

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

Quarterly Technical Progress Report #11

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Prepared by

Dr. Takashi Nakamura

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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 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 2003 in which PSI, Aquasearch and University of Hawaii conducted their tasks. Based on the work during the previous reporting period, PSI delivered its coal reactor to Aquasearch. Aquasearch and PSI continued preparation work on direct feeding of coal combustion gas to microalgae. Aquasearch started their effort on economic analyses of commercial scale photobioreactor. University of Hawaii continued effort on system optimization of the CO₂ sequestration system.

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1. Introduction

Emissions of carbon dioxide are predicted to increase in this century¹ leading to increased concentrations of carbon dioxide in the atmosphere. While there is still much debate on the effects of increased CO₂ levels on global climate, many scientists agree that the projected increases could have a profound effect on the environment. Most of the anthropogenic emissions of carbon dioxide result from the combustion of fossil fuels for energy production. It is the increased demand for energy, particularly in the developing world, which underlies the projected increase in CO₂ emissions. Meeting this demand without huge increases in CO₂ emissions requires more than merely increasing the efficiency of energy production. Carbon sequestration, capturing and storing carbon emitted from the global energy system, could be a major tool for reducing atmospheric CO₂ emissions from fossil fuel usage.

The costs of removing CO₂ from a conventional coal-fired power plant with flue gas desulfurization were estimated to be in the range of \$35 to \$264 per ton of CO₂.² The cost of power was projected to increase by anywhere from 25 to 130 mills/kWh. DoE's goal is to reduce the cost of carbon sequestration to below \$10/ton of avoided net cost.

Photosynthesis has long been recognized as a means, at least in theory, to sequester anthropogenic carbon dioxide. There has been relatively little research aimed at developing the technology to produce a gaseous combustion effluent that can be used for photosynthetic carbon sequestration. However, the photosynthetic reaction process by plants is too slow to significantly offset the point source emissions of CO₂ within a localized area. Aquatic microalgae have been identified as fast growing species whose carbon fixing rates are higher than those of land-based plants by one order of magnitude.

The Department of Energy has been sponsoring development of large-scale photovoltaic power systems for electricity generation. By this analogy, a large-scale microalgae plantation may be viewed as one form of renewable energy utilization. While the PV array converts solar energy to electricity, the microalgae plant converts CO₂ from fossil combustion systems to stable carbon compounds for sequestration and high commercial value products to offset the carbon sequestration cost. The solar utilization efficiency of some microalgae is ~ 5%, as compared to ~ 0.2% for typical land based plants. Furthermore, a dedicated photobioreactor for growth of microalgae may be optimized for high efficiency utilization of solar energy, comparable to those of some photovoltaic cells. It is logical, therefore, that photosynthetic reaction of microalgae be considered as a mean for recovery and sequestration of CO₂ emitted from fossil fuel combustion systems.

Stationary combustion sources, particularly electric utility plants, represent 35% of the carbon dioxide emissions from end-use of energy in the United States.¹ The proposed process addresses this goal through the production of high value products from carbon dioxide emissions. Microalgae can produce high-value pharmaceuticals, fine chemicals, and commodities. In these markets, microalgal carbon can produce revenues of order \$100,000 per kg C. These markets are currently estimated at >\$5 billion per year, and projected to grow to >\$50 billion per year within the next 10 to 15 years. Revenues can offset carbon sequestration costs.

An ideal methodology for photosynthetic sequestration of anthropogenic carbon dioxide has the following attributes:

1. Highest possible rates of CO₂ uptake
2. Mineralization of CO₂, resulting in permanently sequestered carbon
3. Revenues from substances of high economic value
4. Use of concentrated, anthropogenic CO₂ before it is allowed to enter the atmosphere.

In this research program, Physical Sciences Inc. (PSI), Aquasearch, and the Hawaii Natural Energy Institute at the University of Hawaii are jointly developing technologies for recovery and sequestration of CO₂ from stationary combustion systems by photosynthesis of microalgae. The research we propose is aimed primarily at quantifying the efficacy of microalgae-based carbon sequestration at industrial scale. Our principal research activities will be focused on demonstrating the ability of selected species of microalgae to effectively fix carbon from typical power plant exhaust gases. Our final results will be used as the basis to evaluate the technical efficacy and associated economic performance of large-scale carbon sequestration facilities.

Our vision of a viable strategy for carbon sequestration based on photosynthetic microalgae is shown conceptually in Figure 1. In this figure, CO₂ from the fossil fuel combustion system and nutrients are added to a photobioreactor where microalgae photosynthetically convert the CO₂ into compounds for high commercial values or mineralized carbon for sequestration. The advantages of the proposed process include the following:

