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

Quarterly Technical Progress Report for the Period Ending 30 June 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 April to 30 June 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 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.

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 CO₂ into aquatic media; and (3) converting CO₂ efficiently by photosynthetic reactions to materials to be re-used or sequestered.

The work discussed in this report covers the reporting period from 1 April to 30 June 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;
- Tested 21 different strains for tolerance to simulated flue gases;
- Tested 28 strains at the chemostat level for growth and carbon uptake rate;

- Tested 3 different strains for carbon sequestration potential into carbonates for long-term storage of carbon;
- Carried out the first two pilot scale culture to validate the results obtained using the small chemostat are also valid for 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;
- Initiated refurbishing of the PSI coal reactor to be used with the Aquasearch photobioreactor for direct feeding of coal combustion gas to microalgae;
- Developed the diagnostic instrumentation methodology for characterization of coal combustion gas;
- Shared the ASPEN model has been with UH, PSI and Aquasearch for review and discussion;
- Completed planning for a visit to the Aquasearch facility by the UH graduate research assistant (scheduled for late July 2002);
- An alternative model of the photobioreactor subsystem was developed using Excel spreadsheet. Data to calibrate this model will be obtained during a visit to the next visit to Aquasearch scheduled for July 2002;
- A review of the technical literature on tubular photobioreactors was initiated;
- A literature study was initiated 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 Task 1: Supply of CO₂ from Power Plant Gas to Photobioreactor

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 we have worked on finishing up some aspects of Task 2 (Selection of Microalgae). In this period we have specifically worked on assimilating the data obtained on carbon utilization by the different microalgal strains under different growth conditions (Subtask 2.2.1).

3.2.1 Task 2.1: Characterization of Physiology, Metabolism and Requirements of Microalgae

Activities in this subtask were conducted in the previous reporting period. We reported the progress in this subtask in the last quarterly reported, #6.

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

We have previously reported on the techniques used to grow microalgae to accomplish the work in this task (chemostats). We have also previously reported (e.g., Sixth Quarterly Report, Task 2.2) that changes in growth condition at the chemostat scale (such as pH and flue gas conditions) did not have large effects on the growth rate or physiological status (F_v/F_m) of the different strains of microalgae. We have, however, pointed out that, for example, differences in medium pH had profound consequences on the amount of available CO_2 that could be used by the microalgae versus the amount that was degassed (wasted) from the system (Section 1.2.1.2 of our Sixth Quarterly Report). Here we will expand on the results obtained on carbon utilization efficiency and we will extend those results to include those obtained from the gas tolerance experiments and from the outdoor photobioreactors (2,000 liter pilot scale Mera Growth Module (MGM), formerly called Aquasearch Growth Module (AGM)).

3.2.2.1 Microalgal CO_2 Utilization Capacity

Methodology

The automated pH monitoring and control system allows us to closely follow changes in pH in all the chemostat cultures. As an example, Figure 2 shows the changes in pH over the life history of a chemostat culture of strain AQ0022. Changes in pH reflect changes in the concentration of dissolved CO_2 and the total dissolved inorganic carbon ($\text{DIC} = \text{CO}_2 + \text{HCO}_3^- + \text{CO}_3^{2-}$). We make the assumption that increases in DIC in the medium are produced either by respiration by the algae or by the injection of CO_2 . We also make the assumption that decreases in DIC are produced by photosynthetic uptake of carbon and degassing from the culture medium.

Figure 2. Computer generated trace of culture pH in a chemostat culture (strain AQ0022). Showing the periods of time during which the culture's pH was maintained at 6.5, 7.5, and 8.5.

Figure 3 shows an example of such changes. The figure shows two traces. The first trace is the pH of the culture medium over 4 days and nights for a culture of strain AQ0036. Decreases in pH correspond to increases in DIC produced by CO₂ injections and algal respiration. Increases in pH correspond to decreases in DIC caused by photosynthetic uptake of CO₂ by the algae or degassing. Using the changing concentrations of DIC over time we can calculate the net rate of carbon uptake ($\text{mg CO}_2 \text{ l}^{-1} \text{ min}^{-1}$). The results of this calculation, with a resolution of 5 min, are shown in Figure 4. Positive values indicate net uptake of CO₂ by the culture and degassing of CO₂ from the culture medium while negative values indicate injection of CO₂ into the medium and cellular respiration. Note that, in this case, degassing during the night periods (which would be evidenced by a rise in pH) is negligible. If we calculate an average net CO₂ uptake rate, using the values when no CO₂ is being injected, we obtain an average net rate of $0.094 \text{ mg CO}_2 \text{ l}^{-1} \text{ min}^{-1}$. For a 14 hour day this is equivalent to $79 \text{ mg CO}_2 \text{ l}^{-1} \text{ d}^{-1}$ or $21.5 \text{ mg C l}^{-1} \text{ d}^{-1}$.

