates

In our previous quarterly report (QR#13) we showed that as the microalgal cultures grow and take up NO₃⁻ and H₂PO₄⁻ 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). We have made alkalinity and DIC measurements on four more cultures, both at pilot and full scales using two microalgal strain previously untested (AQ0011 and AQ0059). The results are summarized in Figure 3. In all cases, DIC concentration in the medium increased as the cultures grew, even following dilution of the medium. This reflects the fact that photosynthesis does not only capture CO₂ into biomass but into the medium as well. This is illustrated in Figure 4 where we compare the changes in DIC with changes in biomass concentration following photosynthetic growth.

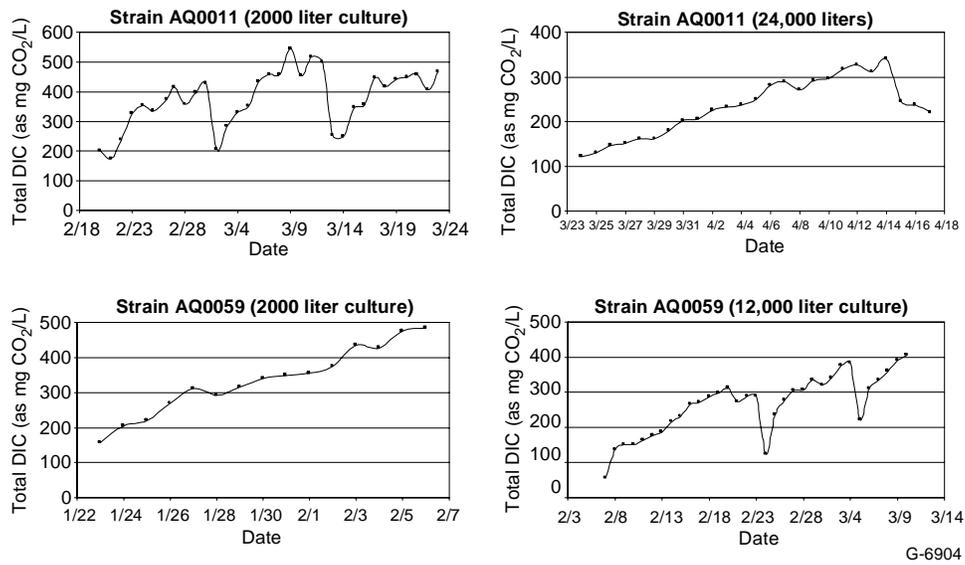


Figure 3. Total dissolved inorganic carbon measured in the medium of four different cultures. Top panels are from cultures of strain AQ0011 grown in either a pilot scale 2,000 liter or a full scale 24,000 liter photobioreactor. Bottom panels are from cultures of strain AQ0059 grown in either a pilot scale 2,000 liter or a full scale 12,000 liter photobioreactor.

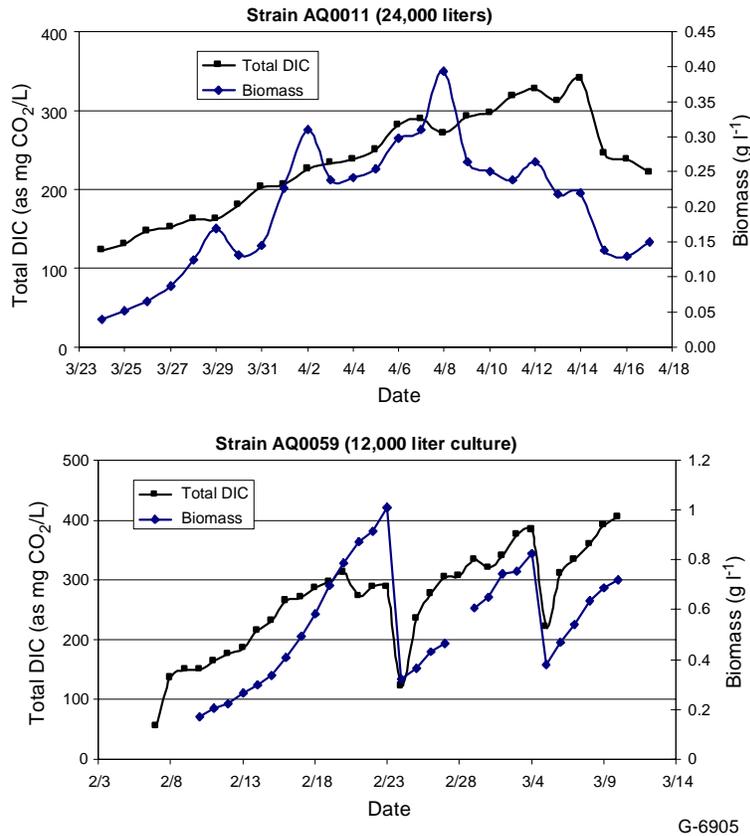


Figure 4. Data on DIC and biomass in large scale cultures of strains AQ0011 and AQ0059.

