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 October to 31 December 2003 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 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	20%	Demonstrate viability of CO ₂ with algae at industrial scale
Subtask 3.1	Pilot Evaluation	25%	Evaluation at 2000 L pilot scale. Experimental work with coal reactor started
Subtask 3.2	Full Scale Production Runs	25%	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 October to 31 December 2003.

3. Experimental

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

In our Quarterly Progress Report #4 (January 31, 2002) we presented a detailed discussion of precipitation of CaCO_3 . 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. 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_2 uptake, the proportion of $\text{CO}_3^{=}$ in the medium increases. The increased availability of $\text{CO}_3^{=}$ in the medium increases the probability that it would react with Ca^{2+} ions to form CaCO_3 , which represents a stable form of carbon useful for long-term sequestration of CO_2 . Furthermore, the concentration of $\text{CO}_3^{=}$ can also be increased without a change in pH if the total alkalinity of the medium increases. Here, we report 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_2 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_3^- and H_2PO_4^- do (Eq. (1)). The stoichiometry of photosynthesis-based cellular growth indicates that for every 106 moles of CO_2 taken up 16 moles of NO_3^- and 1 mole H_2PO_4^- 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 have 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 have 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). The culture was grown as per our standard operating procedures. The culture's pH was controlled (7.4-7.6) by direct injections of CO_2 into the medium. Every morning, pH and alkalinity determinations were conducted on samples from the photobioreactor (PBR) as described in previous Quarterly Reports. Biomass estimates were carried out on the same samples by cell counts. The amount of CO_2 taken up photosynthetically by the cells was estimated from changes in daily cell concentration and assuming a mean cell mass of 8.39×10^{-10} grams and a mean carbon content in the cellular biomass of 45%. These values were derived for our cultures by Mr. Shu Ki Tsang, a student in Dr. Masutani's laboratory and our partner in this project. The calculated carbon taken up by the cells was used to estimate the amount of N and P

taken up by the cells assuming the stoichiometry implied in Equation 1 (106C:16N:1P). Finally, from the estimated consumption of N and P we estimated the expected change in alkalinity after each day of growth. This value was then compared with the actual alkalinity measured in the morning. For morning values following days in which the culture was diluted with fresh medium, the estimated alkalinity value was assumed to be equal to the actual alkalinity measured.

3.2 Task 3.1: Pilot Evaluation of Coal Combustion Gases

During this quarter we have conducted our first experiment with actual combustion gases from coal. The goal of this set of experiments is to determine the suitability of coal combustion gases for microalgal-based carbon capture and sequestration at pilot scale (up to 2,000 liter photobioreactors). A custom built coal combustor (Figure 2) was utilized to burn bituminous coal from the Upper Freeport Mine. A vacuum pump was used to transfer the gases from the combustor to the PBR. The gases from the combustor were introduced into the PBR at the bottom of the “downcomer” leg so that they would raise against the medium current to enhance gas exchange. A 2,000 liter culture of the commercially significant alga *H. pluvialis* was used for the test.

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

During this experiment we used a gas analyzer consisting of a IMR400 gas dryer and a IMR5000 analyzer to measure the concentration of NO_x , SO_x and CO_2 in the gas stream from the coal combustor 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 all three gases. The 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 5 minutes, switch to the photobioreactor exhaust for 30 minutes and again to a 5 minute purge period. Then, the cycle repeated itself.

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 25,000-L 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 5-6 species of microalgae selected for large-scale experiments. Each species will be run at this scale for 6 to 10 weeks, allowing for optimization.

This quarter we have conducted a second full scale experiment with strain *H. pluvialis*. Cultures were grown in our commercial scale MGM PBRs (25,000 liters). Two cultures were grown in parallel, one was fed pure CO₂ as the microalgal carbon source and pH control (M14), the second one was fed the stack gases from a commercial propane water heater as described in our previous quarterly report (M13). 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.

During this experiment we also used a gas analyzer consisting of a IMR400 gas dryer and a IMR5000 analyzer to measure the concentration of NO_x, and CO₂ in the gas stream from the propane combustor before and after the gas was introduced into the photobioreactor. From these values, we have estimated the relative capture efficiency of the microalgal culture. The 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 5 minutes, switch to the photobioreactor exhaust for 30 minutes and again to a 5 minute purge period. Then, the cycle repeated itself.

