PSI-1356

Recovery and Sequestration of CO_2 from Stationary Combustion Systems by Photosynthesis of Microalgae

Quarterly Technical Progress Report #17

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Prepared by

Dr. Takashi Nakamura

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U.S. DEPARTMENT OF ENERGY
National Energy Technology Laboratory
P.O. Box 10940
Pittsburgh, PA 15236

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

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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 CO_2 from stationary combustion systems by photosynthesis of microalgae. The research is aimed primarily at demonstrating the ability of selected species of microalgae to effectively fix carbon from typical power plant exhaust gases.

This report covers the reporting period 1 October to 31 December 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 century[1] leading to increased concentrations of carbon dioxide in the atmosphere. While there is still much debate on the effects of increased CO_2 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 CO_2 emissions. Meeting this demand without huge increases in CO_2 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 CO_2 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.[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 CO_2 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 ~ 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 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.[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 CO_2 uptake
2. Mineralization of CO_2, resulting in permanently sequestered carbon
3. Revenues from substances of high economic value
4. Use of concentrated, anthropogenic CO_2 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 CO_2 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 CO_2 gas is not required for algae culture. It is possible that flue gas containing 2~5% CO_2 can be fed directly to the photobioreactor. This will simplify CO_2 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.

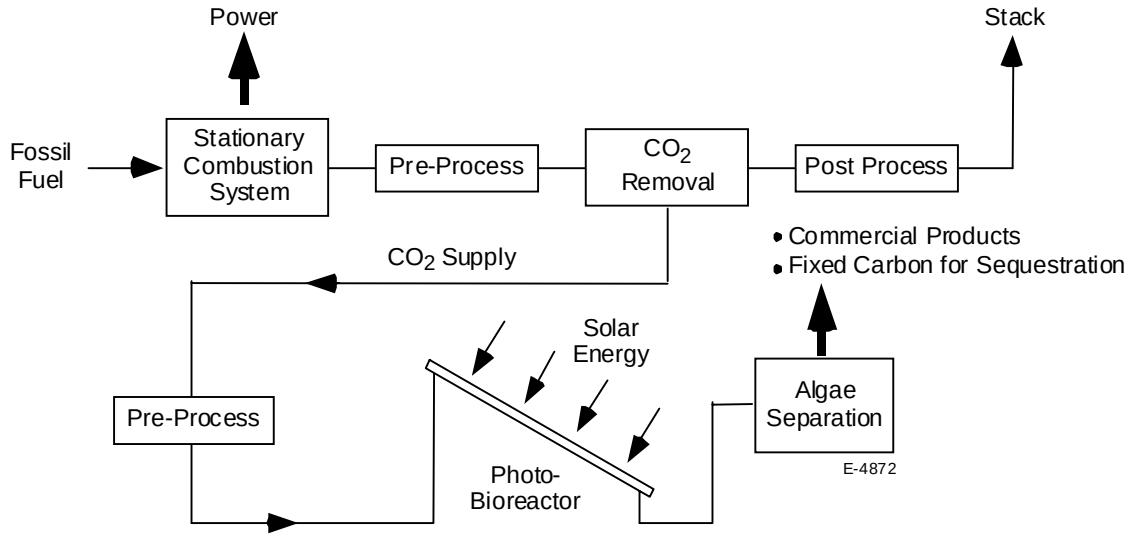

Figure 1. Recovery and sequestration of CO_2 from stationary combustion systems by photo-synthesis of microalgae.

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 CO_2 into aquatic media; and (3) converting CO_2 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 CO_2 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 CO_2 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 stains of microalage (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: CO_2 removal process; CO_2 injection device; photobioreactor; product algae separation process; and process control devices;

- Developed a photobioreactor design concept for biofixation of CO_2 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 CO_2 were developed using multiple regression;

- A review of the technical literature on tubular photobioreactors progressed;

- A literature study progressed to develop the CO_2 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.

During this reporting quarter, we have continued work on Task 3 (Optimization and Demonstration of Industrial Scale Photobioreactor). Specifically we have

- Continue our experiments with actual coal combustion gases with two different strains of microalgae (AQ0073 and AQ0033);

- Commence scaling up cultures of three more strains (AQ0011, AQ0012 and AQ0024) for experimentation with coal combustion gases (scheduled for next quarter); and

- Run further full scale, carbon sequestration tests with actual propane combustion gases using strains AQ0033 and AQ0073.

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	80%	Demonstrate viability of CO_2 with algae at industrial scale
Subtask 3.1	Pilot Evaluation	80%	Evaluation at 2000 L pilot scale. Experimental work with coal reactor started
Subtask 3.2	Full Scale Production Runs	85%	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

Tasks	Title	% Complete	Milestone/Status Description
Task 4.2	System Integration and Simulation Analysis	50%	Analyses of new system concept to be made
Task 5.0	Economic Analysis	15%	Economic analysis of commercial microalgal CO_2 sequestration
Task 5.1	Gas Separation Process	85%	Direct exhaust gas injection option to be assessed
Subtask 5.2	Photobioreactor Carbon Fixation Process	15%	Economic analysis of photobioreactor CO_2 fixation
Subtask 5.3	Product Processing	5%	Economic analysis of product processing

The work discussed in this report covers the reporting period from 1 October 2004 to 31 December 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 CO_2 uptake, the proportion of $CO_3^{=}$ in the medium increases. The increased availability of $CO_3^{=}$ in the medium increases the probability that it would react with Ca^{2+} ions to form $CaCO_3$, which represents a stable form of carbon useful for long-term sequestration of CO_2. Furthermore, the concentration of $CO_3^{=}$ 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 CO_2 produces changes in the pH of the medium but does not change the alkalinity *per se*. However, other growth processes, such as the uptake of NO_3^- and $H_2PO_4^-$ do (Eq. (1)). The stoichiometry of photosynthesis-based cellular growth indicates that for every 106 moles of CO_2 taken up 16 moles of NO_3^- and 1 mole $H_2PO_4^-$ are taken up. At the same time, 17 moles of H^+ are taken up from the medium which results in an equivalent increase in alkalinity.