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.

4.3 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 CO₂ 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.

4.3.1 Task 3.1: Pilot Evaluation of Coal Combustion Gases

As indicated in the 13th 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.

Because of the problems described in earlier reports with the exit of ash and slag from the combustion chamber, a new exit system was designed and built for the coal reactor. A new ceramic restrictor (bottom of combustion chamber) was manufactured, as shown in Figure 5. This system included a new 1inch stainless steel tube, which replaced the original “cross” exit piece, from the reactor exit into the ash collector and an enlarged exit hole in the ceramic constrictor at the furnace exit (Figure 6). The assumption made was that by enlarging the exit diameter and the “cross”, we might stop the exit from becoming blocked with the hard ash build up that has continued to block the flow of flue gas when the reactor is burned (see previous quarterly report). The newly fabricated parts for the furnace exit were not completed until March 9th.

The new furnace exit system was installed in the reactor starting March 18th. When assembled, the reactor was fired for a test run on March 23rd. The coal reactor had all indications of burning, however one of the vacuum pumps in gas analyzer failed. A new vacuum pump was ordered and installed. A new test firing of the reactor was done on March 29th. The reactor was burned for one hour without incident and shut down. A second test firing was started on March 30th. The reactor burned continuously for one hour without problems. However, after one hour of burning, pressure developed between the combustion air inlet and the furnace exit, which indicated there was a solid blockage in the furnace exit.



Figure 5. Photograph of the mold used to cast a new ceramic exit restrictor for the coal combustor (top) and two vies of the new ceramic restrictor after a brief coal burn (middle and bottom).



G-6907

Figure 6. New ceramic restrictor (top), new straight run pipe (middle) and ash can (bottom). The straight pipe run has allowed us to widen the restriction presented by the original “cross” piece at the bottom of the combustion chamber.

Upon disassembly and subsequent inspection of the reactor, it was noted that the ceramic exit piece was completely blocked with slag or hard/solid ash (Figure 7). Up to this point it appears that we have solved all the coal feeding problems however now we must overcome the problem of blockage at the reactor exit. After assessing the situation and discussing a course of action with Joe Morency (PSI engineer), we designed a new furnace exit that includes removing the ceramic constrictor, enlarging the reactor exit to the same size as the alumina retort and enlarging the ash can in order to accept the enlarged exit pipe.



Figure 7. New ceramic restrictor following two hours of coal burning. Note that a very hard slag-like material has completely blocked the exit from the combustion chamber.

The above-mentioned parts are being fabricated and the changes are being made. When these new parts are fabricated, the reactor will be tested again at the earliest opportunity.

4.3.2 Task 3.2: Full Scale Production Runs

During this quarter we have cultured two more microalgal strains (AQ0011 and AQ0059) at 7.5 pH in full scale PBRs being fed pure CO₂ and propane combustion gases. The biomass concentrations achieved in those cultures were shown in Figure 4, Section 4.2. The calculated rates of CO₂ disappearance from the medium are shown in Figure 8. Note that malfunctions in our data collection system (pH) limited the amount of data for available analysis.

We have averaged the CO₂ disappearance rate over each day and night period (Figure 9). The data indicate that as the cultures grew older (more biomass in the culture and higher alkalinity, compare with Figure 4, Section 4.2), the calculated rates of DIC disappearance increased. This is a direct result of increased dissolved CO₂ concentration in the medium and the resulting rate of CO₂ degassing (see below).

We have further averaged the day and night values for each pH condition for each culture for the periods when they were fed either pure CO₂ or propane combustion gases and calculated the difference (ascribed to photosynthesis). The results are shown in Table 2 including the estimated photosynthetic values for the CO₂- and propane-fed periods.