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 last reporting period. We have conducted additional task for Task 2.2: Achievable Photosynthetic Rates, High Value Product Potential and Sequestration of Carbon into Carbonates.

Carbon sequestration into mineral carbonates

Our first step consisted in utilizing Eq. (1) to estimate the expected change in alkalinity, dissolved inorganic carbon (DIC) species and nutrient concentrations (NO₃⁻, H₂PO₄⁻) caused by photosynthetic growth equivalent to 1 mM of carbon. The results are summarized in Table 2 and show decreases in nutrient concentrations as well as in total dissolved inorganic carbon, but an increase in pH, CO₃⁼ and alkalinity. If we run the model in 0.1 mM of carbon uptake steps we can represent the results in graphical form showing the changes in dissolved inorganic carbon (DIC) species (Figure 3).

Table 2. Estimated changes in chemical composition of nutrient medium following photosynthetic growth equivalent to 1 mM C assuming the stoichiometry presented in Eq. (1).

	Concentration in fresh medium	Concentration in medium after growth equivalent to 1mM carbon
H ₂ PO ₄ ⁻ (uM)	20.00	10.57
NO ₃ ⁻ (uM)	320.00	169.06
PH	7.50	10.04
Alkalinity (mEq/l)	2.30	2.47
HCO ₃ ⁻ (mM)	2.25	0.26
CO ₃ ⁼ (mM)	0.027	1.104
Free CO ₂ (nM)	0.094	0.000
Total Dissolved Inorganic C (mM)	2.37	1.37

Figure 3. Modeled changes in medium concentration of alkalinity, HCO_3^- , $\text{CO}_3^{=}$, free CO_2 and total DIC as well as pH following photosynthetic growth of microalgae.

In reality, our cultures are run as pH-stats, that is, we control the pH of the cultures with on-demand injections of CO_2 . Thus, we extended that analysis to a long-term model culture assuming pH control of the culture (accomplished with on-demand CO_2 additions to the medium) and assuming reasonable growth rates as obtained from our experimental cultures. In this exercise, it was assumed that the pH of the cultures was controlled between 7.5 and 8.5: CO_2 is injected when the culture reaches a pH value above 8.5 and the injection stops when the culture's pH reaches 7.5.

The results are shown in Figure 4 and indicate that not only the alkalinity increases over time but also the total DIC concentration. Therefore, according to our model calculations, CO_2 injected into the culture and dissolved in the medium will be used in photosynthesis plus it will accumulate as DIC in the medium. This has the effect of enhancing the CO_2 capture and sequestration capacity of the microalgal culture.

Figure 4. Modeled changes in medium concentration of alkalinity, HCO_3^- , $\text{CO}_3^{=}$, free CO_2 and total DIC as well as pH following photosynthetic growth of microalgae but assuming pH control effected by automatic injections of CO_2 . The arrows indicate injection of CO_2 into the model culture after the culture's pH reached >8.5 .

Finally, we tested the hypothesis that a growing microalgal culture utilizing NO_3^- and H_2PO_4^- as its source of nitrogen and phosphorus would accumulate carbon in biomass as well as DIC in the medium on a 25,000 liter culture of *H. pluvialis*. Figure 5 shows the estimates of microalgal biomass in the culture, calculated from the cell concentration values. The changes in alkalinity estimated from the calculated assimilation of CO_2 by the biomass as well as the actual measured values are shown in Figure 6. The data indicates that both sets of values respond similarly to CO_2 assimilation (and the concomitant assimilation of NO_3^- and H_2PO_4^-) by the biomass. Indeed, the two sets of data are highly correlated (Figure 7), validating our modeling approach.

Figure 5. Changes in biomass concentration (estimated from cell concentration measurements) in a growing culture of *H. pluvialis* in a 25,000 liter photobioreactor. The arrows indicate the days on which the culture was diluted with fresh medium.

Figure 6. Measured and estimated alkalinity concentrations in a growing culture of *H. pluvialis*. On the days following culture dilutions (see Figure 4), the estimated alkalinity was made equal to the measured alkalinity.

Figure 7. Comparison between modeled alkalinity, estimated from biomass assimilation of CO₂ over the previous 24 hours and actual measured alkalinity. The data points obtained in am samples following culture dilution were not considered in this analysis since they are artificially made equal.

