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 July to 30 September 2004 in which PSI, Aquasearch and University of Hawaii conducted their tasks. Based on the work during the previous reporting period, Aquasearch run the first set of experiments with actual coal combustion gases with two different strains of microalgae. In addition further, full scale carbon sequestration tests with propane combustion gases were conducted. Aquasearch continued testing modifications to the coal combustor to allow for longer-term burns.

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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;
- Tested the coal reactor and conducted the first pilot scale production run with coal combustion gases and modified the coal combustor to allow for longer-term burns;
- Run the first set of experiments with actual coal combustion gases with two different strains of microalgae (AQ0073 and AQ0033);
- Completed the first full scale production run and conducted the second full scale run at the 25,000 photobioreactor using propane combustion gas utilizing two different strains of microalgae;
- Carried out preliminary work on biomass separation for two microalgal strains grown in 2000 liter outdoor photobioreactors;
- Started to model the costs associated with biomass harvested from different microalgal strains;
- Conducted work on designing key components including: 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 1 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	60%	Demonstrate viability of CO ₂ with algae at industrial scale
Subtask 3.1	Pilot Evaluation	60%	Evaluation at 2000 L pilot scale. Experimental work with coal reactor started
Subtask 3.2	Full Scale Production Runs	70%	Evaluation at 24,000 L industrial scale with propane combustion gas.
Subtask 3.3	Algae Separation and Final Product	55%	Evaluation of biomass separation
Task 4.0	Carbon Sequestration System Design	50%	Incorporating new system concept
Task 4.1	Component Design and Development	50%	New concept being incorporated
Task 4.2	System Integration and Simulation Analysis	50%	Analyses of new system concept to be made
Task 5.0	Economic Analysis	15%	Economic analysis of commercial microalgal CO 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 July 2004 to 30 September 2004.

3. Experimental

3.1 Task 3: Optimization and Demonstration of Industrial Scale Photobioreactor

Carbon Sequestration into Mineral Carbonates

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

In our previous work, at bench-top scale, we made the argument that as the pH of a culture increases caused by photosynthetic CO₂ uptake, the proportion of CO₃⁼ in the medium increases. The increased availability of CO₃⁼ in the medium increases the probability that it would react with Ca²⁺ ions to form CaCO₃, which represents a stable form of carbon useful for long-term sequestration of CO₂. Furthermore, the concentration of CO₃⁼ can also be increased without a change in pH if the total alkalinity of the medium increases. In our previous reports, we reported our first attempts to model the changes in alkalinity in the medium that results from the cells photosynthetic and growth activities.

Photosynthetic uptake of CO₂ produces changes in the pH of the medium but does not change the alkalinity *per se*. However, other growth processes, such as the uptake of NO₃⁼ and H₂PO₄⁼ do (Eq. (1)). The stoichiometry of photosynthesis-based cellular growth indicates that for every 106 moles of CO₂ taken up 16 moles of NO₃⁼ and 1 mole H₂PO₄⁼ are taken up. At the same time, 17 moles of H⁺ are taken up from the medium which results in an equivalent increase in alkalinity.

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

In this quarter, we have continued the analysis presented in QR#15 to include data obtained from outdoor photobioreactor cultures growing two more microalgal strains (AQ0033, *Porphyridium sp.* and AQ0073, *Botryococcus braunii*) on actual coal and propane combustion gases.

The cultures were grown as per our standard operating procedures. The culture's pH was controlled (7.4-7.6 for AQ0033 and 7.8-8.2 for AQ0073) by direct injections of CO₂ or coal combustion gases into the medium. Every morning, pH and alkalinity determinations were conducted on samples from the photobioreactor (PBR) cultures as described in previous

Quarterly Reports. From the pH and alkalinity values, the concentrations of the different dissolved inorganic carbon species in the medium were calculated as described previously.

3.2 Subtask 3.1: Pilot Evaluation of Coal Combustion Gases

During this quarter we have continued to work with the coal reactor. Specifically we have completed design modifications that allows us longer burn times needed to support microalgal culture growth. The custom-built coal combustor (Figure 2) is utilized to burn bituminous coal from the Upper Freeport Mine. A vacuum pump is used to transfer the gases from the combustor to the PBR. In this report we present the first set of results of large scale microalgal cultures grown on coal combustion gases.