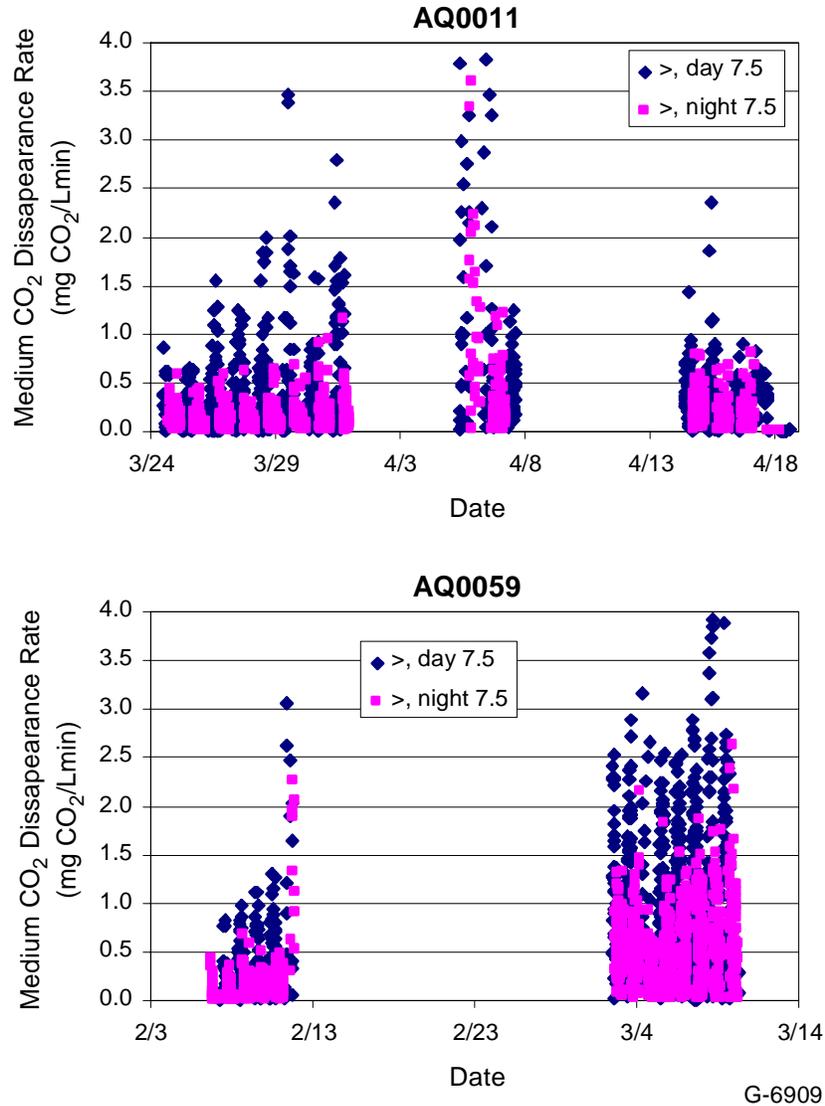


Figure 8. Rates of dissolved inorganic carbon (DIC) disappearance from the medium (photosynthesis and/or degassing) for AQ0011 and AQ0059 cultures. The different symbols indicate the different conditions under which these data were obtained (night vs. day). Gaps in the data were caused by malfunctions in our computer controlled data collection system.