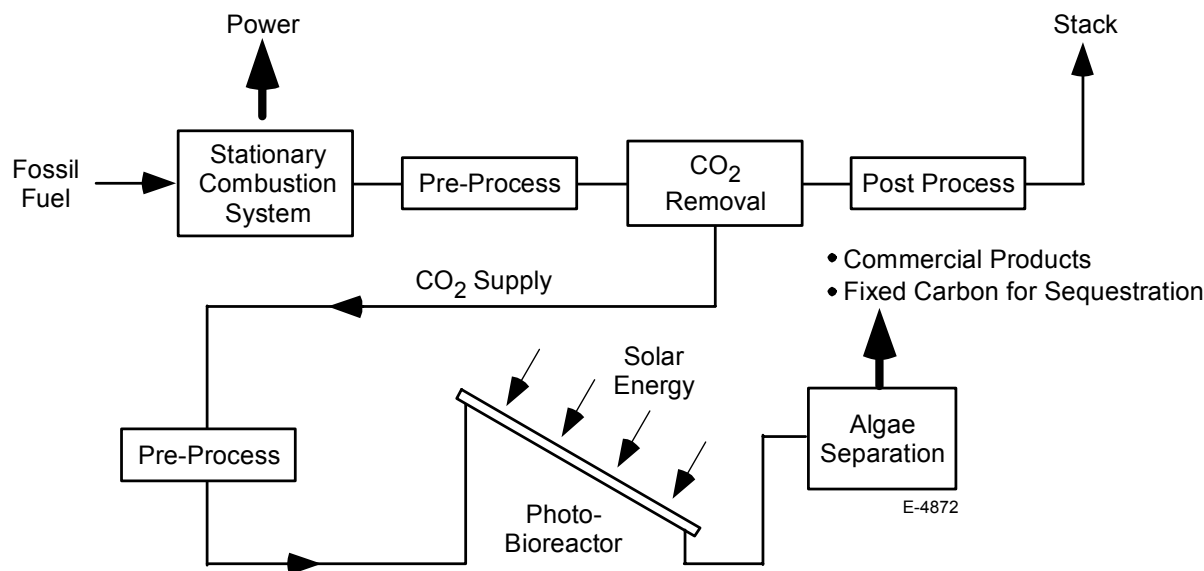


Figure 1. Recovery and sequestration of CO₂ from stationary combustion systems by photosynthesis of microalgae.

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.

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;

- Started preparation of coal combustor for pilot scale production runs with coal combustion gases;
- Started preparation of the full scale production run at the 25,000 photobioreactor using propane combustion gas;
- Carried out preliminary work on biomass separation for two microalgal strains grown in 2000 liter outdoor photobioreactors;
- Conducted work on designing key components including: CO₂ removal process; CO₂ injection device; photobioreactor; product algae separation process; and process control devices;
- Developed a photobioreactors design concept for biofixation of CO₂ and photovoltaic power generation.
- Shared the ASPEN model with UH, PSI and Aquasearch for review and discussion;
- UH research staff visited Aquasearch and worked on-site for one week to gather information on the performance of the photobioreactor;
- Photobioreactor data from Aquasearch were analyzed and simple linear relationships for biomass productivity as a function of solar irradiance and CO₂ were developed using multiple regression;
- A review of the technical literature on tubular photobioreactors progressed;
- A literature study progressed to develop the CO₂ flue gas separation subsystem model for both Aspen Plus and Excel models;
- Conducted economic analysis for photobioreactor carbon fixation process; and
- Continued development of economic model to be used in predictions of carbon sequestration cost for a number of scenarios.

In Table 1, current status of each work scope is summarized.

Table 1. Current Status of Each Work Scope

Tasks	Title	% Complete	Milestone/Status Description
Task 1.0	Supply of CO ₂ from Power Plant Flue Gas	85%	Overall status for Tasks 1.1 through 1.3.
Task 1.1	Power Plant Exhaust Characterization	100%	Most of pertinent exhaust gases were analyzed.
Task 1.2	Selection of CO ₂ Separation and Clean-up Technologies	95%	MEA method identified. Direct injection of exhaust gas into water may be an option.
Task 1.3	Carbon Dissolution Method	75%	Analytical study completed. Direct exhaust gas injection may be studied per our Task 3 outcome.
Task 2.0	Selection of Microalgae	100%	Selection of 6 species out of initial 20.
Subtask 2.1	Characterization of Physiology, Metabolism and Requirements of Microalgae	100%	Test compatibility of 20 species with 5 flue gases.
Subtask 2.2	Achievable Photosynthetic Rates	100%	Productivity parameters of 20 species with 5 flue gases.
Task 3.0	Optimization and Demonstration of Industrial Scale Photobioreactor	15%	Demonstrate viability of CO ₂ with algae at industrial scale.

Tasks	Title	% Complete	Milestone/Status Description
Subtask 3.1	Pilot Evaluation	20%	Evaluation at 2000 L pilot scale. Experimental work with coal reactor to be made.
Subtask 3.2	Full Scale Production Runs	5%	Evaluation at 24,000 L industrial scale.
Subtask 3.3	Algae Separation and Final Product	20%	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	10%	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	0%	Economic analysis of product processing

The work discussed in this report covers the reporting period from 1 April to 30 June 2003.

3. Experimental

3.1 Task 3.1: Pilot Evaluation

During this quarter we have continued preparation of a coal combustor that will allow us to determine the suitability of coal combustion gases for microalgal-based carbon capture and sequestration at pilot scale (up to 2,000 liter photobioreactors). In the Results section we describe the steps that have been taken to accomplish this goal.

3.2 Task 3.2: Full Scale Production Runs

During this quarter we have continued preparation of a propane gas combustor that will allow us to determine the suitability of propane combustion gases for microalgal-based carbon capture and sequestration at commercial scale (up to 25,000 liter photobioreactors).

