Recovery and Sequestration of CO₂ from Stationary Combustion Systems by Photosynthesis of Microalgae

Quarterly Technical Progress Report for the Period Ending 30 September 2002

(Quarterly Report #8)

Reporting Period Start Date: 1 July 2002 Reporting Period End Date: 30 September 2002

Prepared by

Dr. T. Nakamura
Physical Sciences Inc.
20 New England Business Center
Andover, MA 01810-1077

in collaboration with

Dr. Miguel Olaizola Aquasearch Inc. 73-4460 Queen Kaahamanu Highway Suite 110, Kailua-Kona, HI 96740

and

Dr. Stephen M. Masutani Hawaii Natural Energy Institute School of Ocean & Earth Science and Technology University of Hawaii at Manoa 2540 Dole Street, Holmes Hall 246 Honolulu, HI 96822

DOE Contract No. DE-FC26-00NT40934 U.S. DEPARTMENT OF ENERGY National Energy Technology Laboratory P.O. Box 10940 Pittsburgh, PA 15236

December 2002

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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 July to 30 September 2002 in which PSI, Aquasearch and University of Hawaii conducted their tasks. Based on the work conducted during the previous reporting period, PSI initiated work on feasibility demonstration of direct feeding of coal combustion gas to microalgae. Aquasearch continued their effort on selection and characterization of microalgae suitable for CO₂ sequestration. University of Hawaii continued effort on system optimization of the CO₂ sequestration system.

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 CO_2 from a conventional coal-fired power plant with flue gas desulfurization were estimated to be in the range of \$35 to \$264 per ton of CO_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 CO_2 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 $\sim 5\%$, as compared to $\sim 0.2\%$ for typical land based plants. Furthermore, a dedicated photobioreactor for growth of microalgae may be optimized for high efficiency utilization of solar energy, comparable to those of some photovoltaic cells. It is logical, therefore, that photosynthetic reaction of microalgae be considered as a mean for recovery and sequestration of CO_2 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. 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, CO_2 from the fossil fuel combustion system and nutrients are added to a photobioreactor where microalgae photosynthetically convert the CO_2 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 micoralgae. 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.

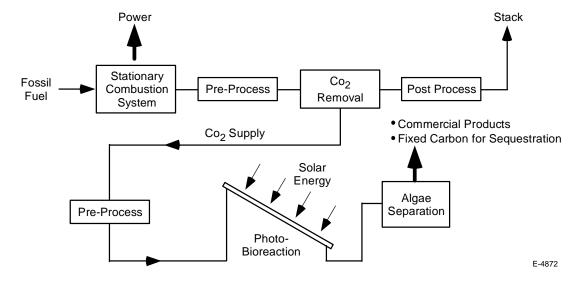


Figure 1. Recovery and sequestration of CO₂ from stationary combustion systems by photosynthesis of microalgae.

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.

2. Executive Summary

The proposed program calls for development of key technologies pertaining to: (1) treatment of effluent gases from the fossil fuel combustion systems; (2) transferring the recovered CO_2 into aquatic media; and (3) converting CO_2 efficiently by photosynthetic reactions to materials to be re-used or sequestered.

The work discussed in this report covers the reporting period from 1 July to 30 September 2002. Up to this point in time we have:

- Tested 50 different strains of microalgae for growth at different temperatures;
- 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 3 different strains for carbon sequestration potential into carbonates for long-term storage of carbon;
- Successfully carried out scale up of the first two microalgal strains to the 2000 liter outdoor photobioreactors;
- Carried out preliminary work on biomass separation for two microalgal strains grown in 2000 liter outdoor photobioreactors;
- Conducted work on designing key components including: CO₂ removal process; CO₂ injection device; photobioreactor; product algae separation process; and process control devices;
- Identified a design concept for photobioreactor incorporating the method for full utilization of solar energy;
- Conducted preparation of 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 diagnostic instrumentation for characterization of coal combustion gas;
- Shared the ASPEN model has been 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.