We use the data thus obtained to understand not only how the physiology and the growth of the microalgal cells may change when grown at different pH but also how the different medium pH affects the degassing of CO₂ from the medium and the uptake of CO₂ by the microalgae. For example, if we consider the changes in pH during the light and dark period (i.e., no photosynthetic carbon uptake) for the AQ0011 culture grown at different pH, both the rate of uptake and the rate of degassing are inversely proportional to the medium pH (Figure 5). At lower pH the concentration of CO₂ is higher in the medium so diffusion of CO₂ out of the medium is expected to be faster (Figure 5). If we compare the calculated rates between the light and dark periods the difference should be that due to photosynthetic uptake of CO₂. The result indicates that the photosynthetic uptake of CO₂ is also pH dependent.

Figure 3. Changes in pH and total DIC over a 4 day period for a chemostat culture of strain AQ0036.

Figure 4. Changes in carbon uptake rate over a four day period for a chemostat culture.

Figure 5. Rates of CO₂ uptake and/or degassing for a chemostat culture.

Microalgal CO₂ Utilization Capacity; Data from the pH Tolerance Experiments

The photosynthetic carbon uptake estimates thus calculated from the data collected during the pH tolerance experiments are summarized in Figure 6. As for strain AQ0011, the results indicate a pH dependency on the uptake/degassing rates calculated. This is expected since at lower pH the degassing of CO₂ from the liquid medium is expected to be faster due to the larger partial pressure of CO₂ in the medium.

Figure 6. Difference between rates of CO₂ uptake and degassing light and dark periods for 19 microalgal strains.

We can take this analysis one step further and calculate what percentage of the total CO₂ that is lost from the medium is taken up by the microalgae photosynthetically (i.e., the data in Figure 5). The results are shown in Figure 7 and indicate that a larger fraction of the available carbon is taken up by the microalgae at the higher pH settings as opposed as being lost back to the atmosphere.

Figure 7. CO₂ uptake as percentage of total CO₂ lost from the growth medium during the light period.

Finally, we can consider the relationship between CO₂ uptake rate by the culture (Figure 6) and %CO₂ uptake from the medium (Figure 7). The relationships at the three pH conditions shown in Figure 8 are positive but have different slopes (Figure 8). The changes in slope indicate that at higher pH the relationship is steeper, thus the efficiency of CO₂ uptake is higher. 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 = 170 at pH 6.5) but increases at increasing pH values (slope = 692 at pH 7.5 and slope = 1131 at pH 8.5). These relationships indicate that the system is most efficient, from a CO₂-capturing point of view, at higher pH since there is less CO₂ wasted or degassed from the medium.

Figure 8. Relationship between photosynthetic CO₂ uptake rate and % of available carbon taken up photosynthetically for the three pH conditions.

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 of the photosynthetic carbon uptake.

Microalgal CO₂ Utilization Capacity; Data from the Gas Tolerance Experiments

The pH traces obtained from the gas tolerance experiments were similarly analyzed to calculate the rates in change of CO₂ 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 CO₂ for the culture was varied by using, besides pure CO₂, five simulated flue gases as described in our previous Sixth Quarterly Report. The results of our analysis are summarized in Figure 9. The relationship 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 505 to 580, all below the slope value of 692 calculated from the pH experiments (Section 1.2, above).

Figure 9. Relationship between photosynthetic CO₂ uptake rate and % of available carbon taken up photosynthetically under pure CO₂ and five simulated flue gases for 19 microalgal strains.

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 (see Section 2.1, Pilot Evaluation, below). We have carried out a preliminary analysis of the data collected during the scale up of two 2,000 liter outdoor cultures. The resulting calculated slope between CO₂ uptake rate by the culture and %CO₂ uptake from the medium is 286 for this limited data set as shown in Figure 10.