The goal of our final set of experiments is to optimize gas delivery systems for photobioreactor performance at present commercial scale. These experiments will be conducted in 25,000-L MGMs, the commercial reactors on which current economic models are based. Flue gas will be supplied by a slipstream from the existing propane combustor can supply flue gas to the pilot and commercial scale bioreactors. The composition of the flue gas can be modified as needed by the addition of more CO₂ and acid gases in order to simulate the flue gas compositions determined in Task 1. Based on the results of Task 1.3, we will optimize the gas injection system for maximum dissolution of CO₂. We will conduct experiments in the 25,000-L MGM using propane combustion product flue gas supplied by the system developed and using only the

5 to 6 species of microalgae selected for large-scale experiments. Each species will be run at this scale for 6 to 10 weeks, allowing for optimization. In the results section we describe the steps that have been taken to accomplish this goal.

3.3 Task 3.3: Algae Separation and Final Product

During the eleventh quarter we have carried out a set of bench scale centrifugation tests to determine the settling characteristics of different species of microalgae. These tests are designed to make relative estimates of centrifugation capacity needed for different species of microalgae. It is expected that different species of microalgae will be more or less difficult to separate from the growth medium by centrifugation because of different physical characteristics such a density and particle size. This information will then be used in our economic model to support our cost estimates of algal biomass harvesting and separation from the growth medium.

Essentially, the tests consist in centrifuging samples of different microalgal cultures in 15 ml tubes for specific amounts of time, noting the volume of pellet formed at those times and estimating the amount of biomass (using fluorescence) left in the supernatant. A digital photograph of the tubes following centrifugation was also be used to record the results.

Microalgal cultures were grown in 250 ml Erlenmeyer flasks under standard conditions (irradiance: $\sim 60 \text{ uE m}^{-2} \text{ s}^{-1}$, 14:10 L:D, temperature: $22 \pm 3 \text{ }^{\circ}\text{C}$). The flasks were manually shaken three times daily. Culture biomass was estimated from *in vivo* fluorescence. A Pulse Amplitude Modulated (MINI PAM, Walz, Germany) fluorometer was used to measure culture *in vivo* fluorescence. The fluorescence measured is proportional to the amount of chlorophyll, and thus biomass, of the culture. Once grown, the cultures were used in our centrifugation experiments as follows.

A 2 to 5 ml sample (approximate) of culture was placed into a glass t-tube and its fluorescence measured. The measurement was repeated twice. The sample was then returned to the Erlenmeyer flask and the flask was thoroughly mixed. Next, six 15 ml samples of the culture were then placed in 15 ml centrifuge tubes. The samples were centrifuged in a Eppendorf 5810R centrifuge programmed for 0, 30", 60", 120", 300" and 600" at 400 rpm. The 0" centrifugation sample was spun up to 400 rpm and immediately stopped. We calculated that the centrifugation force experienced by the samples during speed-up and slow-down was equivalent to 6.5" at 400 rpm so this time was added to all our samples.

After each tube was centrifuged, the tubes were photographed and the pellet volume noted. Finally, a 2 to 3 ml of supernatant was taken from each tube and its fluorescence determined using the MINIPAM fluorometer. The change in fluorescence between pre- and post-centrifugation was used as an estimate of centrifugation efficiency. The values thus calculated were fit to a hyperbolic tangent model to estimate a centrifugation efficiency factor that will later be used in estimating centrifugation needs for a commercial sized facility producing the specific strains.

3.4. Task 5.2: Photobioreactor Carbon Fixation Process

In this quarter we have continued to work on our cost modeling efforts of the carbon fixation process. An economic model for industrial scale algae facilities has been designed. The model includes over 500 variables that go into calculating monthly cost of goods, capital equipment requirements, land requirements and cash flow and balance sheets for 15 years of operation.

As a first step in the design process, we have specified the mass flows of the different materials necessary to run Mera's present microalgal plant in Kona, Hawaii (Figure 20 in Quarterly Report #9). The model has been designed to be flexible and accept parameters for significantly larger microalgal plants that would produce a number of different microalgal products (e.g., astaxanthin from *Haematococcus*, biomass from *Spirulina*, and B-carotene and lutein from *Dunaliella* and *Nannochloropsis* respectively) utilizing open and closed photobioreactors while capturing carbon from smoke stack gases.

4. **Results and Discussion**

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

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

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

4.2 Task 2: Selection of Microalgae

Almost all work in this task was completed in the last reporting period. No additional work was made in this reporting period.

4.3 Task 3: Optimization and Demonstration of Industrial Scale Photobioreactor

The goal for this phase of this research program is to optimize carbon sequestration, high value component production and CO₂ mineralization utilizing microalgal cultures at a commercially significant scale. This will be done in two phases. First, we will conduct a pilot evaluation using 2,000 liter enclosed photobioreactors (pilot scale MGM, Task 3.1) and, second, we will conduct full scale production runs using 24,000 liter enclosed photobioreactors (full scale MGM, Task 3.2). Concurrently, research into the appropriate technologies for harvesting and processing the produced biomass will be conducted (Task 3.3).