The stoichiometry of microalgal growth (Eq. (1)) predicts that for each mole of CO₂ captured by the microalgal biomass, $17/106 = 0.16$ moles of alkalinity are produced in the culture's medium. The increase in alkalinity is reflected in increases in DIC; at our standard culture pH this is further reflected in increases in HCO₃⁻. Thus, microalgal photosynthesis does not only capture CO₂ into biomass but into the medium as well. 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).

4.3.1 Task 3.1: Pilot Evaluation of Coal Combustion Gases

As indicated in the 12th Quarterly Report, a number of technical problems associated with the coal combustor have significantly delayed progress in this part of the research program. In this quarter, new parts were ordered to refit the coal combustor. A new retort and castable refractory material were ordered for the combustor in early November 2003 (Figure 8). We received the parts and commenced casting the ceramic furnace restrictor on November 24. The newly fabricated parts were installed in the combustor starting December 12, 2004. When

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Figure 8. Photographs showing damage to the coal combustor's retort (top), damage to the ceramic furnace restrictor at the bottom of the combustion chamber (middle) and mold manufactured to cast a new ceramic furnace restrictor for the bottom of the combustion chamber (bottom).

assembled, the coal combustor was fired for test runs on 12/12/03 and 12/15/03. Results from these test runs were positive. The reactor was run with and without oxygen added into the combustion air and both tests were reasonably successful. However, by increasing the percentage of oxygen in the combustion air by ~30%, we were able to achieve concentrations of SO_x , NO_x and CO_2 greater than in all previous firings of the reactor.

On December 17, 2003 we ran an experiment with the coal combustor to determine whether the combustor would produce enough CO_2 in the flue gas to control pH in a pilot scale

PBR (2,000 liter). The combustion air feeding was modified for this test in that the coal feed air was stopped and all intake air and make-up oxygen was fed only through the combustion air feeding tube. Shortly after starting the coal feeding into the combustor (4 minutes), we lost the fuel supply to the combustor. It was determined that most likely the loss of fuel supply was caused by a blockage in the top of the combustor, which most likely was caused from not having any pressure on top of the coal as it was being fed into the combustor. The combustor was shut down in order to cool down. After cooling down, the top of the combustor was disassembled. We discovered that indeed the coal feeding tube at the top of the diffuser was clogged with coal. The blockage was cleared and the combustor re-assembled.

On December 18, 2003 we started a second experiment to determine whether the combustor would produce the required CO₂ in the flue gas. The combustor was first fired using no added oxygen in the combustion air stream to determine a baseline of the gas concentrations. This flue gas baseline was established and we stopped the combustor after approximately 10 minutes. The combustor was started up using 100% oxygen as the feed air. We suspected the presence of various small air leaks in the furnace and decided to give the furnace the largest boost possible.

Sets of experiments were run over the time of two complete cycles of the Gas Analyzer (Stack #1 and Stack #2) with results from these experiments being shown below. At the end of the above-mentioned experiments, the coal combustor showed signs of obstructions in the furnace exit. The combustor was shut down and the furnace disassembled for inspection. We discovered that the ceramic restrictor at the exit of the combustor was obstructed with hard ash.

After assessing the situation and discussing a course of action with Joe Morency (PSI engineer), we decided that a new flue gas exit for the combustor must be designed. The new exit design consists of enlarging the diameter of the hole in the ceramic restrictor to 1 in. and replacing the “cross” at the bottom of the combustor with a straight 1-in. stainless steel tube that connects directly into the ash can. A new ceramic restrictor must be cast in order to enlarge the exit diameter and the stainless steel tube and restrictor cup must be custom fabricated.

A new stainless steel exit piece for replacing the “cross” will be designed and we have the material on site to recast the ceramic restrictor. Both of these new parts will be fabricated and the combustor tested at the earliest opportunity.

As noted above, on December 18, 2003, we were able to run the first coal combustion gas injection experiment. The combustion gases were injected into a PBR growing *H. pluvialis*. The gas was injected into the PBR in response to increases in pH caused by photosynthetic CO₂ uptake. Measurements of gas component concentrations were made before injection into the PBR and of the exhaust gas exiting the PBR.