Figure 10. Relationship between photosynthetic CO₂ uptake rate and % of available carbon taken up photosynthetically for two different 2,000 liter photobioreactor cultures.

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 6) 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 0.02 mg L⁻¹ min⁻¹ for cultures kept at 8.5 pH, 0.05 mg L⁻¹ min⁻¹ for cultures kept at 7.5 pH, and 0.37 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 0.05 mg L⁻¹ min⁻¹ for pH chemostats at 7.5 pH (above), the rate averaged 0.07 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 losses of CO₂ from the medium. Indeed, the night-time rate of dissolved CO₂ decrease averaged 0.22 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 11 shows that for a less efficient system (e.g., lower pH, larger amounts of air used) the slope decreases.

Thus, we consider this task nearly finished and we are now shifting our focus to the scale-up of cultures to the outdoor photobioreactor scale. We will continue, however, to carry out small scale work on a few strains that we consider promising on a non-priority basis. These strains will originate from the University of Hawaii Cyanobacterial Collection with whom Aquasearch has negotiated access for drug discovery. A number of strains in this collection have already been identified as producers of molecules with potential therapeutic applications in human health.

Figure 11. 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 Task 3: Optimization and Demonstration of Industrial Scale Photobioreactor

The main goal of this task is to demonstrate the feasibility and to quantify the performance of microalgae for biofixation/sequestration of CO₂ from coal-fired electrical power generating plants. 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 have given serious thought to this requirement and came up with 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 (CO₂, NO_x, SO_x) of the combustion gas.
3. Feed the coal combustion gas directly to the Aquasearch photobioreactor.

Figure 12 shows the scheme of the project.

Figure 12. Coal combustion gas for photobioreactor.

3.3.1 Task 3.1: Pilot Evaluation

3.3.1.1 Preparation for Coal Combustion Gas Generator

In this reporting period we have started preparations for the pilot scale experiment to assess feasibility of using coal flue gas as a feeder for microalgae. For this experiment it is highly desirable to simulate the use of real coal combustion flue gas. The facility for pilot scale evaluation is the Aquasearch 2000 liter photobioreactor. Approximate characteristics of the reactor are given in Table 1.

Table 1. Aquasearch 2000 liter Photobioreactor - Standard Configuration

Photobioreactor area:	30 m ²
Carbon fixation capacity:	225 gram/day
Necessary carbon supply:	1.875 kg/day*
Carbon feed:	1.3 gram/min**

* Based on the empirical overall carbon utilization of 12%

** Based on continuous 24 hour carbon feed

We need to supply coal combustion gas compatible with the specifications required by the photobioreactor discussed above.

About 10 years ago PSI developed a coal combustion test facility to study coal ash characteristics. The facility consists of an auger type pulverized coal feeder, an entrained flow reactor, a six-way cross, and an ash collection system. This facility, as shown schematically in Figure 13, was developed to study coal ash by in-situ X-ray Ash Fine Structure (XAFS) method. It is designed to be separable in two pieces so that each can be wheeled into the experimental hatch. The furnace top section is composed of the furnace, pre-heater, feeder, diffuser, six-way cross, and detector mount. The furnace base section is composed of the ash collection chamber, filter, heat exchanger, and furnace alignment system. For our purpose, the “exhaust gas” which is pumped out of the furnace system is the important product. The six-way cross is not necessary. Table 2 summarizes the air flow rate, preheat temperature and the coal feed rate.

Figure 13. Schematic of the PSI coal reactor system.

Table 2. 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

Combustion of the reactants mixed in the diffuser takes place in the vertically-oriented, electrically-heated furnace placed underneath the diffuser. The furnace is composed of a vertically-oriented 30-in. long, 3-in. ID alumina retort surrounded by 18 silicon carbide heating elements placed inside a brick chamber and has a constant temperature zone of 20 in. A gas temperature profile along the axis of the retort at furnace wall temperature of 1300°C and total gas flow rate of 1 scfm is shown in Figure 14. The residence time of the coal particles is 2.5 seconds. About 90% of coal ash is captured by the ash collection chamber and the rest is captured by a filter placed downstream of the furnace. The heat exchanger is used to condense the moisture in the exhaust stream and cool the exhaust to room temperature.

Figure 14. Axial gas temperature profile along the center of the alumina retort.