4.3.1 Task 3.1: Pilot Evaluation

During this quarter we have continued preparation of a coal combustor that will allow us to determine the suitability of coal combustion gases for microalgal-based carbon capture and sequestration at pilot scale (up to 2,000 liter photobioreactors).

We took delivery of the PSI coal reactor at Mera's facility on 6/19/03. The reactor was unpacked and the initial assembly began on 6/21/03. Joe Morency, principal mechanical engineer for PSI, arrived on site (6/23/03) to lead the installation of the coal reactor. The coal reactor was assembled and was ready for initial testing on 6/24/03 (Figures 2 and 3). We started the reactor late in the day and brought it up to operating temperature. Due to the time of day, all systems, except the coal feeder, were operated and they all tested normal. The reactor was idled down to a safe temperature and secured for the night.

The next morning (6/25/03) we brought the coal reactor up to operating temperature, and then we started the IMR Gas Analyzer in order that the flue gas, which would be produced by the reactor, could be monitored. Upon startup, the gas analyzer's controllers displayed readings that had drifted from the last recorded readings. An attempt was made to calibrate the three different sensors in the gas analyzer, however the NOX sensor could not be set to zero or be calibrated. The SOX and CO₂ sensors did not display stable readings, but were within a range that was expected to give enough of an indication to determine if the reactor was burning coal. Procedures for repairing the gas analyzer were discussed with Dr. Takashi Nakamura and it was decided to ship the instrument back to the manufacturer. A detailed discussion of these repairs will follow in the next quarterly report.



Figure 2. Photograph showing the coal combustor installed at Mera's facility.



G-1457

Figure 3. Photograph showing the pump that delivers the combustion gases from the coal combustor to the gas analyzer and photobioreactor.

After adjusting the gas analyzer to give the most stable readings possible, the coal feeder on the reactor was started. The coal started to feed into the reactor, but very soon after the coal started to burn, the coal feed system clogged with compacted coal. Compressed coal was cleared from the feeding tubes and the auger on the coal feeder was adjusted. The coal feeder was then restarted, however the scenario was repeated and the feed system was again clogged with coal shortly after the reactor started to burn.

We decided the feed system would have to be modified in order for the coal to feed smoothly into the reactor. Three adjustments were outlined. First, it was assumed that the coal had absorbed moisture and should be dried. Second, an air-driven bin vibrator should be installed on the coal feed tubing and third, the feed air should be changed to dry compressed air or nitrogen. These modifications are slated to be implemented during July '03 and will be reported on in the next quarterly report.

4.3.2 Task 3.2: Full Scale Production Run

During this quarter we have continued preparation of a propane gas combustor that will allow us to determine the suitability of propane combustion gases for microalgal-based carbon capture and sequestration at commercial scale (up to 25,000 liter photobioreactors).

We have developed a propane combustion system (see Figure 4 for a schematic diagram) that consists of a Bosch Aquastar 125HX water heater (Figure 5) producing 125,000 BTUs. The

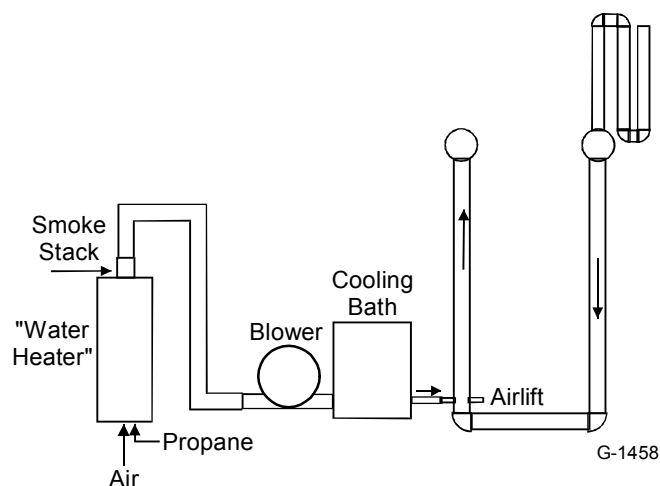


Figure 4. Schematic diagram showing the components of the system used to deliver propane combustion gases to the photobioreactor's airlift.



Figure 5. Propane combuster (a commercial water heater) used to generate combustion gases for photobioreactor operations.

gases from the propane combustion are transported to the photobioreactor via a 4" vent pipe using a 5 horsepower regenerative blower (Figure 6). The gas is then cooled by submerging a carrier pipe into a cold water bath (Figure 7). Finally, the combustion gases are introduced into the photobioreactor at the bottom of the airlift (Figure 8).



G-1460

Figure 6. Regenerative blower used to deliver propane combustion gases to the photobioreactor.



G-1461

Figure 7. Cold water bath used to cool the propane combustion gases before injection into the photobioreactor.



G-1462

Figure 8. Airlift section of the photobioreactor where the propane combustion gases are injected.

We are, at the present time, trouble-shooting the system in preparation for the full scale production runs.

4.3.3 Task 3.3: Algae Separation and Final Product

During this quarter we have carried out a set of bench scale centrifugation tests to determine the settling characteristics of different species of microalgae. These tests are designed to make relative estimates of centrifugation capacity needed for different species of microalgae. It is expected that different species of microalgae will be more or less difficult to separate from the growth medium by centrifugation because of different physical characteristics such as density and particle size. This information will then be used in our economic model to support our cost estimates of algal biomass harvesting and separation from the growth medium.