3. Work Accomplished

The work accomplished during this reporting period reflects the directives we received from the DOE technical contract representative (COTR) as a result of our first annual progress review meeting in February 2002. The DOE directives are summarized as follows:

- An adequate amount of screening for the most promising algal species to be used in CO₂ biofixation/sequestration and in the production of value-added products has been accomplished;
- A concentration of effort on a few of the most promising species of microalgae shall be made;
- Test the most promising algal species with simulated flue gas in bioreactors while varying the appropriate parameters such as pH, temperature, etc.;
- Testing actual flue gas from coal-fired power plants on the most promising algal species should follow this effort, as synthetic flue gas tends not to reflect all of the conditions encountered in actual flue gas from power plants fired with various types of fuels;
- Because of NETL's interest in biofixing/sequestering CO₂ from coal-fired electrical power generating plants, it is imperative that this project demonstrate the effectiveness of various microalgae for removing CO₂ from flue gas from coal-fired power plants and not from oil or natural gas fired power plants; and
- Flue gas from coal-fired power plants should be used on the most promising microalgae in a type of photobioreactor that would allow testing realistically the maximum amount of algal biomass for CO₂ removal.

Our work during this reporting period is to prepare to achieve objectives in compliance with those clear directives. Work accomplished in this reporting period is summarized according to the task structure of the program.

3.1 <u>Task 1: Supply of CO₂ from Power Plant Gas to Photobiorector</u>

Much 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 significant activities were made during the present reporting period.

3.2 Task 2: Selection of Microalgae

During this reporting period, microalgal species have been selected for further scale up and demonstration of algal-based CO₂ sequestration based on:

- Their ability to produce high value compounds;
- Their ability to withstand changes in culture pH;
- Their ability to withstand simulated flue gas mixture; and
- Their capacity to capture CO₂.

For the most part, we have already reported on these aspects in previous reports. During the present reporting period, we have completed the final experimental cultures and finished data assimilation and analysis on CO₂ utilization efficiency. Here we present an updated summary of the data analyzed.

3.2.1 <u>Task 2.1: Characterization of Physiology, Metabolism and Requirements of Microalgae</u> Activities in this subtask were conducted in the previous reporting periods.

3.2.2 <u>Task 2.2: Achievable Photosynthetic Rates, High Value Product Potential and Sequestration of Carbon into Carbonate</u>

3.2.2.1 Microalgal CO₂ Utilization Capacity; Data from the pH Tolerance Experiments

Experiments were designed to test the tolerance of the different microalgal strains to changes in medium pH. Medium pH is driven by the balance between the alga's photosynthetic rate and the rate of CO₂ addition. As described in the 7th quarterly report, we have used our automated pH measurement and control system to estimate the rate of CO₂ disappearance from the medium to obtain photosynthetic carbon uptake and CO₂ degassing rate estimates. The photosynthetic carbon uptake estimates thus calculated from the data collected during the pH tolerance experiments are summarized in Figure 2 for 28 microalgal strains. As shown in previous reports, the results indicate a pH dependency on the uptake rates. This is expected since at lower pH the photosynthetic uptake of CO₂ from the liquid medium is expected to be faster due to the larger partial pressure of CO₂ in the medium.

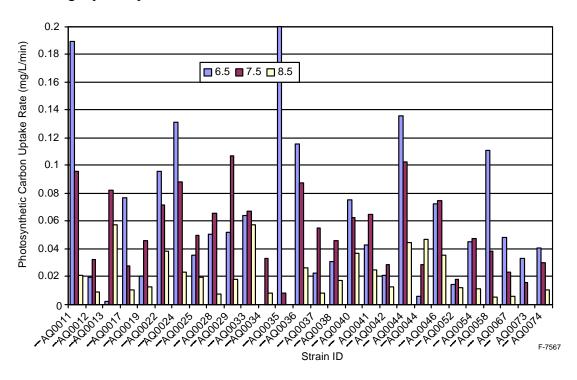


Figure 2. Difference between rates of CO₂ uptake plus degassing in light and in dark periods for 28 microalgal strains under three different ph conditions.

We have taken this analysis one step further and calculated what percentage of the total CO_2 that is lost from the medium is taken up by the microalgae photosynthetically (i.e., the data in Figure 2). The results are shown in Figure 3 and indicate that a larger fraction of the available carbon is taken up by the microalgae at the higher pH settings as opposed to being lost back to the atmosphere.

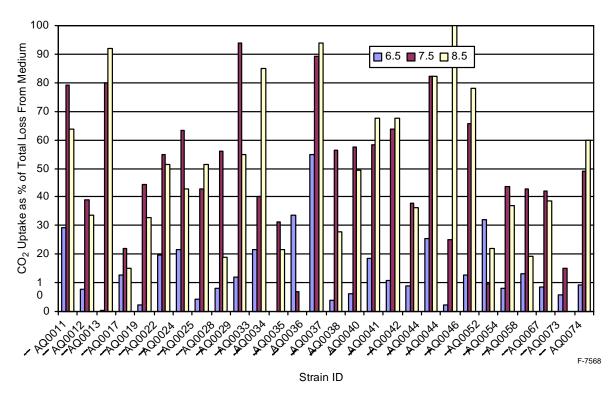


Figure 3. CO₂ uptake as percentage of total CO2 lost from the growth medium during the light period under three different pH conditions.