Equation 1

$$106CO_2 + 16NO_3^- + H_2PO_4^- + 122H_2O + 17H^+ \xrightarrow{photosynthesis} \{C_{106}H_{263}O_{110}N_{16}P_1\} + 138O_2$$

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 and QR#16 to include data obtained from outdoor photobioreactor cultures growing 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 CO_2 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. Modifications carried out during the previous two quarters allow 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.

This quarter we repeated 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 CO_2 and, after a few days, coal combustion gases were used. Gas additions, whether pure CO_2 or stack gases, were made 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 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 CO_2, HCO_3^- and $CO_3^=$ 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.

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

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 further 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 $CO_3^=$ 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.

3.4 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 CO_2 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 CO_2 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 CO_2 mineralization utilizing microalgal cultures at a commercially significant scale. This is being done in two phases. First, we are conducting a pilot evaluation using scale-up 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 NO_3^- and $H_2PO_4^-$ 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 further cultures of strain AQ0033 and AQ0073, including those grown on coal combustion gases.

Experiments with strain AQ0073 grown on CO_2, and coal and propane combustion gases

During the previous quarter (see QR#16) we attempted to grow a culture of this strain although it had become contaminated with another unknown microalga. In this quarter we have repeated the experiment with a clean monoculture of AQ0073. On October 14 we started a 565 liter culture (AQ0073-041014) in one of our scale up PBRs. The culture was initially 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). On October 26th the culture's source of CO_2 was switched from pure CO_2 to coal combustion gases. As can be seen in Figure 3, use of coal combustion gases drove lower the alkalinity of the medium as well as the concentration of the dissolved inorganic species (HCO_3^-, CO_3^{2-} and free CO_2). On November 2nd a reversal in the lowering concentrations can be noted. This was caused by the shutdown of the coal combustor for maintenance and use of pure CO_2 during most of the daylight hours on November 1st.

On November 9th, a large scale culture (AQ0073-041109) was started with the material produce in the previous experiment for a total volume of 25,000 liters. The culture was started with pure CO_2 but was switched to propane combustion gases on the evening of November 12th. The culture was grown for a further 15 days. The results of the alkalinity and dissolved inorganic carbon species analysis indicate continues accumulation of inorganic carbon in the culture's medium, whether when fed pure CO_2 or propane combustion gases (Figure 4).

With these two experiments using strain AQ0073 we have demonstrated that while the use of either pure CO_2 or propane combustion gases as the source of CO_2 for the culture, the medium accumulates inorganic carbon as a result of photosynthetic growth by the microalgal cells. We have also confirmed that when grown on coal combustion gases the medium's concentration of alkalinity and dissolved inorganic carbon decreases caused by the acidity of the NO_X and SO_X components of the gas stream.

Experiments with strain AQ0033 grown on CO_2 and coal combustion gases

In our previous report we showed partial results obtained with culture AQ0033-040901, started on September 1st, through the end of September. This culture was maintained through October 15th . The complete data set is presented here. For the first week of the growth, the culture was fed pure CO_2 on demand and was then switched to coal combustion gases. Over the next several weeks, the culture was fed mainly coal combustion gases except for periods when

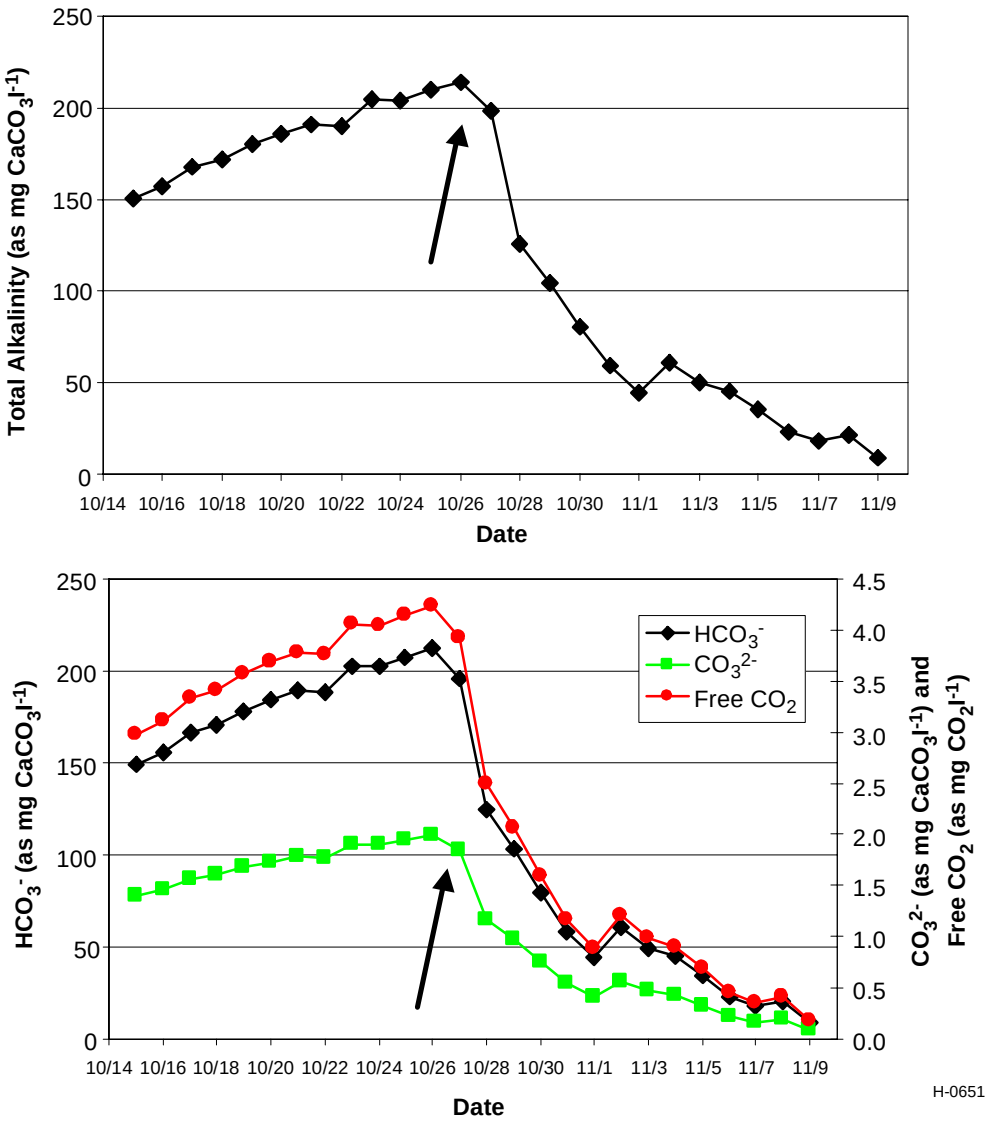

Figure 3. Changes in alkalinity (top panel) and dissolved inorganic carbon species (bottom panel) in the medium during algal growth fed CO_2 for culture AQ0073-041014. The arrows indicate when the gas supply to the culture was switched from pure CO_2 to coal combustion gases.