G-8745

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

This quarter we have attempted two large scale experiment with strains AQ0033 (*Porphyridium sp.*) and AQ0073 (*Botryococcus braunii*). Cultures were grown in our scale-up MGM photobioreactors at pH 7.4-7.6 for AQ0033 and 7.8-8.2 for AQ0073 following our standard operating procedures. The cultures were initially grown using pure CO₂ and, after a few days, coal combustion gases were used. Gas additions, whether pure CO₂ or stack gases, were added to the PBR cultures on demand, i.e., when the pH of the cultures indicated lowering of the concentration of CO₂ in the medium.

Data was collected daily on the concentration of biomass 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

$\text{CO}_3^{=}$ and total dissolved inorganic carbon (DIC). The pH of the cultures was continuously monitored by our computerized monitoring and control system. Changes in pH and alkalinity were used to estimate the rate of carbon assimilation by the microalgal cells as described above.

3.3 Subtask 3.2: Full Scale Production Runs

The goal of our final set of experiments is to optimize gas delivery systems for photobioreactor performance at present commercial scale. These experiments are conducted in Mera Growth Modules (MGM), the commercial PBRs on which current economic models are based. Flue gas is supplied by a slipstream from the existing propane combustor to the commercial scale bioreactors. The composition of the flue gas can be modified as needed by the addition of more CO_2 and acid gases in order to simulate the flue gas compositions determined in Task 1 if needed.

Based on the results of Task 1.3, we will optimize the gas injection system for maximum dissolution of CO_2 . We will conduct experiments in the 25,000-L MGM using propane combustion product flue gas supplied by the system developed and using the species of microalgae selected for large-scale experiments.

This quarter we have conducted two large scale experiment with strains AQ0033 (*Porphyridium sp.*) and AQ0073 (*Botryococcus braunii*). Cultures were grown in our commercial scale MGM photobioreactors at pH 7.4-7.6 for AQ0033 and 7.8-8.2 for AQ0073. The parent cultures used in these experiments were those generated during the coal combustion experiments, above. The cultures were initially grown using pure CO_2 and, after one to a few days, propane combustion gases were used. Gas additions, whether pure CO_2 or stack gases, were added to the PBR cultures on demand, i.e., when the pH of the cultures indicated lowering of the concentration of CO_2 in the medium.

Data was collected daily on the concentration of cells in the cultures to estimate growth rate and carbon capture, the fluorescence yield of the cultures (as described earlier) and the pH and alkalinity of the cultures' medium to estimate the concentration of CO_2 , HCO_3^- and $\text{CO}_3^{=}$ and total dissolved inorganic carbon (DIC). The pH of the cultures was continuously monitored by our computerized monitoring and control system. Changes in pH and alkalinity were used to estimate the rate of carbon assimilation by the microalgal cells as described above. Problems with our data acquisition system limited the amount of useful data available.

3.4 Subtask 3.3: Algae Separation and Final Product

We have not conducted any work under this subtask this quarter.

4. Results and Discussion

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

4.1 Task 1: Supply of CO₂ from Power Plant Gas to Photobioreactor

Most of the work within the two subtasks (Task 1.1: Power Plant Exhaust Characterization and Task 1.2: Selection of CO₂ Separation and Cleanup Technologies) has been conducted during the previous reporting periods. No additional activity was made during the present reporting period.

4.2 Task 2: Selection of Microalgae

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

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 (up to) 2,000 liter enclosed PBRs (pilot scale MGM, Task 3.1) and actual coal combustion gases as the carbon source for the microalgal cultures. Second, we are conducting full scale production runs using 25,000 liter enclosed PBRs (full scale MGM, Task 3.2) and actual combustion gases from a propane burner as the carbon source for the algal cultures. Concurrently, research into the appropriate technologies for harvesting and processing the produced biomass will be conducted (Task 3.3). At the same time we are investigating the scale up of carbon sequestration into relatively stable compounds such as carbonates which would generate a long-lived and easy-to-store form of sequestered carbon.

Carbon sequestration into mineral carbonates

In our previous quarterly reports (QR#14 and #15) we showed that as the microalgal cultures grow and take up NO₃⁻ and H₂PO₄⁻ from the medium, both the alkalinity and concentration of dissolved inorganic carbon increase in the medium. This direct effect of photosynthesis-driven growth constitutes carbon sequestration into dissolved inorganic carbon (DIC). During this quarter we have extended our observations to cultures of strain AQ0033 and AQ0073, including those grown on coal combustion gases.

Experiments with strain AQ0073

The mother culture for these experiments became contaminated with an unknown strain of microalgae. Regardless, we decided to go ahead and run the experiments with the mixed population. On July 17 we started a 1120 liter culture (AQ0073-040717) in one of our scale up

PBRs. The culture was fed CO_2 on demand. As was found on previous cultures fed exclusively CO_2 , the alkalinity of the culture increased over time caused by the uptake of NO_3^- and H_2PO_4^- as it grew (Figure 3 top panel). This translated in an increase in all species of dissolved inorganic carbon (DIC, Figure 3 bottom panel).