Finally, we can consider the relationship between CO_2 uptake rate by the culture (Figure 2) and % CO_2 uptake from the medium (Figure 3). The relationships at the three pH conditions are positive but have different slopes (Figure 4). The changes in slope indicate that at higher pH the relationship is steeper, thus the fraction of CO_2 wasted to the atmosphere is smaller. If we calculate the slope of the regression lines for the different pH values we find that the slope is lowest at the lowest pH (slope = 124 at pH 6.5) but increases at increasing pH values (slope = 755 at pH 7.5 and slope = 1838 at pH 8.5). These relationships indicate that the system is most efficient, from a CO_2 -capturing point of view, at higher pH since there is less CO_2 wasted or degassed from the medium. This information will be used in the final phases of the project, when we undertake the design of a commercial facility for carbon sequestration, since the pH at which that plant is managed will dictate the efficiency carbon sequestration in the photobioreactors.

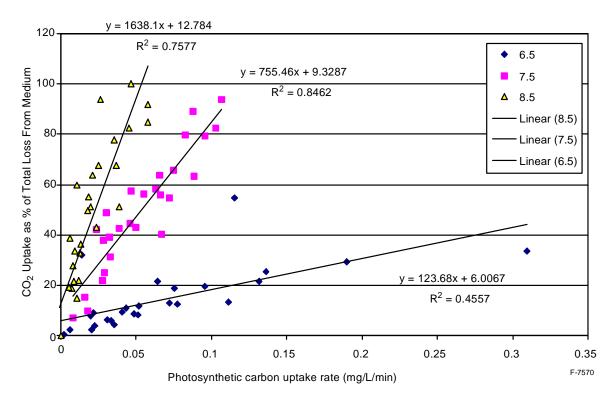


Figure 4. Relationship between photosynthetic CO₂ uptake rate and % of available carbon taken up photosynthetically for the three pH conditions.

3.2.2.2 Microalgal CO₂ Utilization Capacity; Data from the Gas Tolerance Experiments

Experiments were designed to test the tolerance of the different microalgal strains to five different simulated flue gases as described in previous reports. As described in the 7^{th} quarterly report, the pH traces obtained from the gas tolerance experiments were similarly analyzed to calculate the rates in change of CO_2 concentration in the medium. As opposed to the pH tolerance experiments, the pH of the cultures was maintained at approximately 7.5. However, the source of CO_2 for the culture was varied by using, besides pure CO_2 , five simulated flue gases as described in our previous 6^{th} quarterly report.

The results of our updated analysis are summarized in Figure 5. The relationship between CO₂ uptake rate by the culture and %CO₂ uptake from the medium is independent of the simulated gas mixture used to provide carbon to the cultures. The slopes of the linear regressions from each gas range from 496 to 627, all below the slope value of 755 calculated from the 7.5 pH experiments (see above).

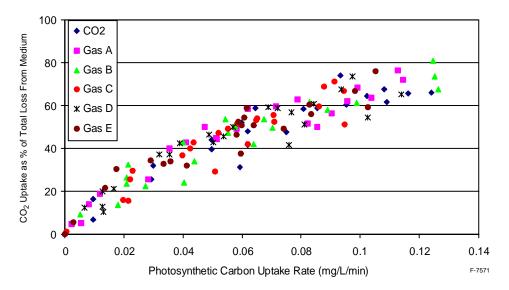


Figure 5. Relationship between photosynthetic CO₂ uptake rate and percent of available carbon taken up photosynthetically under pure CO₂ and five simulated flue gases for 22 microalgal strains.

3.2.2.3 Microalgal CO₂ Utilization Capacity; Data from the Module Scale Experiments

We have also analyzed the pH traces from the scale up experiments carried out in the pilot scale MGMs. We have carried out a preliminary analysis of the data collected during the scale up of five 2,000 liter outdoor cultures (see Task 3.1, below). The resulting calculated slope between the photosynthetic CO₂ uptake rate by the culture and %CO₂ loss from the medium is 266 for this limited data set (Figure 6).