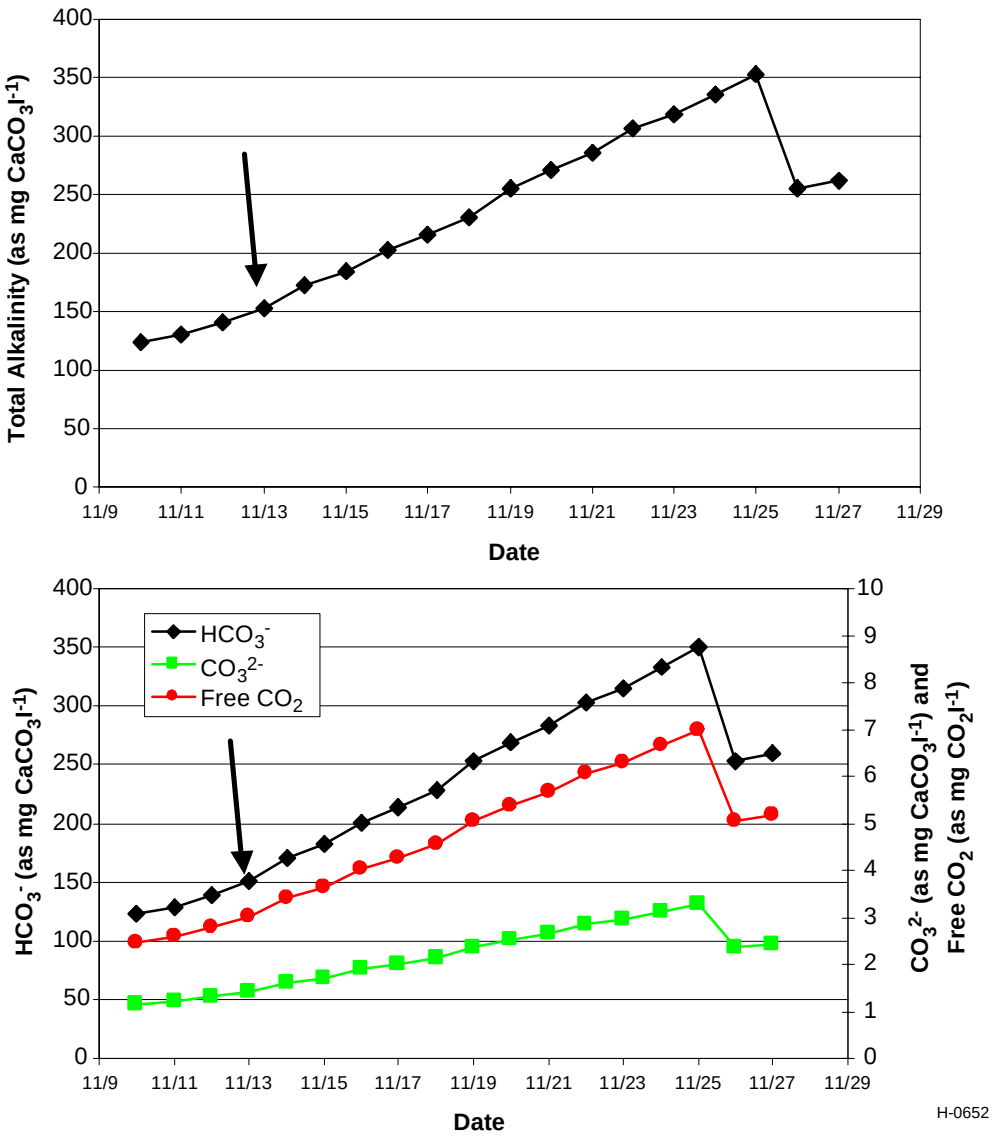

Figure 4. Changes in alkalinity (top panel) and dissolved inorganic carbon species (bottom panel) in the medium during algal growth fed CO_2 and propane combustion gases for culture AQ0073-041109. The drop in alkalinity and inorganic carbon species on November 26th was caused by dilution of the culture with fresh medium. The arrow indicates the switch from CO_2 to propane combustion gases.

the coal combustor needed maintenance and/or repairs. We found that, on days when the culture was fed pure CO_2, the alkalinity increased (periods marked in black in Figure 5 top panel). On days when the culture was fed coal combustion gases, the alkalinity dropped (periods marked in red in Figure 5 top panel). On two occasions part of the culture was harvested and the rest was diluted with fresh culture medium which increased the alkalinity (September 22nd and October 6th, arrows in Figure 5). The changes in the concentration of the dissolved inorganic carbon species paralleled the changes in alkalinity (Figure 4 bottom panel).