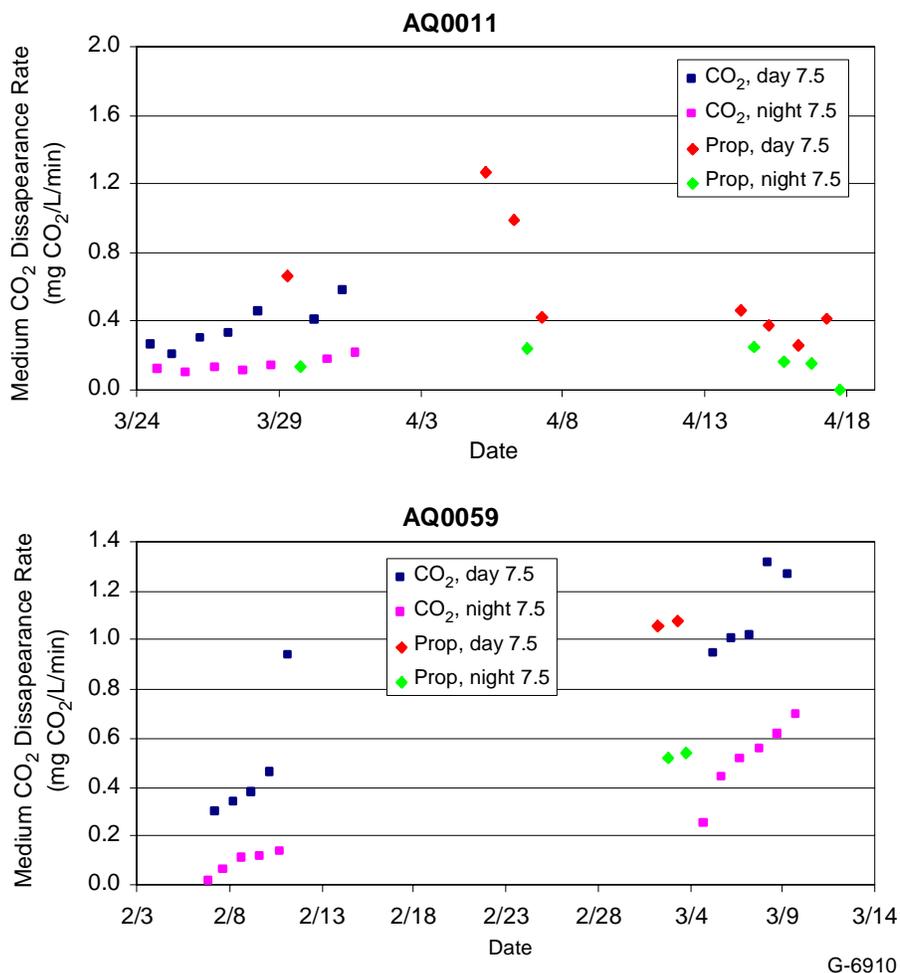


Figure 9. Calculated daily averages of DIC disappearance from the medium (photosynthesis and/or degassing) for AQ0011 and AQ0059 cultures. The different symbols indicate the different conditions under which these data were obtained (night vs. day, CO₂ vs. propane fed).

Table 2. Average rates of DIC disappearance from the medium (mg CO₂/L/min) for cultures of strains AQ0011 and AQ0059 for the periods when the cultures were fed pure CO₂ or propane combustion gases. The difference is assumed to be the photosynthetic rate.

pH	CO ₂			Propane			
	Strain	Day	Night	Difference	Day	Night	Difference
	AQ0011	0.36	0.12	0.24	0.63	0.19	0.44
	AQ0059	0.79	0.32	0.48	1.01	0.53	0.54

Finally, we have considered the effect of CO₂ concentration in the culture medium on CO₂ degassing rate during the night periods (i.e., in the absence of photosynthesis). The results are shown in Figure 10 and corroborate the dependency of degassing of CO₂ from the medium on the concentration of CO₂ in the medium as was reported in previous experiments (QR#12 and QR#13). In all cases, and as was the case for the pilot scale experiment (previous reports), more CO₂ is lost from the medium at higher CO₂ concentrations in the medium.