The recommended feed rate of the pulverized coal (4 gram/min) shown in Table 2 translates to approximately 2.8 gram/min of carbon (assuming 70% of coal is carbon). This indicates that the PSI coal reactor is capable of supplying adequate carbon to the Aquasearch Photobioreactor as shown in Table 1. At the writing of this report the PSI coal reactor is being refurbished for operation. Figure 15 shows the reactor and the flow control unit. On the far right is the bottom rack that contains the filter unit and other equipment.

Figure 15. Photo of the PSI coal reactor.

3.3.1.2 Coal Combustion Gas Diagnostics

PSI has also been preparing the instruments to measure the combustion gas composition: CO_2 , NO_x ; and SO_x . The expected composition of the coal combustion gas is given in Table 3 below.

Table 3. Typical Flue Gas Compositions for Coal Combustion Systems

	Bituminous Coal	Sub-Bituminous Coal	Combustion Gas Diagnostics Measurement Range
CO_2	12.7%	15.1%	0 ~ 100%
H_2O	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_x [ppm]	50-500	50-500	0 ~ 500

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 16. The current concept is to inject the coal combustion gas through the port which was used for injection of pure CO_2 . As the volume of the coal combustion gas is expected to be about five

Figure 16. Coal combustion gas diagnostics.

times larger than the pure CO₂, it is possible that the coal combustion gas cannot be injected through the port for the counter flow dissolution section. If this is the case, the coal combustion gas may have to be injected at the air lift port.

The diagnostic instruments will be delivered to PSI in October. PSI will purchase the instruments by its own fund as part of the cost share contribution to the program.

3.3.1.3 Initial Algae Growth in Photobioreactor

During this quarter we have started to scale up the first candidate species to the 2,000 liter pilot scale Mera Growth Modules (MGMs), formerly called Aquasearch Growth Module (AGM). 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 two EPBs with strain AQ0011 and one 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. Initially, following inoculation of the MGMs we can estimate a maximal growth rate from changes in daily biomass estimated from fluorescence measurements. This estimated growth rate is considered 'maximal' since during that period in the cultures' life neither light nor nutrients are limiting (Figure 17). The

Figure 17. Initial biomass levels in pilot scale MGMs used to estimate the average maximal growth rate.

average maximal growth rates are 0.88 d^{-1} and 0.57 d^{-1} for the AQ0011 and 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 Sixth Quarterly Report).

Potential for Carbon Sequestration in MGMs

Our calculations of CO_2 consumption by the MGM cultures indicate consumption rates (i.e., photosynthetic rates) similar to those obtained in chemostat cultures (e.g., Figures 7, 8, and 9). However, from the limited data available thus far it is clear that the capturing efficiency of dissolved CO_2 in the EPBs is lower than the capturing efficiency in chemostat cultures kept at the same pH (Figure 11). In Section 3.2.2.1 it was argued that this difference is caused by the design of the system since the EPBs are dependent on airlifts to provide turbulence. The large amount of air used is expected to strip dissolved CO_2 from the medium. It is expected that changes in the design of the EPBs may result in increased capturing efficiency of dissolved CO_2 . The results also suggest that changes in cultivation strategy (e.g., raising the pH of the culture) would similarly increase the efficiency of the EPBs. These questions will be taken up during year three of the project as they will impact the final design of a microalgal-based CO_2 -sequestration facility.

3.4 Task 4: Carbon Sequestration System Design

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. Process simulations will be performed for conventional coal-fired and gas turbine power stations and natural gas boilers.

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 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, we have conducted analysis of engineering aspects of solar utilization by microalgae. As reported in the last progress report, PSI believes that a key to successful CO₂ sequestration is efficient use of solar energy. The area required for photosynthetic process by microalgae is a key cost driving factor. Therefore, we need to develop a photobioreactor design which makes efficient use of solar light. Progress in this area is under way.

3.4.2 Task 4.2: System Integration

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. This onsite research is scheduled for July 2002. Preparations for this visit, including prioritization of desired information, were undertaken during the present reporting period. The results of the site visit to Aquasearch will be summarized in the next Quarterly Report.

Performance characteristics of CO₂ flue gas separation systems are generally available in the literature and a literature review was initiated to secure the information needed for submodel development (see below). A summary of technical activities conducted by UH during this quarter is provided below.