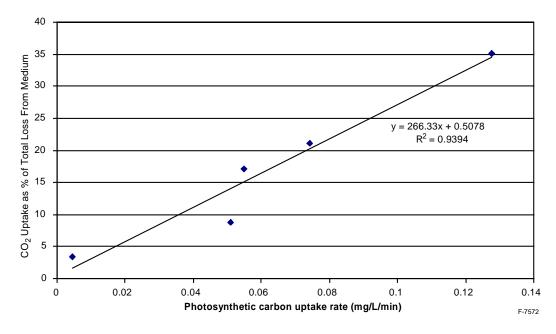


Figure 6. Relationship between photosynthetic CO₂ uptake rate and percent of available carbon taken up photosynthetically for five different 2,000 liter photobioreactor cultures.

3.2.2.4 Microalgal CO₂ Utilization Capacity; Conclusions Thus Far

While the absolute amount of CO₂ that a culture may take up may depend on the strain used (e.g., Figure 2) and, ultimately, on the amount of light irradiance (i.e., energy) available for photosynthesis, our preliminary analysis indicates that the efficiency of the system is dependent on the design of the cultivation vessel and culture technique.

We have now analyzed CO₂ utilization data for three different types of culture vessels. First, we have data from the pH experiments carried out in 3.3 liter chemostats where CO₂ (pure) was provided, on demand, to control the pH of the culture. In these vessels, continuous addition of nutrients and removal of culture is carried out using peristaltic pumps. The results indicate that the rate of degassing in these cultures is dependent on the pH of the culture. When averaged for all strains tested, the calculated rates of night-time dissolved CO₂ decrease averaged 0.026 mg L⁻¹ min⁻¹ for cultures kept at 8.5 pH, 0.056 mg L⁻¹ min⁻¹ for cultures kept at 7.5 pH, and 0.467 mg L⁻¹ min⁻¹ for cultures kept at 6.5 pH.

Second, we have data from the simulated gas addition experiments, also carried out in 3.3 liter chemostats but with one important difference. In these experiments we used pumps for the continuous nutrient additions but not for the removal of culture (for logistic reasons). Instead we maintained positive air pressure inside the vessel to, using a level tube, blow out the excess culture. This had the effect of continuously renovating the gas phase inside the chemostat with low CO₂ (atmospheric) air. By lowering the partial pressure of CO₂ in the gas phase of the chemostat we would expect faster degassing of CO₂ from the medium itself. Our data reflects this difference; while the night-time rate of dissolved CO₂ decrease averaged 0.056 mg L⁻¹ min⁻¹ for the gas chemostats at 7.5 pH (above), the rate averaged 0.064 mg L⁻¹ min⁻¹ for the gas chemostats, also at 7.5 pH.

Third, we have analyzed the first data set from the 2,000 liter photobioreactors. Here, culture circulation is accomplished by blowing massive amounts of air through the culture medium (airlift). This is expected to produce even larger loses of CO_2 from the medium. Indeed, the night-time rate of dissolved CO_2 decrease averaged 0.29 mg L^{-1} min⁻¹ for the module cultures.

The differences in system efficiency are reflected in the slopes of the relationships between CO₂ uptake rate by the culture and %CO₂ uptake from the medium. Figure 7 shows that for a less efficient system (e.g., lower pH, larger amounts of air used) the slope decreases.

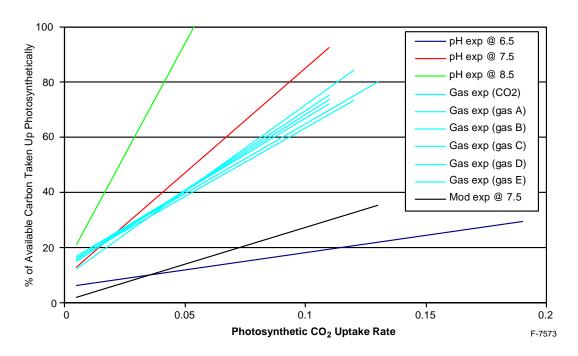


Figure 7. Summary of relationships obtained between photosynthetic CO₂ uptake rate and percent of available carbon taken up photosynthetically for all systems tested so far.

3.3 <u>Task 3: Optimization and Demonstration of Industrial Scale Photobioreactor</u>

The main goal of this task is to demonstrate the feasibility and to quantify the performance of microalgae for biofixation/sequestration of CO₂ at a commercially significant scale. This will be done in two phases. First, we will conduct a pilot evaluation using 2,000 liter enclosed photobioreactors (pilot scale MGM, Task 3.1) and, second, we will conduct full scale production runs using 24,000 liter enclosed photobioreactors (full scale MGM, Task 3.2). Concurrently, research into the appropriate technologies for harvesting and processing the produced biomass will be conducted (Task 3.3).