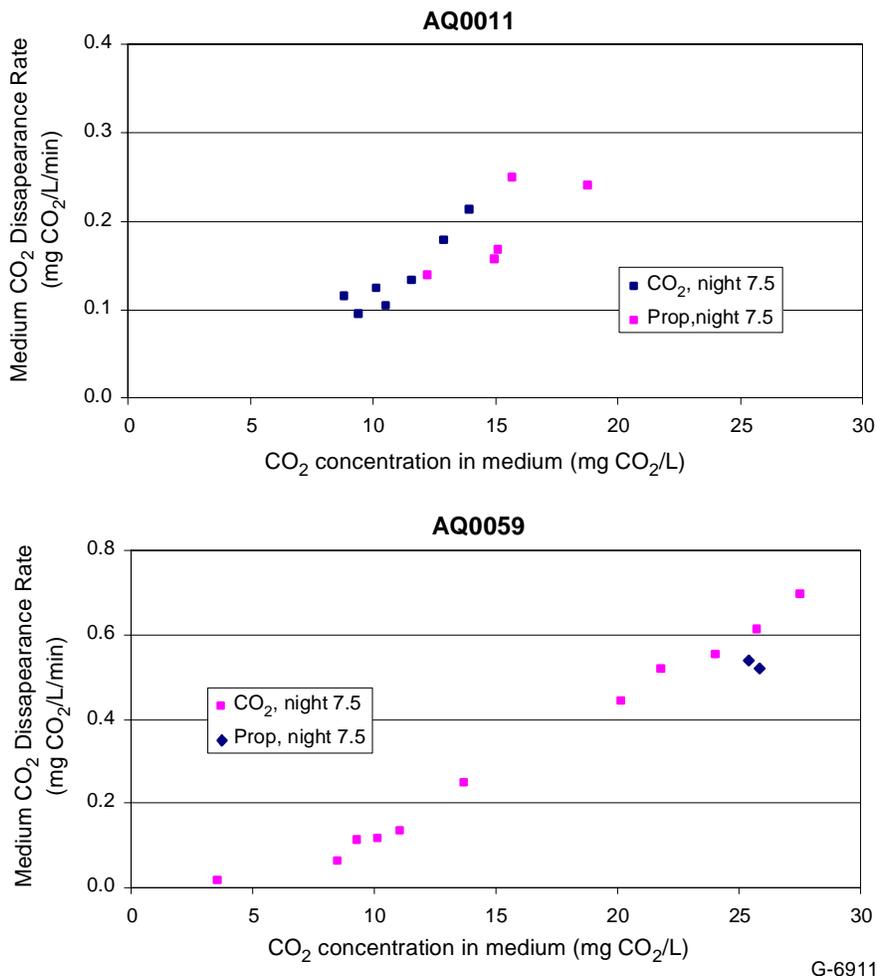


Figure 10. Relationship between CO₂ concentration in the culture medium and night-time rate of dissolved inorganic carbon (DIC) disappearance from the medium (degassing) for AQ0011 and AQ0059 cultures.

4.4 Task 4.1: Component Design and Development

The purpose of this subtask is to develop design concepts for each of the key components of the industrial scale photosynthetic sequestration of CO₂. Key components to be designed include: CO₂ removal process; CO₂ injection device; photobioreactor; product algae separation process; and process control devices. As the proposed system depends on the solar energy to photosynthetically convert CO₂ to products compounds, optimization of the photobioreactor is an

important part of this task. In the reporting period, PSI evaluated the concept to (i) assess feasibility of the concept for large scale photobioreactor, (ii) quantify cost benefit, and (iii) address technical issues for commercial applications. Results of the evaluation will be given in the next quarterly report.

4.5 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 CO₂ flue gas separation system. In order to obtain data on the performance characteristics of the Aquasearch photobioreactor, the graduate research assistant (GRA), Mr. Simon Tsang, visited Mera Pharmaceuticals' facilities in Kona to collect data on microalgal cells growing in a photobioreactor fed with combustion gases from a pulverized coal furnace. Cells were collected over 6 days and these samples were analyzed to determine cell dry weight, organic carbon content, and other properties relevant to modeling photobioreactor performance.

4.5.1 Total Inorganic Carbon Analysis

Work continued to determine total inorganic carbon in the photobioreactor from data collected by Mera Pharmaceuticals, Inc. Samples were analyzed to investigate the influence of the carbon source on the growth of *Haematococcus pluvialis*. Experiments were performed at the Mera Pharmaceuticals, Inc. facility in which either flue gases from a propane combustor or pure CO₂ gas was sparged into two different photobioreactors identified, respectively, as M13A-031107 and M14A-031025. Samples of the *Haematococcus pluvialis* cultures were collected during these experiments between 11/08/04 and 11/25/04 and subsequently analyzed by the Agricultural Diagnostic Service Center of the University of Hawaii for % total organic carbon on a dry mass basis (% TOC). % TOC was determined for several replicates of many of the samples and the associated average values and standard deviations (indicated by the vertical bars) are plotted in Figures 11 and 12.