Typical concentrations of gas components produced by the combustion of coal and injected into the PBR were CO₂ = 3.2 %, NO_x = 275 ppm, and SO_x = 325 ppm (Figure 9). The rate of gas flow into the PBR was 70 SCFH. Typical concentrations of gas components exiting into the PBR reactor were CO₂ = 0.1 %, NO_x = 2 ppm and SO_x = 1 ppm. The flow rate of gas out of the PBR was 720 SCFH. Note that the volume of combustion gas into the PBR is

Figure 9. Gas analysis of coal combustion gases before (IN) and after (OUT) passage through the pilot scale photobioreactor.

70 SCFH but the exhaust gas is made up of that volume plus the air volume used in the airlift for a total of 720 SCFH. Thus, we can calculate the actual volumes of each individual gas, in and out of the PBR by multiplying the measured concentration times the flow rate. The results are shown in Table 3 and show that the microalgal culture was able to capture nearly 70% of the available CO_2 and over 90% of the NO_x and SO_x components.

Table 3. Measured Concentrations and Mass Flow Balance of CO_2 , NO_x and SO_x Introduced Into and Exiting the Photobioreactor

	Conc IN	Conc OUT	Flow IN (total=70SCFH)	Flow OUT (total=720SCFH)	%Captured
CO2	3.2 %	0.1 %	2.24 SCFH	0.72 SCFH	68 %
NOx	275 ppm	2 ppm	0.01925 SCFH	0.00144 SCFH	93 %
SOx	325 ppm	1 ppm	0.02275 SCFH	0.00072 SCFH	97 %

During the next quarter we intend to make the necessary modifications to the coal combustor that will eliminate the obstructions caused by ash so that longer run times, and experiments, will be possible.

4.3.2 Task 3.2: Full Scale Production Runs

During this quarter we have carried out a second direct comparison of microalgal performance in full scale PBRs being fed either pure CO_2 or actual combustion gases from a propane combustor utilizing *H. pluvialis*.

Figure 10 shows the pH values measured during the duration of the experiment in both photobioreactors. M13 was fed propane combustion gases while M14 was fed pure CO_2 both on demand. As is shown in the figure, M14 was started with pH set points around 7.5 (7.4-7.6) while M13 was started with set points around 8.5 (8.4-8.6). The set points were switched as the experiment progressed.

Figure 10. pH traces obtained for M14 (fed CO₂) and M13 (fed propane combustion gases).

The cultures in both PBRs accumulated biomass consistently (Figure 11); no deleterious effects were noted in M13, the photobioreactor fed propane combustion gases. Growth rates were calculated from the changes in cell concentration and averaged for the each photobioreactor for the periods when the PBRs were maintained at either 7.5 or 8.5 pH. For M14 (running on CO₂) the average growth rates were 0.26 d⁻¹ and 0.29 d⁻¹ at pH 7.5 and 8.5 respectively. For M13 (running on propane combustion gases) the average growth rates were 0.21 d⁻¹ and 0.29 d⁻¹ at pH 7.5 and 8.5 respectively.

The calculated rates of CO₂ disappearance from the medium are shown in Figure 12. As was the case in the previous experiments (QR#12), it is clearly seen that the rates are larger when the culture pH is maintained at 7.5 than when maintained at 8.5 in both PBRs. These results reflected those obtained in our chemostat scale experiments reported on earlier. We have then averaged the CO₂ disappearance rate over each day and night period, eliminating those during which culture dilutions took place. We have further averaged the day and night values for each pH condition for each PBR. Finally, we subtracted the disappearance rates obtained during the night periods from those obtained for the daylight periods to calculate average photosynthetic rates. The results are shown in Table 4 and indicate that while the photosynthetic rates are higher for cultures maintained at 7.5 pH, the amount of CO₂ that is lost to the atmosphere from the medium is about 10 times higher at 7.5 pH than at 8.5 pH. These results agree well with those obtained, reported previously, in the pilot scale PBRs and in chemostat-scale experiments.

Figure 11. Fluorescence-based estimates of daily biomass for M13 (propane fed) and M14 (CO₂ fed).

Figure 12. Rates of dissolved inorganic carbon (DIC) disappearance from the medium (photosynthesis and/or degassing) for M14 and M13. The different symbols indicate the different conditions under which these data were obtained (night versus day, pH 7.5 versus pH 8.5).