We recognize that it is imperative that this project demonstrate the effectiveness of various microalgae for removing CO₂ from the flue gas from coal-fired electrical power generating power plants. To fully implement this objective, it is necessary to conduct a series of tests using actual coal combustion gas. Synthetic flue gas tends not to reflect all of the conditions encountered in actual flue gas from power plants fired with various types of fuels. We will accomplish our objectives by means of the following scheme:

- 1. Employ a coal combustor which can operate with different types of pulverized coal.
- 2. Use diagnostic instruments to monitor and quantify chemical constituents (CO_2 , NO_x , SO_x) of the combustion gas.
- 3. Feed the coal combustion gas directly to the Aquasearch photobioreactor.

Figure 8 shows the scheme of the project.

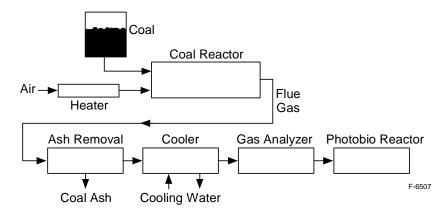


Figure 8. Coal combustion gas for photobioreactor.

3.3.1 Task 3.1: Pilot Evaluation

3.3.1.1 Initial Algae Growth in Photobioreactor

During this quarter we have continued to scale up the first candidate species to the 2,000 liter pilot scale MGMs. We have chosen strain AQ0011 as our first candidate. AQ0011 is a locally isolated green algal strain. In previous reports we indicated that AQ0011 contains commercially significant amounts of lutein and zeaxanthin, two high value carotenoids with applications in human health. The second chosen candidate is AQ0012, a Cyanobacterium that we have shown accumulates zeaxanthin. So far we have grown three MGM cultures with strain AQ0011 and two with strain AQ0012.

Initial Growth Rates in MGMs

Cultures used to inoculate MGMs are grown in chemostats. The biomass produced in the chemostats is then used to inoculate 20 liter carboys. Once the cultures in the carboys reach appropriate density, the biomass is transferred to the MGMs for grow out.

Initially, following inoculation of the MGMs, we can estimate a maximal growth rate from changes in daily biomass estimated from fluorescence measurements (as described in previous reports). This estimated growth rate is considered 'maximal' since during that period in the cultures' life neither light nor nutrients are limiting (Figure 9). The average maximal growth rates over the ramp-up period are 0.88, 0.40 and 0.45 d⁻¹ for strain AQ0011 and 0.57 and 0.31 d⁻¹ for strain AQ0012 cultures respectively which are comparable to the growth rates obtained during the initial ramp-up in the chemostat cultures for these strains (as reported in the 6th quarterly report).

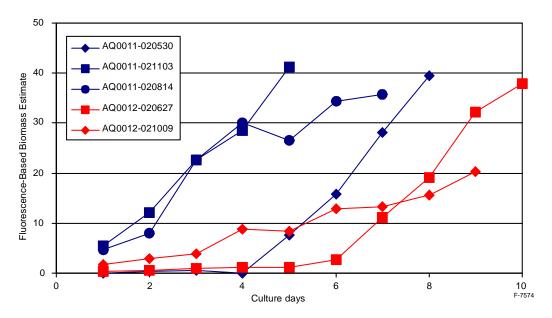


Figure 9. Initial biomass levels for two species in pilot scale MGMs used to estimate the average maximal growth rate.

Potential for Carbon Sequestration in MGMs

Our calculations of CO₂ consumption by the MGM cultures indicate consumption rates (i.e., photosynthetic rates) similar to those obtained in chemostat cultures (e.g., Figures 4, 5, and 6). However, from the limited data available thus far it is clear that the capturing efficiency of dissolved CO₂ in the MGMs is lower than the capturing efficiency in chemostat cultures kept at the same pH (Figure 7). Previously, we have argued that this difference is caused by the design of the system since the MGMs are dependent on airlifts to provide turbulence. The large amount of air used in the airlift is expected to strip dissolved CO₂ from the culture medium. It is expected that changes in the design of the MGMs may result in increased capturing efficiency of dissolved CO₂. The results also suggest that changes in cultivation strategy (e.g., raising the pH of the culture) would similarly increase the efficiency of the MGMs. These questions will be taken up during the last phase of the project as they will impact the final design of a microalgal-based CO₂-sequestration facility (Task 5).