Figure 3. Changes in alkalinity (top panel) and dissolved inorganic carbon species (bottom panel) in the medium during algal growth fed CO_2 for culture AQ0073-040717.

On July 30, a second culture (AQ0073-040730) was started with material grown in the previous experiment with a total volume of 1690 liters. The culture was fed CO_2 for 2 days initially and then switched to coal combustion gases. Our measurements indicate that while the

alkalinity in the culture medium increased during the first 2 days (while being fed CO_2), it slowly decreased after that. On August 10 a malfunction with the coal combustor forced us to switch the culture back to pure CO_2 . On August 11, part of this culture was used to start up another culture (AQ0073-040811, below) and, thus, it was diluted with fresh growth medium (1000 L). As the data indicates, the alkalinity started increasing again following the switch to pure CO_2 (Figure 4 top panel). The concentration of the different DIC species followed the same pattern (Figure 4 bottom panel).

Figure 4. Changes in alkalinity (top panel) and dissolved inorganic carbon species (bottom panel) in the medium during algal growth fed CO_2 and coal combustion gases for culture AQ0073-040730.

On August 19, a third culture (AQ0073-040819) was started with biomass from culture AQ0073-040730. We had been concerned that the coal combustor could not produce enough CO_2 for a large photobioreactor so, in this case, we used a smaller one (900 liter capacity). The culture was fed pure CO_2 on demand. In this case, the alkalinity of the culture increased over the next few days (Figure 5 top panel) as well as the concentrations of the DIC species (Figure 5 bottom panel).

Figure 5. Changes in alkalinity (top panel) and dissolved inorganic carbon species (bottom panel) in the medium during algal growth fed CO_2 for culture AQ0073-040819.

On August 11, another culture (AQ0073-040811) was started from AQ0073-040730 in a 25,000 liter photobioreactor (24,000 L of culture). After 1 day of feeding CO_2 to the culture, it was switched to propane combustion gases. In this culture, the alkalinity as well as the DIC species, increased continuously during growth of the culture (Figure 6 top and bottom panel).

Figure 6. Changes in alkalinity (top panel) and dissolved inorganic carbon species (bottom panel) in the medium during algal growth fed CO_2 (1 day) followed by propane combustion gases for culture AQ0073-040811.

Experiments with strain AQ0033

On September 1, a 695 liter culture of strain AQ0033 was started in a scale up photobioreactor (AQ0033-040901). For the first week, the culture was fed pure CO_2 on demand and was

then switched to coal combustion gases. Over the next 4 weeks, the culture was fed mainly coal combustion gases except for periods when the coal combustor needed maintenance and/or repairs. We found that, on days when the culture was fed pure CO₂, the alkalinity increased (periods marked in black in Figure 6 top panel). On days when the culture was fed coal combustion gases, the alkalinity dropped (periods marked in red in Figure 7 top panel). On one occasions, part of the culture was harvested and the rest diluted with fresh culture medium, which increased the alkalinity (9/22, arrows in Figure 7). The changes in the concentration of the dissolved inorganic carbon species paralleled the changes in alkalinity (Figure 7 bottom panel).

Figure 7. Changes in alkalinity (top panel) and dissolved inorganic carbon species (bottom panel) in the medium during algal growth fed CO₂ (days in black on top panel) or coal combustion gases (days in red on top panel) for culture AQ0033-040901. Arrows indicate harvest and dilution of the culture with fresh medium.

On September 22, a 24,000 liter culture of strain AQ0033 (AQ0033-040922) was started with biomass harvested from AQ0033-040901, above. During the first 5 days, the culture was fed pure CO₂ on demand. As it occurred in the previous cultures, the alkalinity and dissolved inorganic carbon species increased daily (Figure 8 top and bottom panels). After the first 5 days a catastrophic failure of the photobioreactor forced us to loose the culture.

Figure 8. Changes in alkalinity (top panel) and dissolved inorganic carbon species (bottom panel) in the medium during algal growth fed CO₂ for culture AQ0033-040922.