Table 4. Average Rates of DIC Disappearance from the Medium (mg CO₂/L/min) for M14 (fed pure CO₂) and M13 (fed propane combustion gases) at either 7.5 or 8.5 pH and Either During the Day or Night Periods. The difference is assumed to be the photosynthetic rate.

pH	7.5			8.5		
Period	Day	Night	Difference	Day	Night	Difference
M14 (CO ₂)	0.41	0.21	0.19	0.17	N/A	>0.17
M13 (propane)	0.35	0.15	0.20	0.11	N/A	>0.11

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 13 and indicate a dependency of degassing of CO₂ from the medium on the concentration of CO₂ in the medium. The results are shown again in Figure 14 but superimposed on the results obtained from the commercial scale photobioreactors reported on previously (QR#12). In all cases, and as was the case for the pilot scale experiment (QR#12), more CO₂ is lost from the medium at higher CO₂ concentrations.

Figure 13. Relationship between CO₂ concentration in the culture medium and night-time rate of dissolved inorganic carbon (DIC) disappearance from the medium (degassing) for M14 and M13.

Figure 14. Relationship between CO₂ concentration in the culture medium and night-time rate of dissolved inorganic carbon (DIC) disappearance from the medium (degassing) for M14 and M13 super imposed on the data obtained from a previous run of the same experiment, as reported in QR#12.

Gas analysis data

Figure 16 shows the gas concentrations measured for >2 weeks of photobioreactor operation (M13, propane combustion gases). The top panel shows the concentrations of CO₂ (%) measured at the inlet and outlet of the PBR. The bottom panel shows the concentrations of NO_x measured at the inlet and outlet of the photobioreactor. The data indicate that the concentration of CO₂ in the combustor exhaust is about 8% (v:v) but only about 4.5% in the photobioreactor's exhaust when the coal combustor is running. Similarly, the concentration of NO_x is about 85 ppm in the combustor exhaust but only about 72 ppm in the photobioreactor's exhaust. This means that about 44% of the CO₂ and about 15% of the NO_x is scrubbed from the flue gas by passage through the photobioreactor. The results confirm those obtained last quarter (see QR#12) where we estimated that 45% of the CO₂ and 18% of the NO_x were scrubbed during passage of the propane combustion gases through the culture.

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Figure 15. Concentration of CO₂ and NO_x in the gas stream supplied from the propane combustor into the photobioreactor (IN) and in the gas stream leaving the photobioreactor (OUT) for a > 2 week period.

Figure 16. Concentration of CO₂ and NO_x in the gas stream supplied from the propane combustor into the photobioreactor (IN) and in the gas stream leaving the photobioreactor (OUT) for a > 2 week period.

4.4 Task 4: Carbon Sequestration System Design

To evaluate the potential for application of photosynthetic sequestration of CO₂ to industrial-scale combustion systems, we are conducting a system-level design study. The purposes of this study are:

- (1) Identify design concepts for components and the integrated system of the proposed concept.
- (2) Optimize and evaluate performance of the components and the system.

- (3) Develop deployment methodologies.
- (4) Identify key technology issues for further development.

This task consists of two sub-tasks: Task 4.1: Component Design and Development, and Task 4.2: System Integration.

4.4.1 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 continued to focus its effort on preparation of the PSI coal reactor delivered to Aquasearch, and no significant progress was made in Task 4.1. In the following quarters, we will evaluate 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.

4.4.2 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.

Total Inorganic Carbon Analysis

Work continued to determine total inorganic carbon in the photobioreactor from data collected by Mera Pharmaceuticals, Inc. Effort during this reporting period focused on identifying the appropriate constants to use in the relationships for total inorganic carbon concentration. Photosynthetic CO₂ fixation can be used to estimate the quantity of carbon that is metabolized and bound in the cell biomass pool. This information is required to estimate carbon sequestration efficiency.