So far, we have tested 22 different microalgal strains. Figure 9 shows examples of data obtained from four different strains of microalgae. The data obtained was fit to a model of the form:

$$\%Harvest = \%Harvest_{max} * \left(1 - e^{\left(\frac{-a * time}{\%Harvest_{max}} \right)} \right) * \left(e^{\left(\frac{-b * time}{\%Harvest_{max}} \right)} \right)$$

where:

%Harvest is the fraction of biomass harvested from the medium after a specific amount of time,

$\%Harvest_{max}$ is the maximum harvestable biomass (up to 100%),

- a is the harvest efficiency factor (larger for easier to harvest strain),
- b is a modifier that reflects the fact that since microalgal populations are heterogeneous (e.g., some cells are larger than others) it is expected that larger cells will harvest faster than smaller cells of the same population, thus affecting the efficiency of the process, and

time is the amount of time for which the specific sample was centrifuged.

For example, for the data shown in Figure 8 the calculated efficiency factors (a) are 0.046, 0.120, 2.046, and 39.3 for AQ0011 (3 μ m coccoid cells), AQ0052 (3 x 6 μ m ovoid cells), AQ0024 (4-cell chain forming ovoid cells 4 x 8 μ m), and AQ0030 (a filamentous Cyanobacterium) respectively (Figure 9). Our calculated centrifugation efficiency factors thus reflect the differences in cell size and morphology. Figure 10 summarizes the centrifugation harvest efficiencies obtained for 22 strains thus far.

These values will be used in our economic model to estimate the costs, in capital equipment as well as running costs (manpower, supplies, utilities), of processing biomass from different microalgal strains.

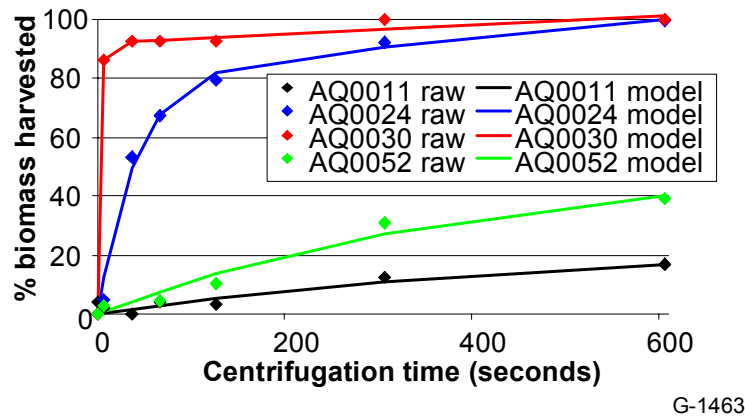


Figure 9. Four data sets obtained from four morphologically different strains of microalgae (see also Figure 10).