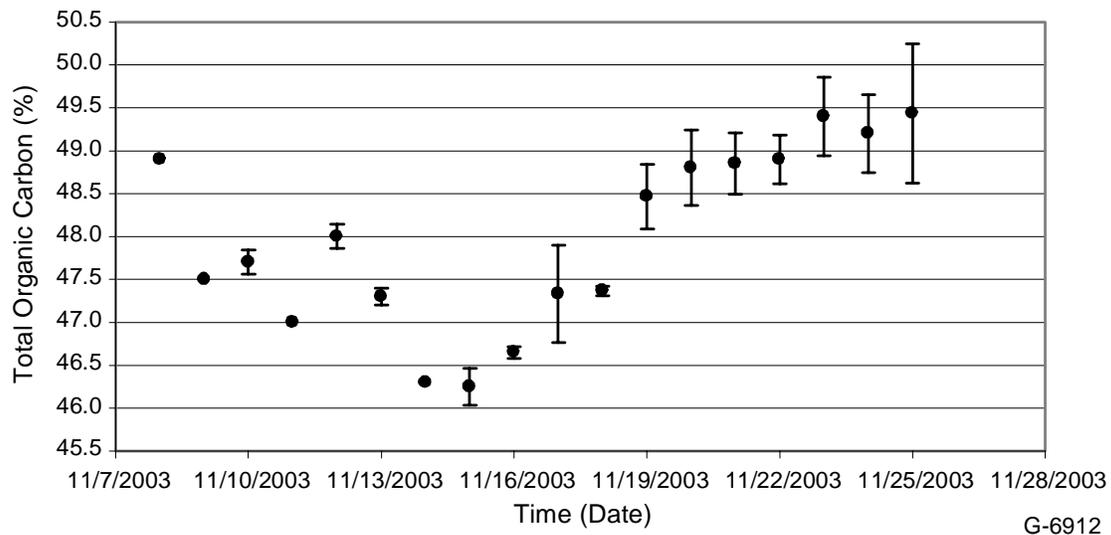


Figure 11. % Total Organic Carbon for M13A-031107 (propane flue gas injection).

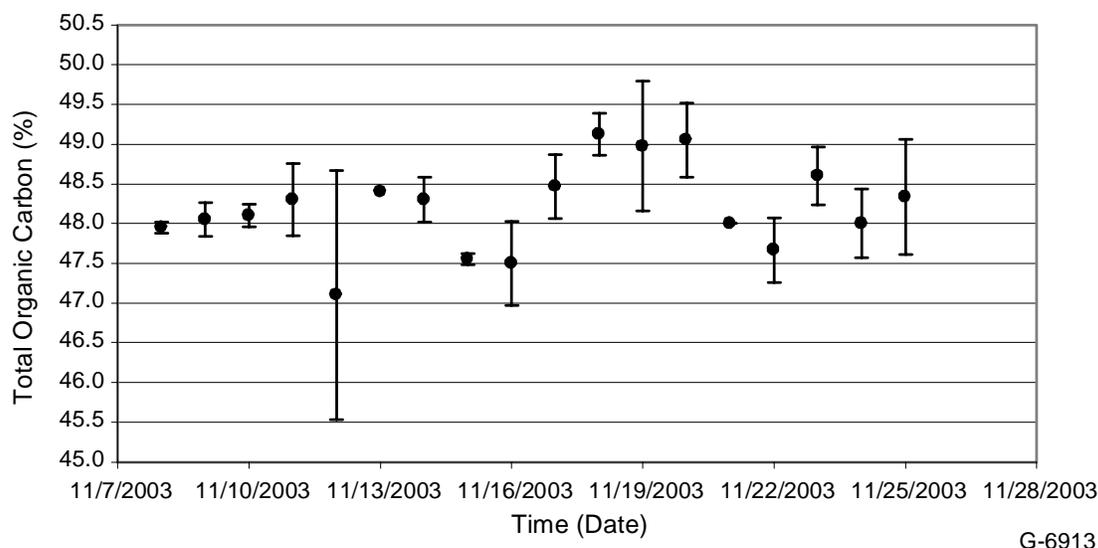


Figure 12. %Total Organic Carbon for M14A-031025 (pure CO₂ gas injection).

In these experiments, the amount of flue gas or CO₂ that was sparged into the liquid media controlled to maintain the same target solution pH. For the case where propane flue gases served as the carbon source for microalgae growth, Figure 11 indicates that %TOC of the collection of cells on a dry mass basis varied between 46.3% to 49.4% over the 17 day test period. Over this same period, the data in Figure 12 indicates that cells collected from the photobioreactor fed with pure CO₂ gas had %TOC between 47.1% to 48.2%.