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). Results presented in previous reports indicated that cultures grown with either pure CO₂ or propane combustion gases resulted in increased alkalinity and dissolved inorganic carbon in the culture medium, indirectly driven by photosynthetic NO₃⁻ and H₂PO₄⁻ uptake. Those results have been confirmed with further microalgal strains. We have now found that the reverse is true in cultures fed coal combustion gases. In every case when a culture was fed coal combustion gases, the alkalinity and dissolved inorganic carbon concentration dropped. This means that the secondary benefit of capturing inorganic carbon in the culture medium found in CO₂- and propane-fed cultures is non existing in coal-fed cultures. Furthermore, the loss of alkalinity in those cultures represents a lowering of the efficiency in carbon capture and sequestration. At this point, we assume that this is an effect of the acid gases (NO_x and SO_x) produced by the combustion of coal. Data from the gas analyzer monitoring the output of the coal combustor during the experiments with AQ0073-040730 and AQ0073-040819 indicated that while the concentration of CO₂ in the flue gas varied between 2% and 4%, the concentrations of NO_x and SO_x ranged between 100 and 200 ppm (NO_x) and up to 500 ppm (SO_x) (Figure 9). In the next quarter, more culture experiments will be carried out with coal combustion gases as well as a modeling effort to understand the effect of SO_x and NO_x on the medium alkalinity.

Figure 9. Analysis of the flue gas produced by the coal reactor during experiments with cultures AQ0073-040730 and AQ0073-040819.

4.4 Subtask 3.1: Pilot Evaluation of Coal Combustion Gases

As indicated in previous Quarterly Reports, a number of technical problems associated with the coal combustor have significantly delayed progress in this part of the research program. During this quarter, further modifications to the coal combustor have been carried out that have resulted in burns of sufficient length to allow growing cultures with actual coal combustion gases.

As was indicated in our previous report, during testing in early June we discovered that the furnace thermocouple and wiring showed signs of wear and the furnace elements did not measure at the proper resistance. A new thermocouple, furnace heating elements and wiring material were ordered from the factory. Unfortunately, these parts were not in stock and had to be manufactured. The parts finally arrived in late June.

The first firing of the coal reactor, with the new large ash box, enlarged furnace exit pipe installed, and heating elements occurred on July 2nd. Subsequent test burns were conducted through July 12th with only minor problems. The most significant of which was that the coal feeder clogged and the diffuser at the top of the reactor had to be cleaned. After approximately 20 hours of operation the furnace pressure and the furnace pressure drop indicated that the furnace was plugged. The furnace was shut down for inspection.

Upon inspection we discovered ash build up at the top and bottom of the alumina retort as well as in ash can. The furnace and ash can were cleaned and reassembled. It is noted that the furnace and ash box must be cleaned after approximately 20 hours of operation (5 days to 1 week of supplying flue gas to a growth module). Test burns to determine optimum-burning parameters and conditions continued without incident through the 21st of July.

The coal reactor was fitted with automatic controls so that the pH in the growth module would control the coal feeder and the compressed air to the coal feeder vibrator. Then from August 2nd the coal reactor was hooked to an active growth module.

During the weekly cleaning on August 10th, the Alumina Retort and some of the heating elements were broken. New parts were ordered. However, an extremely long lead-time to manufacture the heating elements prompted us to rewire the furnace to operate on only 14 elements (normally 18). However, with only 14 heating elements operating the amperage draw was too great for the existing main electrical feed. The main electrical feed was upgraded from #10 AWG copper wire to #6 AWG copper wire.

Regular burns and normal weekly cleaning occurred from the 20th of August to September 7th. The main vacuum pump delivering air and flue gas to the growth module and the gas analyzer failed on September 7th, however we were able to switch to a spare. The spare only lasted long enough for the repair of the primary vacuum pump to be completed (approximately two hours) and then the spare also failed. We discovered that the pump failures were caused by a unique characteristic of the algae being cultivated in the growth module to form large “clumps”, which over time blocked the flow of flue gas into the growth module and created undue backpressure on the main vacuum pump. We modified the dispersion tube to accommodate a

higher volume of gas flow, which allowed for proper gas flow into the module and kept the “clumped” algae from blocking the gas dispersion tube in the module.

The CO₂ sensor in the gas analyzer failed on September 17th. A new sensor was ordered and then installed on September 27th.

Operating problems with the coal reactor and the gas analyzer have plagued this project from the beginning, however at this point both the gas analyzer and the coal reactor are operating smoothly enough to produce usable data.

During this quarter, two outdoor photobioreactor cultures were exposed to coal combustion gases, AQ0073-040730 and AQ0033-040901. In both cases, the cultures were started with pure CO₂ as the carbon source and later switched. The fluorescence-based biomass estimates indicate that the cultures grew as well under both conditions (Figure 10).