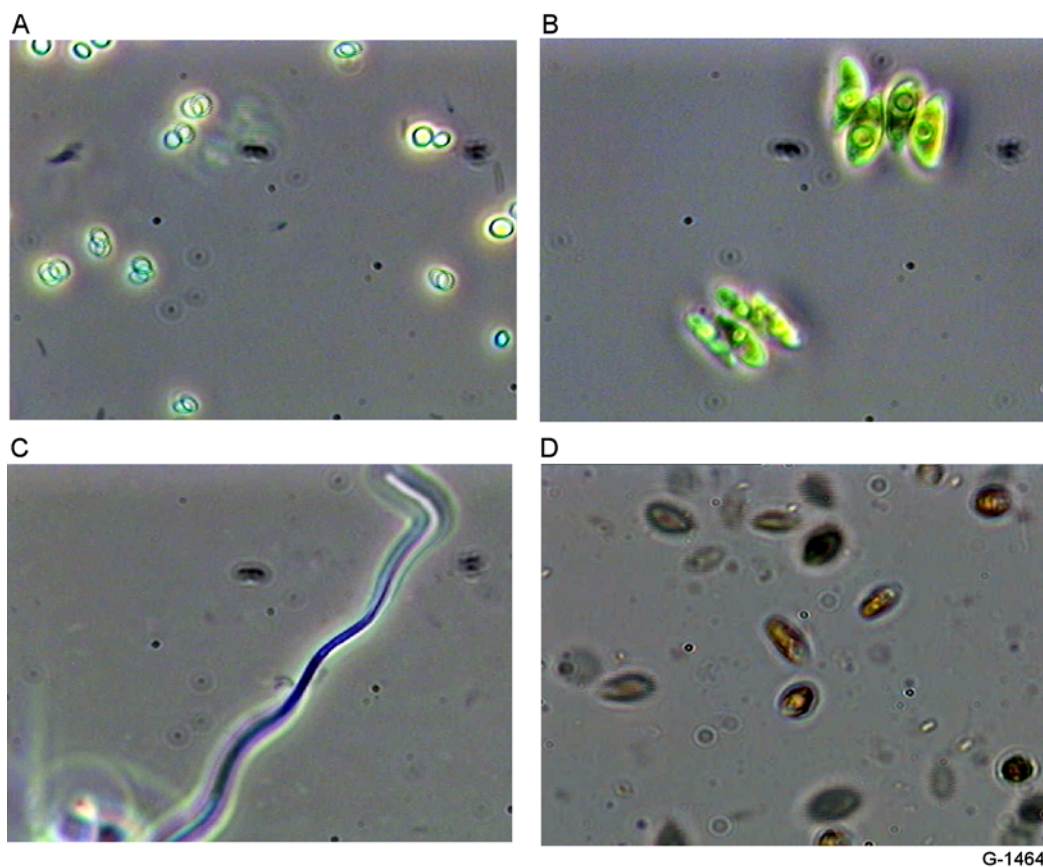


Figure 10. Microphotographs (400x) of strains AQ0011 (A), AQ0024 (B), AQ0030 (C) and AQ0052 (D) showing differences in size and morphology.

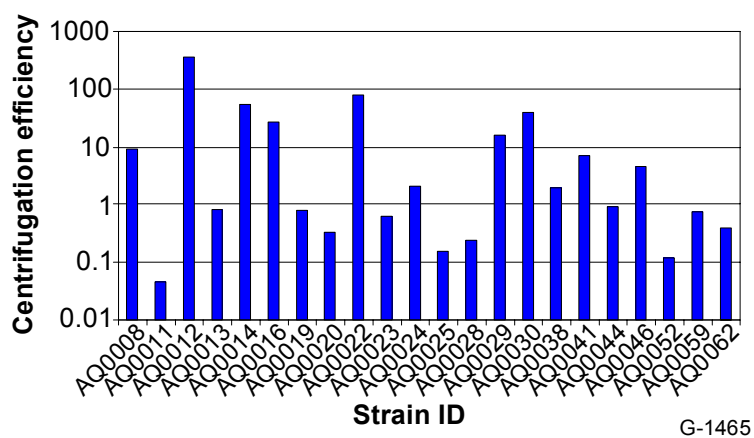


Figure 11. Summary of centrifugation efficiency factors obtained for 22 microalgal strains so far.

4.4 Task 4: Carbon Sequestration System Design

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

- (1) Identify design concepts for components and the integrated system of the proposed concept.
- (2) Optimize and evaluate performance of the components and the system.
- (3) Develop deployment methodologies.
- (4) Identify key technology issues for further development.

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

4.4.1 Task 4.1: Component Design and Development

The purpose of this subtask is to develop design concepts for each of the key components of the industrial scale photosynthetic sequestration of CO₂. Key components to be designed include: CO₂ removal process; CO₂ injection device; photobioreactor; product algae separation process; and process control devices. As the proposed system depends on the solar energy to photosynthetically convert CO₂ to products compounds, optimization of the photobioreactor is an important part of this task. In the reporting period, PSI focused its effort on preparation of the PSI coal reactor to be shipped to Aquasearch, and no significant progress was made. In the following quarters, we will evaluate the concept to (i) assess feasibility of the concept for large scale photobioreactor, (ii) quantify cost benefit, and (iii) address technical issues for commercial applications.

4.4.2 Task 4.2: System Integration

The integrated process model being developed by UH requires submodels that accurately represent the behavior of key components, notably, the photobioreactor and the CO₂ flue gas separation system. In order to obtain data on the performance characteristics of the Aquasearch photobioreactor, UH personnel visited the Aquasearch facility in July 2002. The work continued on the data obtained since the visit. A description of technical activities conducted by UH during this reporting period is provided below.

Samples of *Haematococcus Pluvialis*

Mera Pharmaceuticals, Inc. provided two sets of dry samples of *Haematococcus pluvialis* to the University of Hawaii. These samples were collected from bioreactors which hereafter will be referred to as Mera Growth Modules (MGMs). Samples collected from the MGMs are identified by the prefix “M.” For the first set of samples, *Haematococcus pluvialis* cells from the MGM were collected at different times during the same day cycle. Table 2 summarizes the data provided with the first set of samples, including sample identities, sampling dates and times, ages of the MGM, average cell count, liters of culture and media sampled, and dry weights. These

Table 2. First Set of *Haematococcus Pluvialis* Samples

Sample Identity	Date	Time	Age (days)	Average Cell Count (cells/mL)	Liters used	Dry Weight (g)
M13A-030215	2/28/03	8:15	13	528657	2	0.9949
M13A-030215	2/28/03	12:15	13	566680	2	1.0021
M13A-030215	2/28/03	15:30	13	584302	2	1.3462

samples were analyzed to determine the variation in %total organic carbon (TOC) of the cells during the day cycle.

A second set of *Haematococcus pluvialis* cells from the MGM were sampled over a period of 6 days at different times during both the day and night cycles. Table 3 summarizes the data on this second set of samples that was provided by Mera Pharmaceuticals. These samples were analyzed to determine the variation in %TOC of the cells in the MGM during the day and night cycles. Data on total organic carbon is needed to determine the quantity of carbon bound in the biomass produced between two sampling dates.