To aid in the interpretation of these results, the %TOC data were converted to average mass of carbon per cell using corresponding information on cell counts. A comparison of the average mass of carbon per cell for the two cases is plotted in Figure 13. The mass of carbon per cell for M13A-031107 (flue gas injection) varied over time between 2.41×10^{-10} g and 4.54×10^{-10} g. The mass of carbon per cell for M14A-031025 (pure CO₂ injection) varied between 2.47×10^{-10} g and 6.99×10^{-10} g. Except for the final days of the experiments, the average mass of carbon per cell was similar in the two bioreactors and did not seem to depend on the source of carbon. It is unclear whether the higher carbon content per cell observed at the end of the experiment for the culture in the photobioreactor fed with pure CO₂ represents a real effect or instead reflects the experimental uncertainty associated with the cell count provided for these samples (i.e., errors associated with manual counting of a large collection of cells). This issue is currently under investigation.

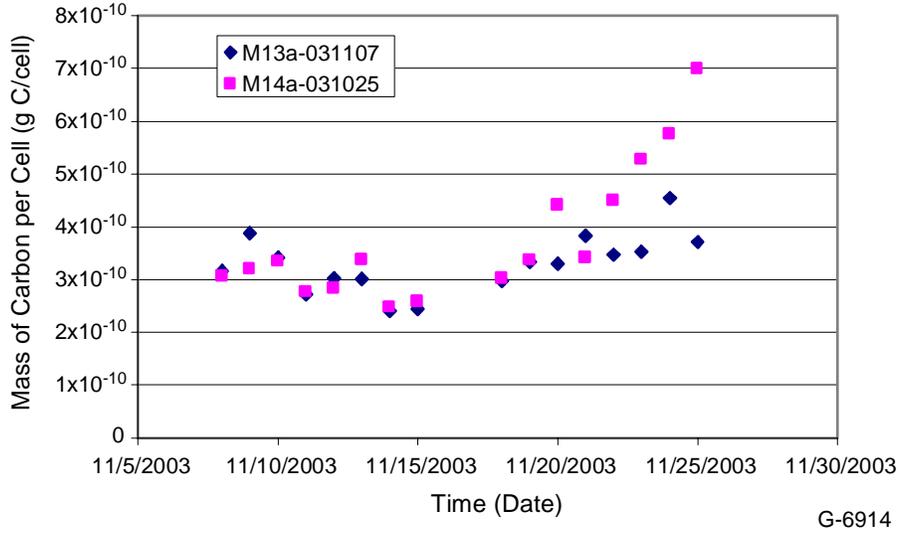


Figure 13. Average mass of carbon per cell for the two test cases.

4.5.2 Photobioreactor Carbon Mass Balance

Dr. Gérard Nihous, an Associate Researcher at HNEI (UH), who has been investigating carbon sequestration since 1989, assisted the GRA in identifying an appropriate relationship for the carbon balance on the photobioreactor. The relationship describes the partitioning of carbon between the biomass, media, and the gas headspace of the photobioreactor. The carbon mass balance will be used to determine the carbon sequestration efficiency of the microalgae. The carbon balance relationship 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_{in} is the mass flow rate of carbon from both CO_2 and air injections into the photobioreactor (g/min), C_{out} is the mass flow rate of carbon out of the photobioreactor via venting (g/min), V_l is the volume of the media (L), M_c 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 should provide sufficient information to apply Eq. (2). Results will be reported in the future.

4.5.3 Analysis of Chlorella

As part of a complementary effort to carbon sequestration using *Haematococcus pluvialis*, Mera Pharmaceuticals, Inc. provided UH with dry samples of a different species, *Chlorella*, grown in their photobioreactors. These samples were collected from photobioreactor M13A-040206 between 02/10/04 and 03/10/04. Table 3 summarizes information on sampling dates, average cell count, liters of culture and media sampled, and dry weights.