Photosynthetic CO₂ fixation can be inferred from net total inorganic carbon concentration. Assuming that the inorganic carbon system is in equilibrium, the total inorganic carbon is determined by

$$[TCO_2] = [CA] \frac{1 + K_2^1 / H^+ + H^+ / K_{L1}^1}{1 + 2K_2^1 / H^+} \quad (2)$$

where $[TCO_2]$ is the total inorganic carbon concentration in meq/L, $[CA]$ is the carbonate alkalinity in meq/L, H^+ is the hydrogen ion activity (*i.e.*, 10^{-pH}), K_{L1}^1 is the first apparent dissociation constant for carbonic acid in water, and K_2^1 is the second apparent dissociation constant for carbonic acid in water (Geider and Osborne, 1992).

In order to use Eq. (2), the values of carbonate alkalinity must be estimated. Carbonate alkalinity represents the ability of carbonate solutes (bicarbonate and carbonate) in a filtered water sample (filter membrane with a pore size of $\leq 0.45 \mu m$) to neutralize acid (Radtke *et al.*, 1998). Carbonate alkalinity is defined as

$$[CA] = Alk - [OH^-] + [H^+] \quad (3)$$

where $[CA]$ is the carbonate alkalinity in meq/L, Alk is the alkalinity in meq/L, $[OH^+]$ is the hydroxyl anion normality in meq/L, and $[H^+]$ is the hydrogen cation normality in meq/L (Geider and Osborne, 1992; Reinfelder, 2003). Mera Pharmaceuticals, Inc. has collected data on the alkalinity and pH of the media in the photobioreactor which can be applied to calculate the corresponding values of carbonate alkalinity.

Other quantities that must be known to use Eq. (2) are the first and second apparent dissociation constants. Expressions for the first and second dissociation constants are:

$$K_1' = 10^{-\left[\left(-14.8435 + \frac{3404.71}{T} + T * 0.032786 \right) + \left(-0.0230848 + \frac{-14.3456}{T} \right) * S^{\frac{1}{2}} + \left(0.000691881 + \frac{0.429955}{T} \right) * S \right]} \quad (4)$$

and

$$K_2' = 10^{-\left[\left(-6.4980 + \frac{2902.39}{T} + T * 0.02379 \right) + \left(-0.458898 + \frac{41.24048}{T} \right) * S^{\frac{1}{2}} + \left(0.0284743 + \frac{-2.55895}{T} \right) * S \right]} \quad (5)$$

where S is the salinity of the media and T is the absolute temperature (Regnier *et al.*, 2000).

Since *Haematococcus pluvialis* is a freshwater species, salinity is assumed to be zero. Therefore, Eqs. (4) and (5) can be simplified:

$$K_1' = 10^{-\left(-14.8435 + \frac{3404.71}{T} + T * 0.032786 \right)} \quad (6)$$

and

$$K_2' = 10^{-\left(-6.4980 + \frac{2902.39}{T} + T * 0.02379 \right)} \quad (7)$$

In our application, the first and second apparent dissociation constants for carbonic acid in water depend only on the media temperature. These data have been collected by MeraPharmaceuticals, Inc.

To summarize, total inorganic carbon concentration in the photobioreactor media can be estimated employing Eqs. (2), (3), (6), and (7) and operational data on alkalinity, pH, and temperature.

Photobioreactor Operational Data

Operational data for two photobioreactors identified as M13A-031107 and M14A-031025, that were collected during the recent propane combustion experiments, have been requested from Mera Pharmaceuticals, Inc. Those data sets include media temperature in each photobioreactor (at 1 min intervals), the duration of the seawater flows (to cool the photobioreactors), daily solar irradiance (at 1 min intervals), media pH (at 1 min intervals), duration of the CO₂ injections, and microalgae harvesting and sampling information. Analysis of these data will be included in the next Quarterly Report.

Samples of Haematococcus Pluvialis

During the present reporting period, Mera Pharmaceuticals, Inc. provided dry samples of *Haematococcus pluvialis* to UH. These samples were collected from photobioreactors M13A-031107 and M14A-031025, for which operational data have been requested (see preceding section). Table 5 summarizes information on sample identities, sampling dates, average cell count, liters of culture and media sampled, and dry weights. As noted in the Table, the cell counter experienced technical failure on 11/16/03 and manual counts were recorded from 11/18/03 to 11/25/03.

The *Haematococcus pluvialis* samples have been sent to the Agricultural Diagnostic Service Center of UH Manoa for analyses of total organic carbon content on a dry weight basis. Results from the analyses will be included in the next Quarterly Report.