Table 3. Second Set of *Haematococcus Pluvialis* Samples

Sample Identity	Date	Time	Age (days)	Average Cell Count (cells/mL)	Liters used	Dry Weight (g)
M13a-030423	4/26/03	5:40	3	156513	3	0.3498
M13a-030423	4/26/03	18:45	3	237617	3	0.6309
M13a-030423	4/27/03	5:40	4	211803	3	0.4901
M13a-030423	4/27/03	18:30	4	298501	3	0.6839
M13a-030423	4/28/03	6:05	5	304173	3	0.6213
M13a-030423	4/28/03	18:50	5	336370	1.95	0.6501
M13a-030423	4/29/03	5:30	6	410071	3	0.9152
M13a-030423	4/29/03	18:45	6	441130	2	0.7105
M13a-030423	4/30/03	6:00	7	431003	2	0.7581
M13a-030423	4/30/03	19:00	7	538085	2	1.0871
M13a-030423	5/1/03	5:25	8	520702	2	0.9908

Sample Analysis and Results

The Agricultural Diagnostic Service Center of the University of Hawaii analyzed the *Haematococcus pluvialis* samples for total organic carbon content on a dry weight basis. Results of the analyses of the first and second set of samples are provided in Tables 4 and 5, respectively. The quantity of carbon bound in the biomass generated between sampling dates was estimated from these data and is plotted in Figures 12 and 13 for, respectively, the first and second sets of samples from the MGM.

Table 4. Total Organic Carbon Content for First Set of Samples

Sample Identity	Date	Time	Age (days)	Total Organic Carbon (%)
M13A-030215	2/28/03	8:15	13	48.4
M13A-030215	2/28/03	12:15	13	48.7
M13A-030215	2/28/03	15:30	13	48.1

Table 5. Total Organic Carbon Content for Second Set of Samples

Sample Identity	Date	Time	Age (days)	Total Organic Carbon (%)
M13a-030423	4/26/03	5:40	3	40.03
M13a-030423	4/26/03	18:45	3	41.41
M13a-030423	4/27/03	5:40	4	42.17
M13a-030423	4/27/03	18:30	4	42.70
M13a-030423	4/28/03	6:05	5	43.18
M13a-030423	4/28/03	18:50	5	42.82
M13a-030423	4/29/03	5:30	6	43.15
M13a-030423	4/29/03	18:45	6	43.79
M13a-030423	4/30/03	6:00	7	43.74
M13a-030423	4/30/03	19:00	7	45.23
M13a-030423	5/1/03	5:25	8	46.01

Figure 12 indicates that the %TOC of the cells on a dry weight basis varied only slightly over the course of a single day cycle, between approximately 48.1% to 48.7%. Figure 13 indicates that the %TOC on a dry weight basis increased steadily between 40.03% and 46.01% over six days. In order to better understand these results, the %TOC was employed, to estimate the mass of carbon per cell. The mass of carbon per cell for the first and second sets of samples are tabulated in Tables 6 and 7 and plotted in Figures 14 and 15, respectively. Figure 14 indicates that the mass of carbon per cell varied slightly, between 4.31×10^{-10} gm to 5.54×10^{-10} gm during the day cycle. Figure 15 indicates that the mass of carbon per cell varied between 2.98×10^{-10} gm to 4.57×10^{-10} gm over 6 days, generally increasing during the day via photosynthesis and decreasing at night due to respiration. There appears to be an increasing trend over time.

These TOC data will be applied to determine the quantity of carbon bound in the biomass produced between two sampling dates. Results will be employed in our ongoing systems modeling effort.

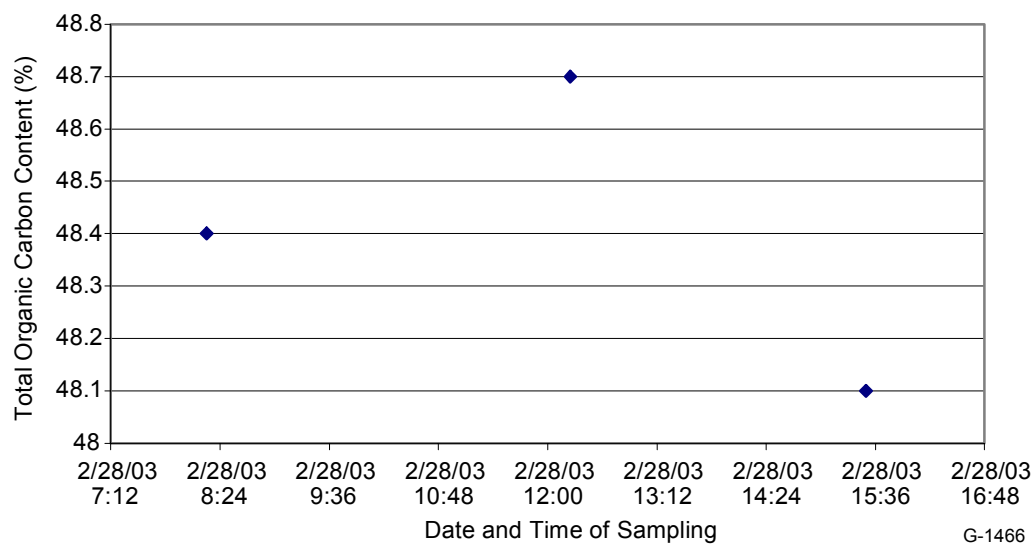


Figure 12. Total organic carbon of first set of samples.