3.3.1.2 Preparation for Coal Combustion Gas Generator

In this reporting period we have continued preparation for PSI coal reactor as discussed in the previous quarterly report. Schematic representation of the coal reactor is given in Figure 10. Specification of the reactor is given in Table 1.

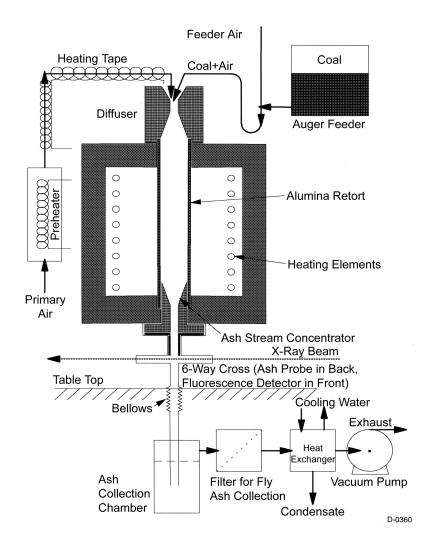


Figure 10. Schematic of the PSI coal reactor system.

Table 1. Specifications of the PSI Coal Reactor System

Total gas flow rate:	~ 1 scfm
Primary air:	~ 0.8 scfm
Feeder air:	~ 0.2 scfm
Preheat temperature:	up to 550°C
Coal feed:	1 ~ 10 gram/min;
	4 gram/min recommended

To date all key components were tested and integrated into the system. Several new components have been ordered. Figure 11 shows the coal reactor being tested at PSI coal laboratory. The main component is the electric heater to heat the pulverized coal to 1200°C. At that temperature the pulverized coal reacts with the air to form coal combustion gas. We have measured the reactor temperature up to 1350°C (see Figure 12) to confirm that the heater operates at the specified condition. We are also testing the coal feeder which supplies the reactor with the prescribed amount of coal (Figure 13). The control system to regulate the reactor temperature, air flow, and coal mass flow rate (Figure 14) was also tested. At the writing of this report we are finalizing the performance test.



Figure 11. Coal reactor system at PSI coal laboratory.



Figure 12. Reactor temperature measurement.

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Figure 13. Coal feeder located at the top of the coal reactor.



Figure 14. Control system.

3.3.1.3 Coal Combustion Gas Diagnostics

PSI has been preparing the instruments to measure the composition of the coal combustion gas: CO_2 , NO_x ; and SO_x . The expected composition of the coal combustion gas is given in Table 2 below.

Bituminous Coal		Sub-Bituminous Coal	Combustion Gas Diagnostics Measurement Range		
CO_2	12.7%	15.1%	0 ~ 100%		
H ₂ O	5.0%	12.2%			
O_2	6.0%	6.0%			
N ₂	76.9%	71.0%			
SO ₂ [ppm]	50-500	300-500	0 ~ 4000		
NO, [nnm]	50-500	50-500	0 ~ 500		

Table 2. Typical Flue Gas Compositions for Coal Combustion Systems

We will measure the composition of the coal combustion gas at the inlet and the vent of the photobioreactor. The locations of the gas composition measurement are shown in Figure 15.

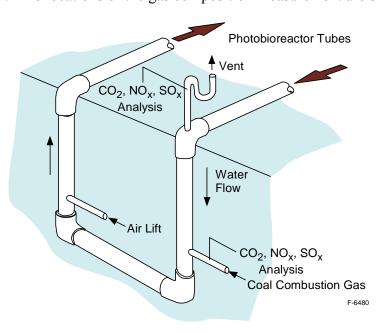


Figure 15. Coal combustion gas diagnostics.

The diagnostic instruments was delivered to PSI in October. The instruments consists of the gas dryer main box, IMR 400 Gas Dryer Main Box shown in Figure 16. There are two sets of heated hose which takes gas sample from the inlet and the outlet of the photobioreactor (Figure 17). The sample gas is dried in the dryer box and is sent to IMR5000 Gas Analyzer Main Box shown in Figure 18. Concentration of CO₂, NO_x and SO₂ will be determined.



Figure 16. IMR 400 gas dryer main box.



Figure 17. Gas sample hoses, probes and flanges.



Figure 18. IMR5000 gas analyzer main box.

3.3.2 <u>Task 3.2: Full Scale Production Run</u>

This task is scheduled after Task 3.1.