Table 3. *Chlorella* Samples

Unit ID	Date	Average Cell Count (cells/mL)	Liters Used	Sample Dry Weight (g)
M13A-040206	2/10/2004	6166666	3.6	0.6223
M13A-040207	2/11/2004	7333333	3.6	0.742
M13A-040208	2/12/2004	11666666	3.6	0.8065
M13A-040209	2/13/2004	10166666	3.6	0.9567
M13A-040210	2/14/2004	12375000	3.6	1.0681
M13A-040211	2/15/2004	12875000	3.6	1.204
M13A-040212	2/16/2004	15750000	3.6	1.474
M13A-040213	2/17/2004	20208333	3.6	1.7698
M13A-040214	2/18/2004	27125000	3.6	2.1025
M13A-040215	2/19/2004	42875000	3.6	2.5133
M13A-040216	2/20/2004	47583332	3.6	2.8322
M13A-040217	2/21/2004	51291665	3.6	3.141
M13A-040218	2/22/2004	53833332	3.6	3.3012
M13A-040219	2/23/2004	57125000	1.2	1.2125
M13A-040220	2/24/2004	11166666	2.4	0.7695
M13A-040221	2/25/2004	18500000	3.6	1.3204
M13A-040222	2/26/2004	19208333	2.4	1.0388
M13A-040223	2/27/2004	19166666	2.4	1.1133
M13A-040224	2/29/2004	23125000	2.4	1.4534
M13A-040225	3/1/2004	24833333	2.4	1.5578
M13A-040226	3/2/2004	31333333	2	1.4917
M13A-040227	3/3/2004	35416665	2	1.5061
M13A-040228	3/4/2004	47583333	2	1.6533
M13A-040229	3/5/2004	25458332	2	0.7551
M13A-040230	3/6/2004	28208302	2	0.9371
M13A-040231	3/7/2004	26416665	2	1.082
M13A-040232	3/8/2004	30291665	1.2	0.7611
M13A-040233	3/9/2004	33708333	1.2	0.8251
M13A-040234	3/10/2004	37125000	1.2	0.8643

The *Chlorella* samples will be sent to the Agricultural Diagnostic Service Center of UH for analyses of total organic carbon content on a dry mass basis. Results of the analyses will be included in the next Quarterly Report.

4.6 Task 5: Economic Analysis

Our aim in the economic analysis is to identify those components of the carbon sequestration process that have the greatest associated costs, given the design based on current data. Subsequent modeling will explore alternative technologies and procedures that might enable significant reduction in both capital and operating costs.

4.6.1 Task 5.1: Gas Separation Process

Much of work pertaining to this subtask has been completed in the previous reporting periods. We will address this issue again after we complete Tasks 3 and 4.

4.6.2 Task 5.2: Photobioreactor Carbon Fixation Process

We have no new results to report here at this time.

4.6.3 Task 5.3: Product Processing

We are continuing the development of an economic model for industrial scale algae facilities, specifically, we are now starting to incorporate costs associated with biomass harvesting (Subtask 3.3) into the model (Figure 20 in Quarterly #9). We will continue to fine-tune our modeling efforts as the results from Task 2 and 3 are incorporated for a larger number of microalgal species and microalgal products. We expect to present updated results of our efforts in the next quarterly report.

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 CO₂ capture does not only results in assimilation of organic carbon but also increases the concentration of inorganic carbon in the medium using two more microalgal strains,
- Carried out modifications on the coal combustor, and
- Extended our observations of carbon capture by microalgae from actual propane combustion gases to two previously untested strains.

Within the next quarter we expect to:

- Further modify several parts for the coal combustor and continue experiments with microalgal strains fed carbon exclusively from coal combustion,
- 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 4: Carbon Sequestration System Design

- Samples were analyzed to investigate the influence of the carbon source on the growth of *Haematococcus pluvialis*. Experiments were performed at the Mera Pharmaceuticals, Inc. facility in which either flue gases from a propane combustor or pure CO₂ gas was sparged into two different photobioreactors.
- Samples of the *Haematococcus pluvialis* cultures were collected during these experiments and subsequently analyzed by the Agricultural Diagnostic Service Center of the University of Hawaii for % total organic carbon on a dry mass basis (%TOC). Cell count data were used to convert sample %TOC to mass of carbon per cell. The results suggest that the carbon content per cell is not affected significantly when combustor flue gas is substituted for pure CO₂ as the primary carbon source.
- The appropriate relationship for the carbon mass balance on the photobioreactor was identified and will be applied using the operational and %TOC data to estimate the carbon sequestration efficiency of the *Haematococcus pluvialis* cultivation system.
- *Chlorella* samples grown in the same photobioreactors as the *Haematococcus pluvialis* were received from Mera Pharmaceuticals, Inc. and will be analyzed to determine %TOC. These data will complement the information that has been obtained for the *Haematococcus pluvialis* cultivation system.

5.3 Task 5: Economic Analysis

In this quarter we have not advanced in the development of an economic model for industrial scale algae facilities. However, within the next quarter 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,
- Carry out large scale centrifugation 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>]