Table 5. *Haematococcus Pluvialis* Samples

Unit ID	Date	Average Cell Count (cells/mL)	Liters Used	Sample Dry Weight (g)
M13a-031107	11/8/2003	154967	4	0.4004
M14a-031025	11/8/2003	212190	4	0.5408
M13a-031107	11/9/2003	171890	4	0.5606
M14a-031025	11/9/2003	285726	3	0.5697
M13a-031107	11/10/2003	243722	4	0.6983
M14a-031025	11/10/2003	341407	3	0.712
M13a-031107	11/11/2003	375383	3	0.6515
M14a-031025	11/11/2003	500138	3	0.8588
M13a-031107	11/12/2003	440587	3	0.8312
M14a-031025	11/12/2003	573918	3	1.038
M13a-031107	11/13/2003	163063	4	0.4145
M14a-031025	11/13/2003	164305	4	0.458
M13a-031107	11/14/2003	205724	4	0.4276
M14a-031025	11/14/2003	273798	4	0.5607
M13a-031107	11/15/2003	286744	4	0.6061
M14a-031025	11/15/2003	331054	4	0.7194
M13a-031107	11/16/2003	counter experienced technical failure	3	0.6652
M14a-031025	11/16/2003	counter experienced technical failure	3	0.8021
M13a-031107	11/17/2003	counter experienced technical failure	3	0.7768
M14a-031025	11/17/2003	counter experienced technical failure	3	0.9533
M13a-031107	11/18/2003	463333	3	0.8723
M14a-031025	11/18/2003	495000	3.55	1.0793
M13a-031107	11/19/2003	378333	3.55	0.9245
M14a-031025	11/19/2003	441666	3.55	1.0779
M13a-031107	11/20/2003	423333	3.55	1.0144
M14a-031025	11/20/2003	383333	3.55	1.2234
M13a-031107	11/21/2003	243333	3.15	0.6017
M14a-031025	11/21/2003	316666	3.15	0.7092
M13a-031107	11/22/2003	321667	3.15	0.7188
M14a-031025	11/22/2003	285000	3.15	0.846
M13a-031107	11/23/2003	336700	3.55	0.8529
M14a-031025	11/23/2003	238350	3.55	0.9175
M13a-031107	11/24/2003	290000	3.55	0.9496
M14a-031025	11/24/2003	233333	3.55	0.9932
M13a-031107	11/25/2003	376666	3.55	1.0029
M14a-031025	11/25/2003	191666	3.55	0.9845

4.5 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.

4.5.1 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.

4.5.2 Task 5.2: Photobioreactor Carbon Fixation Process

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

4.5.3 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, above) into the model (Figure 17). 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 the second full scale propane combustion experiments. Specifically we have:

- Determined 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,
- Determined that passage of coal combustion flue gas through a pilot scale microalgal photobioreactor removes nearly 70% of the CO₂ and over 90% of the NO_x, and SO_x present in the flue gas,
- Confirmed carbon capture by microalgae from actual propane combustion gases, and

- Confirmed that passage of propane flue gas through a commercial scale microalgal photobioreactor removes about 45% and 18% of the CO₂ and NO_x, respectively, from propane flue gas and that this can be improved following photobioreactor changes.

Within the next quarter we expect to

- Finalize design and manufacture of modified 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.

5.2 Task 4: Carbon Sequestration System Design

- Continued carbon balance analyses and estimation of CO₂ sequestration efficiency for the Aquasearch facility.
- Continued total organic carbon content analysis of *Haematococcus pluvialis* samples. A sampling protocol was developed and submitted to Mera Pharmaceuticals, Inc. along with a request for additional samples.
- Relationships and constants were identified to calculate total inorganic carbon concentration in the photobioreactor media from operational data on alkalinity, pH, and temperature.
- *Haematococcus pluvialis* samples collected during the propane combustion experiments were received from Mera Pharmaceuticals, Inc. and sent to the Agricultural Diagnostic Service Center of UH Manoa for analyses of total organic carbon content on a dry weight basis.

During the next reporting period we plan to conduct the following.

- Evaluate feasibility of large scale photobioreactor with photovoltaic electric power generation.
- Quantify the benefits of the above photobioreactor.

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.

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