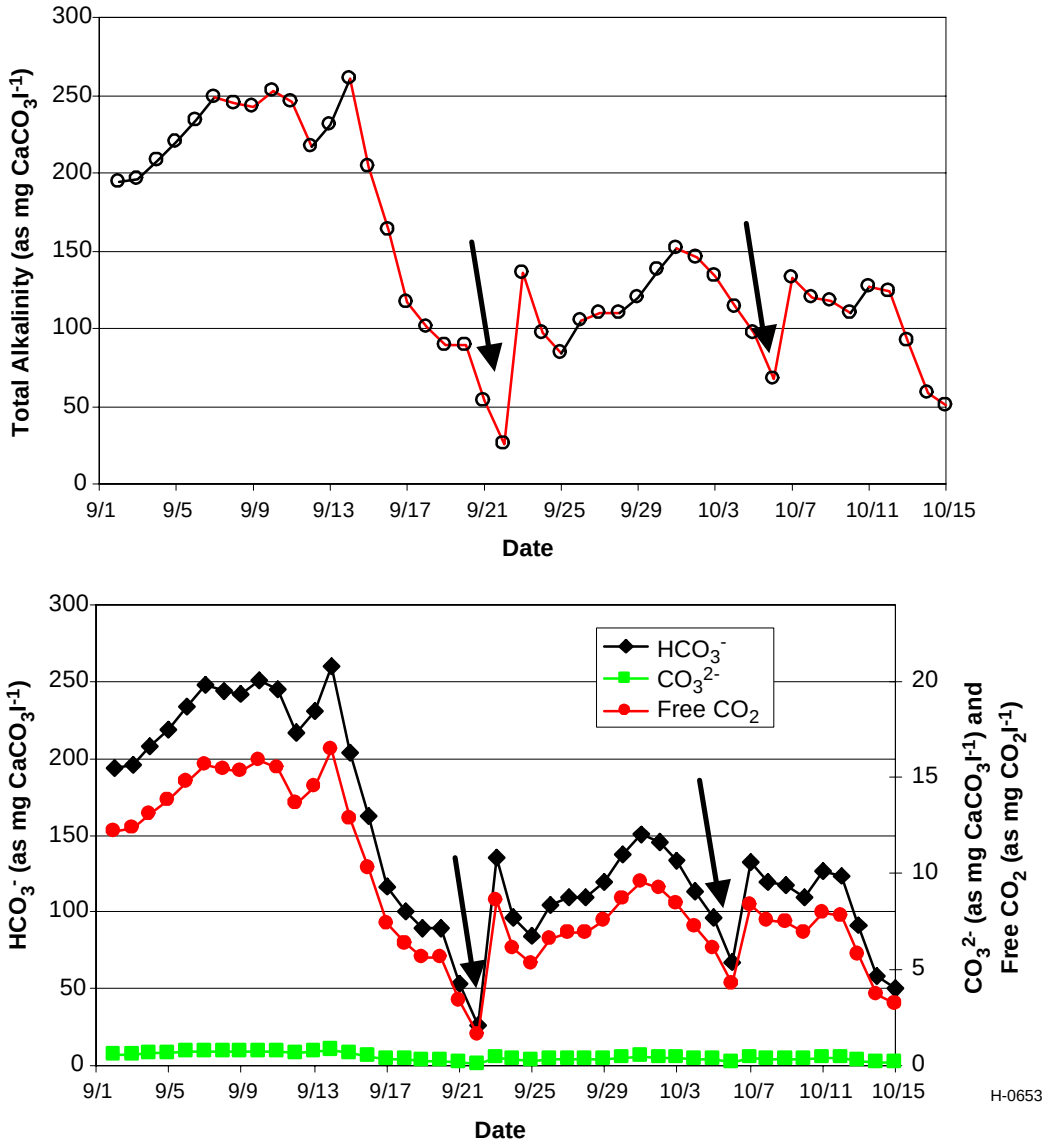

Figure 5. Changes in alkalinity (top panel) and dissolved inorganic carbon species (bottom panel) in the medium during algal growth fed CO_2 (days in black on top panel) or coal combustion gases (days in red on top panel) for culture AQ0033-040901. Arrows indicate harvest and dilution of the culture with fresh medium.

A second experiment with AQ0033 and coal combustion gases was started on November 29th on a scale-up photobioreactor (685 liter, AQ0033-041129). The culture was grown on pure CO_2 until December 22nd when the gas source was switched to coal combustion products. On December 13th the culture was diluted with fresh medium. The results of inorganic carbon species analysis indicates that the alkalinity and dissolved inorganic carbon content of the medium increased caused by growth. As noted elsewhere, dilution with fresh medium decreased the alkalinity and inorganic carbon content of the medium (Figure 6). Unexpectedly, the alkalinity did not rise as rapidly following the medium dilution. After December 22nd, following the change to coal combustion gases, the alkalinity and inorganic content of the medium decreased. On January 2nd, the culture was fed pure CO_2 for the last three days which resulted in slight increases in alkalinity and dissolved inorganic carbon in the medium.