3.4.2.1 Carbon Dioxide Supply, Separation, and Biological Uptake System

Photobioreactors

During this reporting period, significant effort was invested in the development of an alternative photobioreactor model using an Excel spreadsheet. Renewal of our Aspen Plus academic license has proceeded very slowly; in consideration of this recurrent complication, we have decided to pursue parallel modeling strategies using Aspen Plus and Excel in order to avoid excessive delays.

The Excel photobioreactor model consists of three submodels. The first submodel predicts the daily volume of seawater used for cooling the photobioreactor based on media temperature inside the photobioreactor. Seawater flow is activated when the media temperature exceeds 17°C and deactivated when the media temperature drops below 17°C. This submodel tracks the duration seawater flow is activated. The daily volume of seawater is determined from the flow duration and seawater flow rate.

The second submodel predicts the daily volume of CO₂ gas injected into the media based on media pH. CO₂ injection is activated when the media pH exceeds 7.5 and the flow ceases when the media pH drops below 7.5. The model tracks the duration of CO₂ injection. The daily volume of CO₂ injected is determined from the duration of CO₂ injection and CO₂ flow rate.

The last submodel predicts daily biomass productivity based on solar irradiance and CO₂ injection calculated in the second submodel. The daily biomass productivity is determined from the linear multiple regression equation developed earlier. Data needed to calibrate the aforementioned submodels will be obtained during the visit to Aquasearch in July 2002.

Carbon Dioxide Flue Gas Separation

A literature study was initiated to develop the CO₂ flue gas separation subsystem model. Carbon dioxide separation processes being considered include membrane separation, cryogenic fractionation, air separation/flue gas recycling, and separation using a recyclable solvent. Using a recyclable solvent is the most common commercial process and a model of this separation system will probably be given highest priority. Recyclable solvent separation involves: (1) scrubbing the carbon dioxide from the flue gas with a solvent, (2) stripping the carbon dioxide from the solvent, and (3) recycling the solvent.³ The most common solvent used is aqueous monoethanolamine, a primary amine, which is reactive and inexpensive.⁴ Studies have been conducted using a mixture of methyldiethanolamine, a tertiary amine, and monoethanolamine as the solvent. The mixed amine solvent combines the high reaction rate of the primary amine with the high equilibrium loading capacity of the tertiary amine.⁴ Ammonia has been evaluated as an alternative solvent. Ammonia has a higher equilibrium loading capacity than monoethanolamine and the energy requirement for regenerating ammonia is lower than for monoethanolamine.⁵

Information from the literature study of recyclable solvent CO₂ flue gas separation systems is being applied to develop the Excel and Aspen Plus models of this component.

4. Summary and Future Plans

4.1 Task 2: Selection of Microalgae

In this report period, 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 Task 3: Optimization and Demonstration of Industrial Scale Photobioreactor

Preparation for pilot scale experiment using PSI coal reactor has been initiated. Carbon requirement by the Aquasearch pilot scale photobioreactor was compared with the supply capability of PSI coal reactor. It was found that the CO₂ supply from the PSI coal reactor is sufficient for the pilot scale test to be conducted at Aquasearch. Refurbishing of PSI coal reactor is in progress.

Diagnostic system to measure chemical components of the coal combustion gas: CO₂, NO_x, and SO_x have been developed. The diagnostic system will characterize the coal combustion gas at the inlet of the photobioreactor. It will also measure the components of the vented gas from the photobioreactor. With this diagnostic system, complete characterization of the feed gas can be made for assessment of photosynthetic efficiency of microalgae.

We have also carried out the first two pilot scale cultures. The preliminary results obtained with these two 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 refurbishing the PSI coal reactor and developing diagnostic system.
- Continue scaling up of promising strains to the 2000 L outdoor photobioreactor scale.
- 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 the following technical activities were pursued:

1. An alternative model of the photobioreactor subsystem was developed using an Excel spreadsheet. Data to calibrate this model will be obtained during a visit to Aquasearch scheduled for July 2002.

2. A literature study was initiated to develop the CO₂ flue gas separation subsystem model. Both Aspen Plus and Excel models will be developed. A recyclable solvent process will probably be assigned highest priority.
3. Preparations were completed for the onsite study at Aquasearch to gather critical bioreactor model information.

5. References

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