Figure 10. Fluorescence-based biomass estimates for culture AQ0073-040730. Green lines indicate periods during which the culture was fed coal combustion gases.

From the pH and alkalinity data, we have estimated the rate at which CO₂ disappears from the medium in both cultures. The rate, at night, represents degassing of CO₂ from the culture while the rate during the day represents the both degassing of CO₂ plus photosynthetic uptake by the algal biomass. The results are presented in Figure 11. The disappearance rates tend to be higher for the AQ0073-040901 culture since this culture was kept at 7.5 pH (versus 8.0). The lower pH indicates higher CO₂ concentration in the medium which results in higher degassing rates, although it is also dependent on the alkalinity of the medium (see Figures 4 and 7).

Figure 11. Rates (daily averages) of CO₂ disappearance from the culture medium during the day and night periods.

Finally, we have considered the difference in the degassing rates between night and day to obtain estimates of photosynthetic CO₂ capture by the algal biomass. We have normalized those estimates to the fluorescence-based biomass estimates in those cultures. We present those results in Figure 12. Based on this limited data set it is difficult to state whether coal combustion gases lower the photosynthetic capacity of the cultures (versus CO₂). As further experiments are carried out in the next two quarters, we expect to be able to make that determination.

Figure 12. Biomass-normalized rates of photosynthetic carbon capture by the microalgal cultures for periods when the cultures were fed CO₂ versus coal combustion gases.

4.5 Subtask 3.2: Full Scale Production Runs

During this quarter we have attempted to culture two microalgal strains (AQ0033 and AQ0073) in full scale PBRs being fed pure CO₂ and propane combustion gases. We had tried to run such an experiment with AQ0073 during the last reporting period but were unsuccessful. This time around, after a structural failure of the photobioreactor used for AQ0033, we had to stop the experiment after 4 days. We expect to continue the work with AQ0033 in the next quarter and limit ourselves to reporting the results obtained with the AQ0073 culture at this time. As in previous experiments, we have averaged the CO₂ disappearance rate over each day and night period for this culture. As in previous experiments, the data indicate that as the cultures grew older (more biomass in the culture and higher alkalinity, see Figure 6), the calculated rates of DIC disappearance increased (Figure 13). This is a direct result of increased dissolved CO₂ concentration in the medium and the resulting rate of CO₂ degassing during the night periods (see below) and degassing plus photosynthetic carbon capture during the day.

Figure 13. Daily-averaged rates of CO₂ disappearance from the medium during day and night periods. The culture was fed propane combustion gases after the first day of culture.

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 14 and corroborate the dependency of degassing of CO₂ from the medium on the concentration of CO₂ in the medium as was reported in previous experiments (QR#12-QR#15). In all cases, and as was the case for the pilot and full scale experiments (previous reports), more CO₂ is lost from the medium at higher CO₂ concentrations in the medium.

Figure 14. Relationship between CO₂ concentration in the culture medium and nighttime rate of CO₂ disappearance from the medium (degassing).

4.6 Subtask 3.3: Algae Separation and Final Product

No activity under this subtask was performed during this reporting period.

4.7 Task 4.2: System Integration

No activity under this subtask was performed during this reporting period.

5. **Conclusion and Future Plans**

5.1 Task 3: Optimization and Demonstration of Industrial Scale Photobioreactor

In this quarter, we have been able to run the first set of experimental cultures fed coal combustion gases. We have found that such cultures do not sequester carbon in the growth medium (as opposed to cultures fed pure CO₂ or propane combustion gases).

Specifically we have:

- Extended our observations that microalgal photosynthetic CO₂ capture does not only results in assimilation of organic carbon but also increases the concentration of inorganic carbon in the medium using more microalgal strains, when the cultures are fed pure CO₂ or propane combustion gases, but not when fed coal combustion gases.
- Run the first set of experimental cultures fed coal combustion gases.
- Extended our observations of carbon capture by microalgae from actual propane combustion gases at commercial scale.

Within the next quarter we expect to

- Continue full experimental runs with microalgal cultures fed coal combustion gases.
- Continue propane-fed, full scale, photobioreactor experiments with further strains of microalgae.
- Produce a model to account for the loss of alkalinity in cultures fed coal combustion gases.

5.2 Task 5: Economical Analysis

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

- Continue development of the economic model to be used in predictions of carbon sequestration cost for a number of different scenarios.
- Incorporate productivity parameters for the different microalgal strains as determined during Tasks 2 and 3 of this project.

- Continue large scale centrifugation and separation experiments that will test our cost predictions based on our centrifugation cost models presented in previous quarterly reports.

6. References

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