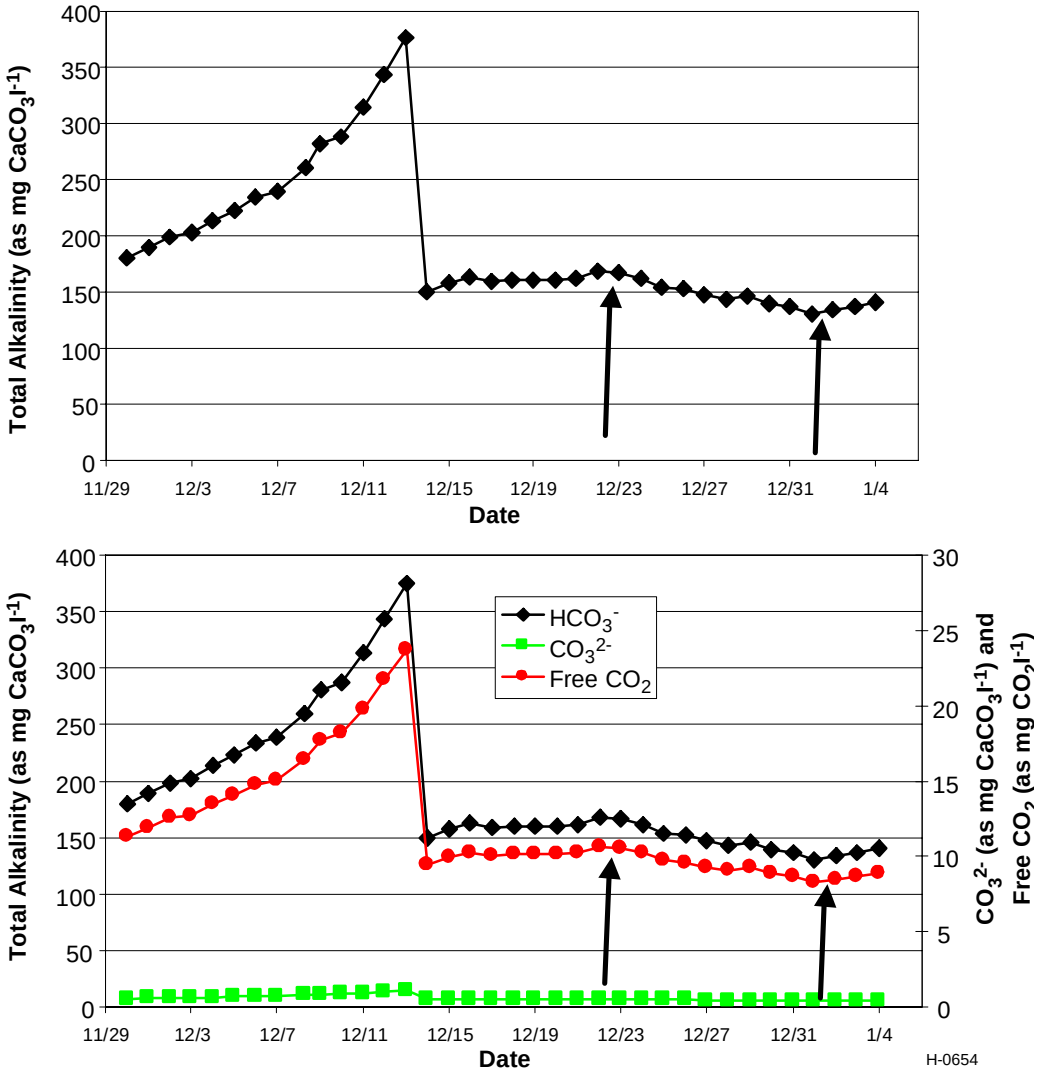

Figure 6. Changes in alkalinity (top panel) and dissolved inorganic carbon species (bottom panel) in the medium during algal growth fed CO_2 and coal combustion gases for culture AQ0033-041129. The period between the arrows indicate the time during which coal combustion gases were used to provide CO_2 to the culture.

On October 6th, we started a culture with strain AQ0033 for a full scale experiment (AQ0033-041006, 24500 liters). The culture was fed pure CO2 and allowed to grow in preparation for a propane combustion gases experiment. Unfortunately, the culture needed to be terminated before the switch to propane combustion gases. The inoculum for this experiment was obtained from culture AQ0033-040901, which had been grown on coal combustion gases (see Figure 5). While the parent culture's alkalinity and inorganic carbon content decreased in response to coal combustion gases, this culture's growth resulted in increases in alkalinity and dissolved inorganic carbon (Figure 7).

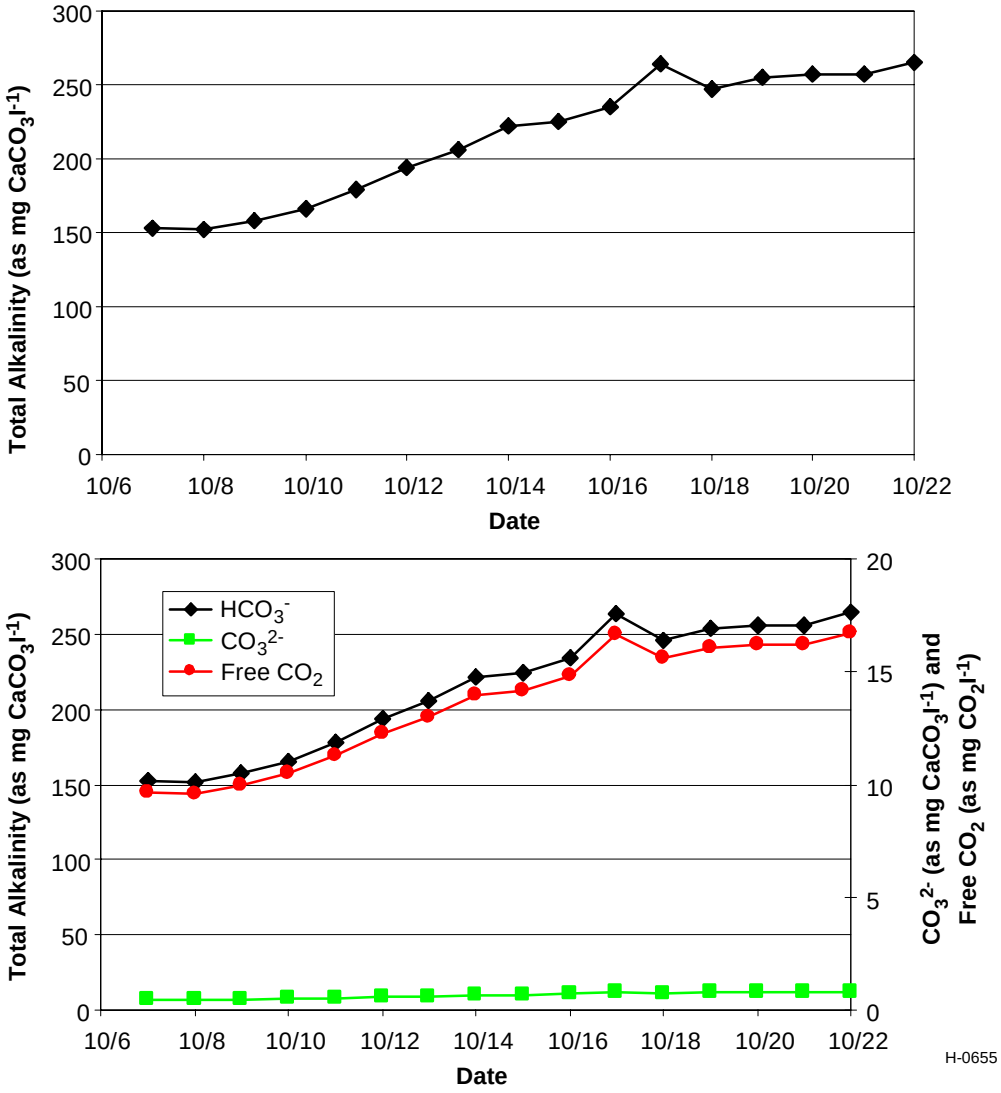

Figure 7. Changes in alkalinity (top panel) and dissolved inorganic carbon species (bottom panel) in the medium during algal growth fed CO_2 for culture AQ0033-041006.