3.3.3 Task 3.3: Algae Separation and Final Product

During this quarter we have carried out the first two separations of algal biomass produced in 2000 L MGMs. We have harvested 500 L volumes of cultures of strains AQ0011 and AQ0012 utilizing pilot scale industrial centrifuges (Clinton Separators, Model # 9021). The centrifugation of the algal biomass is carried out by placing the volume of culture in a feed tank about two feet above the centrifuge. The material is fed by gravity and the amount of feed (liters per minute) adjusted via the feed tank's drain valve.

The optimum rate of flow into the centrifuge is arrived to empirically. It is expected that cells of different physical characteristics (density, size, shape) will present different settling rates and, thus, will affect the capacity of the centrifuge. AQ0011 is a small (about 4 to 6 μ m diameter) unialgal strain while AQ0012 is a multicellular, filamentous strain. We adjust the flow into the centrifuge to the point where less than 10% (estimated optically) of the feed biomass appears in the outflow (i.e., >90% capture of biomass). The respective flow rates were 1.5 and 1.8 liters per minute for AQ0011 and AQ0012. From 500 liter of culture we obtained 0.88 and 2.43 kg of wet biomass respectively.

We will continue conducting harvest experiments on the 2000 L MGM pilot scale cultures during the following quarters.

3.4 <u>Task 4: Carbon Sequestration System Design</u>

To evaluate the potential for application of photosynthetic sequestration of CO_2 to industrial-scale combustion systems, we will conduct a system-level design study. The purposes of this study are as follows:

- (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.

3.4.1 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 CO_2 . Key components to be designed include: CO_2 removal process; CO_2 injection device; photobioreactor; product algae separation process; and process control devices. As the proposed system depends on the solar energy to photosynthetically convert CO_2 to products compounds, optimization of the photobioreactor is an important part of this task.

In the reporting period, no significant progress was made in this task as PSI focused its effort on the coal reactor and the diagnostic system.

3.4.2 <u>Task 4.2: System Integration</u>

3.4.2.1 On-Site Research at Aquasearch

As reported previously, 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. Due to the complexity of the processes involved, these submodels are expected to be empirical in nature, rather than based on first principles. In order to obtain data on the performance characteristics of the Aquasearch photobioreactor, it was decided to send UH personnel to the Aquasearch facility.

The Graduate Research Assistant supported by this project, Mr. Simon Tsang, as well as HNEI Junior Researcher, Dr. Brandon Yoza, visited and worked at Aquasearch's facilities in Kona, Hawaii for one week in July 2002. Dr. Yoza is a microbiologist who had previous experience with the UH photobioreactor that was used for hydrogen production from microalgae.

Mr. Tsang gathered information on the performance of the Aquasearch photobioreactor to calibrate and refine the submodels described in the previous Quarterly Report. He received data on its 25,000 L photobioreactors that were collected by Aquasearch during the first 6 months of 2002. The data included media temperature in the photobioreactor (at 5 min intervals), duration seawater flow is activated (for cooling the photobioreactors), daily solar insolation, media pH (at 5 min intervals), duration of CO₂ injection, and microalgae harvesting and sampling data. Operational parameters such as flow rates of air, CO₂, media, and seawater, and the Reynolds number of the media were determined. Also, the specific growth rate of the microalgae, average microalgae dry weight, and the dimensions of the photobioreactor were extracted from a publication by Dr. Miguel Olaizola.

3.4.2.2 Data Analysis

Averages and standard deviations of the daily volume of seawater, media temperature, CO₂ injected, media pH, daily insolation, and daily biomass productivity are presented in Table 3. Table 3 shows that the average daily media temperature (16.94 °C) was maintained within the desired range, 15 °C to 17 °C, and that the standard deviation of the media temperature (1.96 °C) was small due to temperature regulation by cold upwelled seawater. When the media temperature rises above 17 °C, a controller allows seawater to flow over the photobioreactor tubes to reduce media temperature. When the media temperature drops below 17 °C, seawater flow ceases. The average and standard deviation of the daily volume of seawater used for cooling were 192,848 L/day and 81,504 L/day, respectively.

CO₂ gas is injected into the media to control media pH. Table 3 shows that the average media pH (7.38) fell within the desired range, 6.5 to 7.5, and the standard deviation of the media pH (0.28) was small. When media pH exceeds 7.5, CO₂ gas is injected and pH decreases. Once the media pH drops below 7.5, CO₂ injection ceases. The average and standard deviation of the daily volume of CO₂ injected into the media were 118 ft³/day and 32 ft³/day, respectively.