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 CO_2 or

propane combustion gases resulted in increased alkalinity and dissolved inorganic carbon in the culture medium, indirectly driven by photosynthetic NO_3^- and $H_2PO_4^-$ uptake. Those results have been confirmed with further microalgal strains. We have now confirmed 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 CO_2- 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 experiment with culture AQ0033-040901 indicated the gas stream to contain 3-4.5% CO_2, 150-350 ppm NO_X and 200-500 ppm SO_X (Figure 8). The concentrations of the gases exiting the photobioreactor were lower in all cases. To determine whether any of the three components are more likely to be captured by the photobioreactor we calculated the ratios of NO_X/CO_2, SO_X/CO_2 and SO_X/NO_X before and after passage through the photobioreactor. The results are shown in Figure 9. We have calculated the average ratios for the period shown in Figure 9 which are:

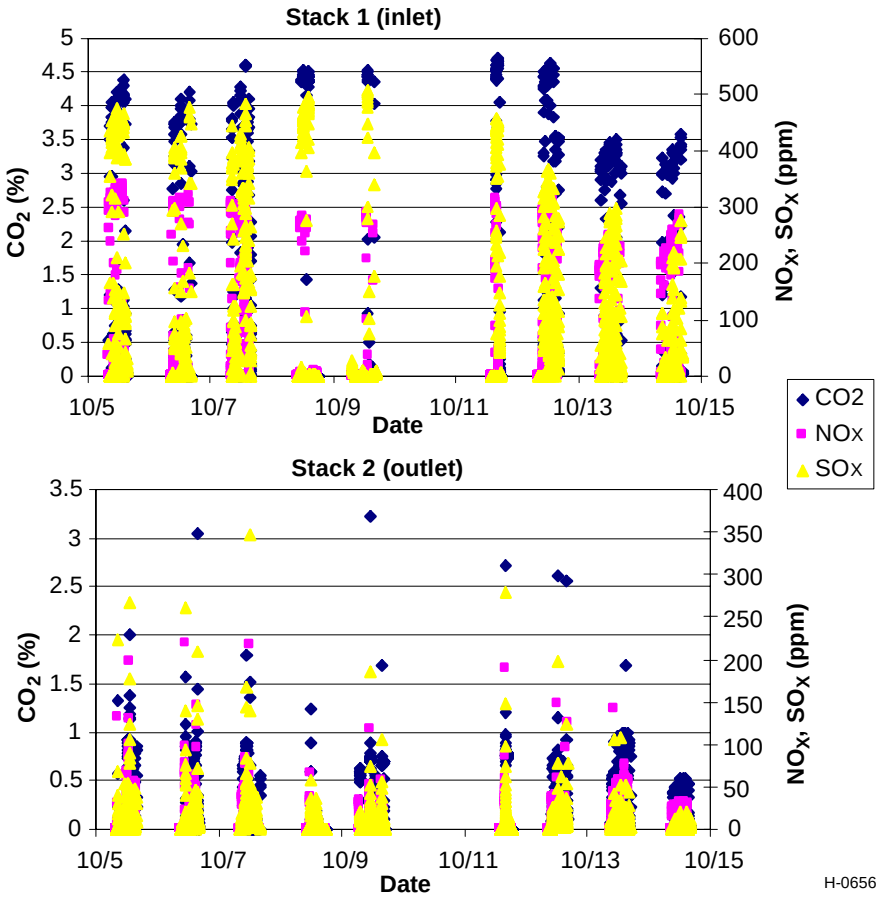

Figure 8. Analysis of the *flue gas produced by the coal reactor during experiments with culture AQ0033-04090 (top panel) and of the gas exiting the photobioreactor.*

	NO_X/CO_2	SO_X/CO_2	SO_X/NO_X
Before passage	87.98	171.89	2.48
After passage	64.01	54.39	0.83

The decrease in NO_X/CO_2 SO_X/CO_2 after passage through the photobioreactor indicates that NO_X and SO_X are taken up preferentially by the culture medium over CO_2.
We are now starting to incorporate these observations into a simple model to understand the effects of SO_X and NO_X on the medium alkalinity.

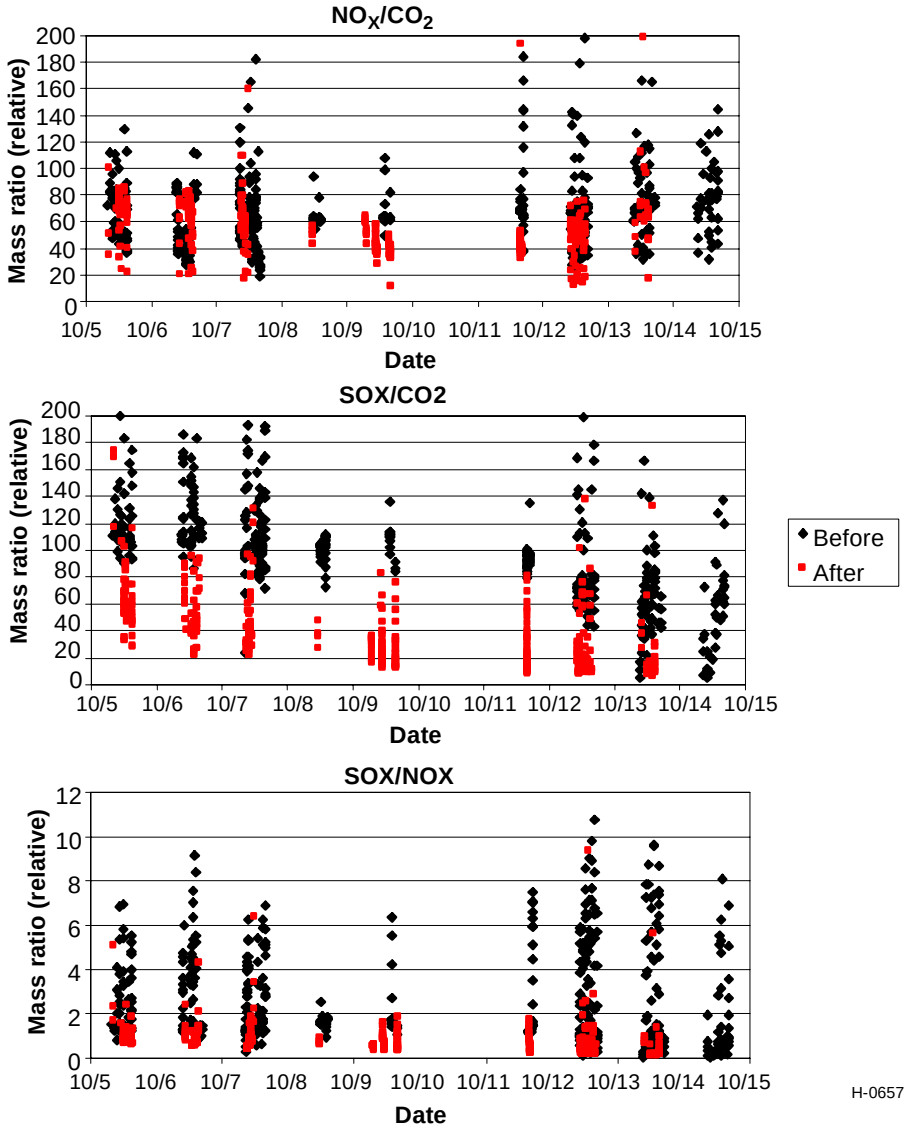

Figure 9. Relative mass ratios of NO_X/CO_2, SO_X/CO_2 and SO_X/NO_X in the gas stream before and after passage through the photobioreactor.

4.4 Subtask 3.1: Pilot Evaluation of Coal Combustion Gases

During this quarter, as noted above, three different cultures were grown while exposed to coal combustion gases (AQ0073-041014, AQ0033-040901 and AQ0033-041129)

In all cases, the cultures were started with pure CO_2 as the carbon source and later switched coal combustion gases. The fluorescence-based biomass estimates indicate that the cultures grew as well under both conditions (Figure 10). It is not clear why AQ0033-041129 grew slower following the culture's dilution with fresh medium but both under CO_2 and coal combustion gases it grew slower than AQ0033-040901.

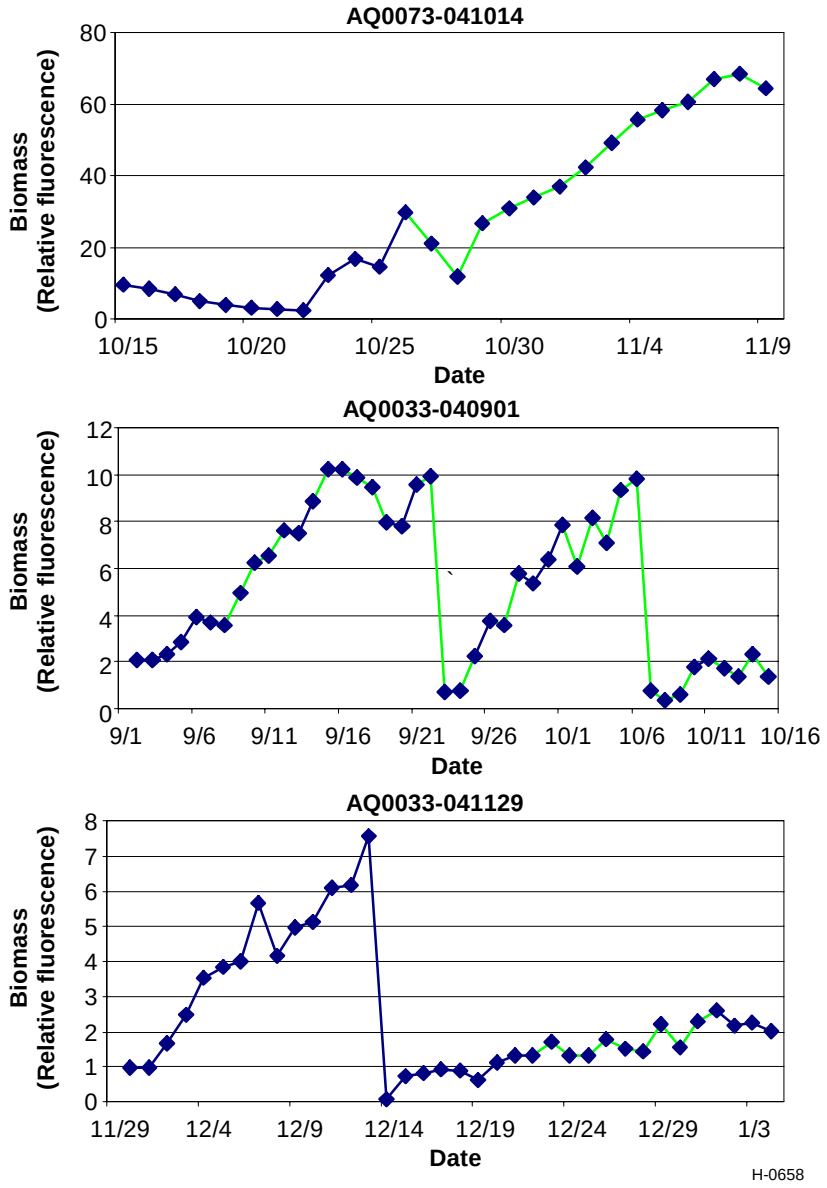

Figure 10. Fluorescence-based biomass estimates for culture AQ0073-040730. Green lines indicate periods during which the culture was fed coal combustion gases instead of pure CO_2. Large, 1-day, drops in biomass indicate dilution of the culture with fresh medium.