Table 3. Averages and Standard Deviations of Daily Volume of Seawater, Media Temperature, Daily Volume of CO₂, Media pH, Daily Solar Irradiance, and Daily Biomass Productivity

		Standard
	Average	Deviation
Volume of seawater (L/day)	192,848	81,504
Media temperature (°C)	16.94	1.96
Volume of CO ₂ (ft ³ /day)	117.53	31.69
Media pH	7.38	0.28
Solar irradiance (E/m²/day)	18.85	10.36
Biomass productivity (g/day)	1346.98	995.74

The average daily biomass productivity was determined from the harvesting and sampling data. In some instances, the calculated biomass productivity was negative. This anomaly probably occurred because the microalgae in the photobioreactor media was dispersed heterogeneously, and while most samples contained high cell density, a few contained low cell

density. The negative values were ignored in the computations. The average daily biomass productivity and its standard deviation were 1347 g/day and 996 g/day, respectively.

Microalgae are autotrophs that require sunlight and CO_2 to produce sugar via photosynthesis. Sugar provides energy for cell synthesis and cell maintenance. Biomass productivity (i.e., cell synthesis) is related to solar insolation and CO_2 concentration. This relationship will be used to develop a photobioreactor model. A linear relationship between the output, biomass productivity, and the inputs, solar irradiance and CO_2 , was developed using multiple regression. The coefficients of the solar irradiance, CO_2 , and constant terms for the linear regression equation were 26.71, 10.41, and -914.8, respectively (Table 4). The multiple regression analysis is summarized in Tables 5 and 6.

Table 4. Coefficients of the Multiple Regression

	Coefficient	Std Err	t-value	p-value	Lower Limit	Upper Limit
Constant	-914.7902	530.6652	-1.7239	0.0891	-1972.9070	143.3266
Volume of CO ₂ (ft ³)	10.4149	3.3408	3.1175	0.0026	3.7536	17.0763
Solar irradiance (E/m²/day)	26.7085	10.2207	2.6132	0.0109	6.3290	47.0879

Table 5. Summary Measures of the Multiple Regression

Multiple R	0.4597
R-square	0.2113
Adj R-square	0.1891
StErr of est	896.6491

Table 6. ANOVA Table of the Multiple Regression

Source	df	SS	MS	F	p-value
Explained	2	15297240.6654	7648620.3327	9.5135	0.0002
Unexplained	71	57082552.0000	803979.6056		

4. Summary and Future Plans

4.1 <u>Task 2: Selection of Microalgae</u>

In this report period, we have finished working on assimilating the data obtained on carbon utilization by the different microalgal strains under different growth conditions. We have now tested the compatibility of over 20 microalgal species with 5 different flues gases. Similarly, we have determined the productivity parameters for over 20 different algae with 5 different flue gases. We have further analyzed the data on carbon utilization obtained from the pH, gas, and pilot scale experiments to show that changes in design and culture strategies affect the carbon capturing potential of microalgal cultures.

4.2 <u>Task 3: Optimization and Demonstration of Industrial Scale Photobioreactor</u>

We have carried out the first five pilot scale cultures. The preliminary results obtained with these cultures (2,000 liter) show close agreement with results obtained with the same strains at much smaller scale (3.3 liter chemostats) validating our early assumption that we can extrapolate data obtained in laboratory experiments to outdoor photobioreactors.

Within the next quarter we expect to

- Continue scaling up of promising strains to the 2000 liter outdoor photobioreactor scale.
- Test and install gas measuring equipment, and
- Install a coal combusting unit (provided by PSI) to provide coal combustion waste gases to the MGM cultures.

Preparation for pilot scale experiment using PSI coal reactor has progressed. To date all key components were tested and integrated into the system. Several new components have been ordered. At the writing of this report we are finalizing the performance test. Diagnostic system to measure chemical components of the coal combustion gas: CO₂, NO_x, and SO_x have been developed. The diagnostic instruments were delivered to PSI in October. After inspection and testing, the instruments were shipped to Aquasearch Inc. in Hawaii.

Within the next quarter we expect to

- Continue scaling up of promising strains to the 2000 liter outdoor photobioreactor scale,
- Test and install gas measuring equipment, and
- Install a coal combusting unit (provided by PSI) to provide coal combustion waste gases to the MGM cultures.

4.3 Task 4: Carbon Sequestration System Design

During the present reporting period (07/01/02 - 09/30/02) the following technical activities were pursued:

1. The Graduate Research Assistant supported by this project and UH research staff worked at Aquasearch for one week in July 2002 to gather information on the performance of the photobioreactor to calibrate and refine the submodels described in the previous Quarterly Report.

2. 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.

5. 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]