As in previous experiments, we will estimate the rate at which CO_2 disappears from the medium in the cultures from the pH and alkalinity data. The rate, at night, represents degassing of CO_2 from the culture while the rate during the day represents the both degassing of CO_2 plus photosynthetic uptake by the algal biomass. Those results will be presented in our next quarterly report.

4.5 Subtask 3.2: Full Scale Production Runs

During this quarter we have repeated our attempts to culture two microalgal strains (AQ0033 and AQ0073) in full scale PBRs being fed pure CO_2 and propane combustion gases.

On October 6th we started a 25000 liter culture with strain AQ0033 (AQ0033-041006). We had tried to run such an experiment with AQ0033 during the last reporting period but were unsuccessful due to a structural failure of the photobioreactor. This time around, a green alga contaminated the culture growing AQ0033 and, similarly, we stopped the experiment before switching the culture from CO_2 to propane combustion gases. We will attempt to run this experiment a third time during the next quarter. The biomass levels measured in this culture are shown in Figure 11. The rapid increase in biomass noted during the last few days of culture were caused by the contaminating organism.

On November 9th we started a 25,000 liter culture with strain AQ0073 (AQ0073-041109). Initially, the culture was grown on pure CO_2, which was switched to propane combustion gases on the evening of November 12th. The levels of biomass achieved are shown in Figure 10. According to that data, AQ0073 grew nearly as fast during the first few days following the switch to propane gases as it had with pure CO_2. However, after November 18th, the fluorescence-based biomass estimates indicate a drop. At this point, it is not clear what caused this since, according to the alkalinity data, the culture continued to grow (Figure 4). The continued increase in alkalinity indicates that NO_3^- and $H_2PO_4^-$ were still being consumed.

As in previous experiments, we will estimate the rate at which CO_2 disappears from the medium in the cultures from the pH and alkalinity data. The rate, at night, represents degassing of CO_2 from the culture while the rate during the day represents the both degassing of CO_2 plus photosynthetic uptake by the algal biomass. Those results will be presented in our next quarterly report.

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.

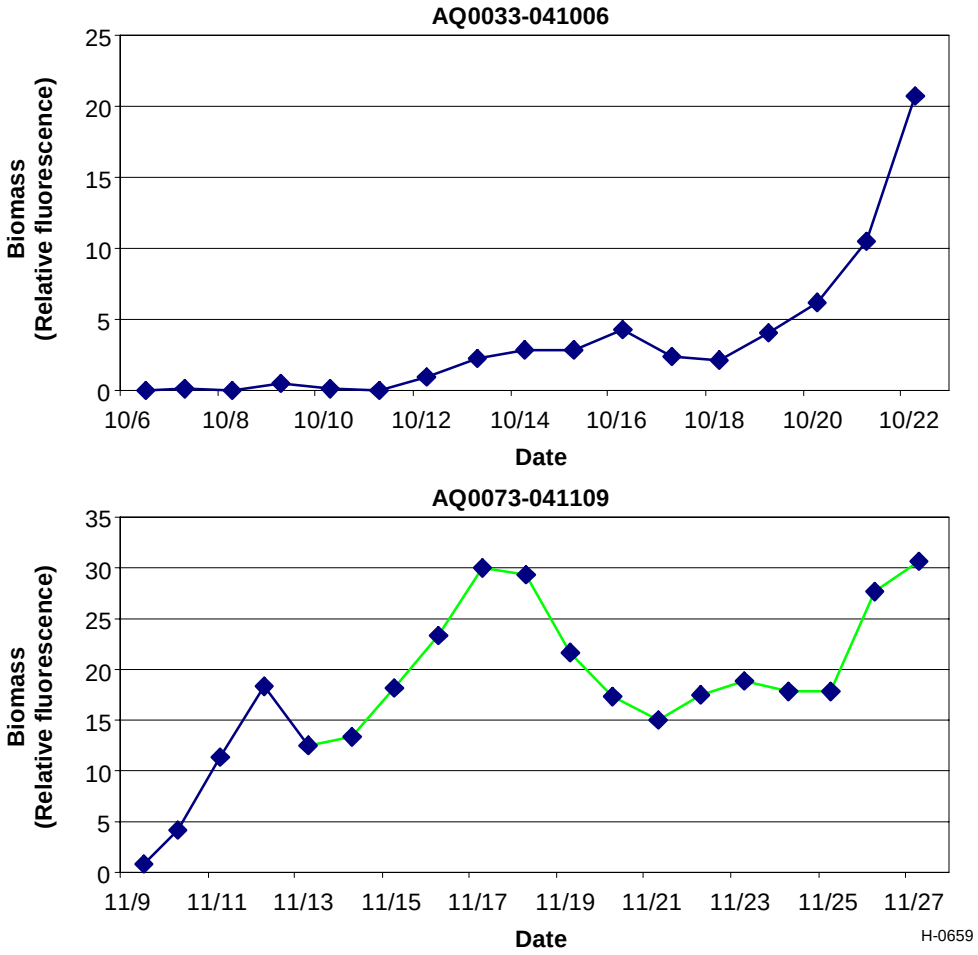

Figure 11. Fluorescence-based biomass estimates for cultures AQ0073-041109 and AQ0033-041006. Green lines indicate periods during which the culture was fed propane combustion gases instead of pure CO_2. Due to slow growth and contamination we terminated the experiment with strain AQ0033 before switching to propane combustion gases.

5. Conclusion and Future Plans

5.1 Task 3: Optimization and Demonstration of Industrial Scale Photobioreactor

In this quarter, we have continued to run experimental cultures fed coal and propane combustion gases. We have confirmed that cultures fed coal combustion gases do not sequester carbon in the growth medium (as opposed to cultures fed pure CO_2 or propane combustion gases).

Specifically we have:

- Run a second set of experimental cultures fed coal combustion gases.

- Extended our observations of carbon capture by microalgae from actual propane combustion gases at commercial scale.

- Extended our observations that microalgal photosynthetic CO_2 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 CO_2 or propane combustion gases, but not when fed coal combustion gases.
  Within the next quarter we expect to

- Continue full experimental runs with microalgal cultures fed coal combustion gases using strains AQ0011 and AQ0012.

- 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]