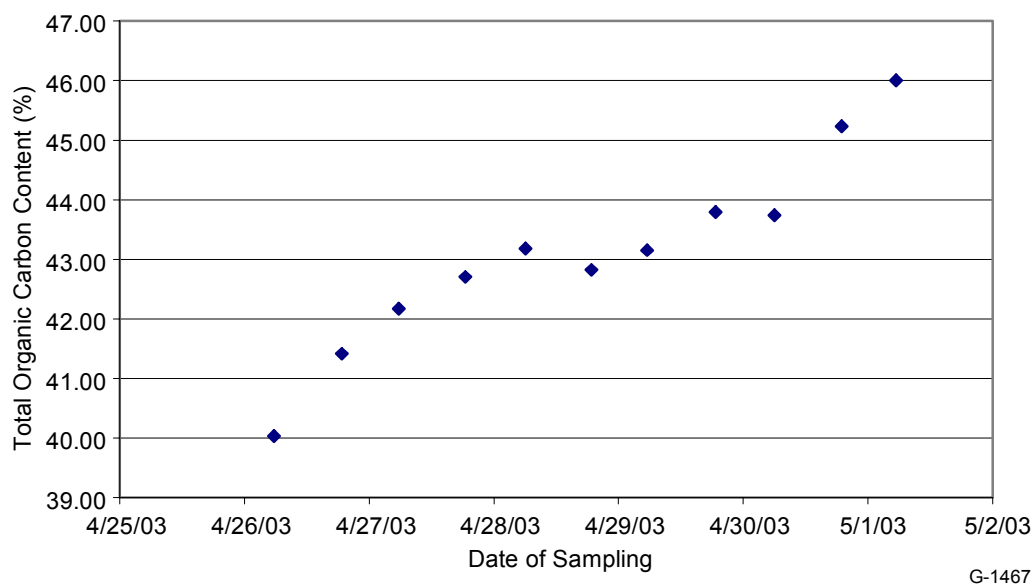


Figure 13. Total organic carbon of second set of samples.

Table 6. Mass of Carbon Per Cell for First Set of Samples

Sample Identity	Date	Time	Age (days)	Mass of Carbon Per Cell (g/cell)
M13A-030215	2/28/03	8:15	13	4.55E-10
M13A-030215	2/28/03	12:15	13	4.31E-10
M13A-030215	2/28/03	15:30	13	5.54E-10

Table 7. Mass of Carbon Per Cell for Second Set of Samples

Sample Identity	Date	Time	Age (days)	Mass of Carbon Per Cell (g/cell)
M13A-030423	4/26/03	5:40	3	2.98E-10
M13A-030423	4/26/03	18:45	3	3.66E-10
M13A-030423	4/27/03	5:40	4	3.25E-10
M13A-030423	4/27/03	18:30	4	3.26E-10
M13A-030423	4/28/03	6:05	5	2.94E-10
M13A-030423	4/28/03	18:50	5	4.24E-10
M13A-030423	4/29/03	5:30	6	3.21E-10
M13A-030423	4/29/03	18:45	6	3.53E-10
M13A-030423	4/30/03	6:00	7	3.85E-10
M13A-030423	4/30/03	19:00	7	4.57E-10
M13A-030423	5/1/03	5:25	8	4.38E-10

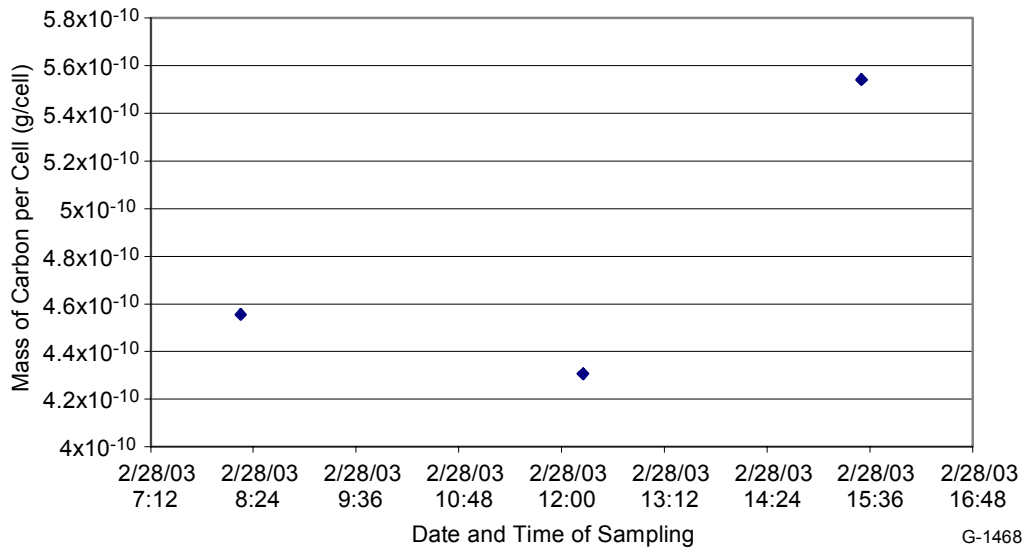


Figure 14. Mass of carbon per cell for first set of samples.

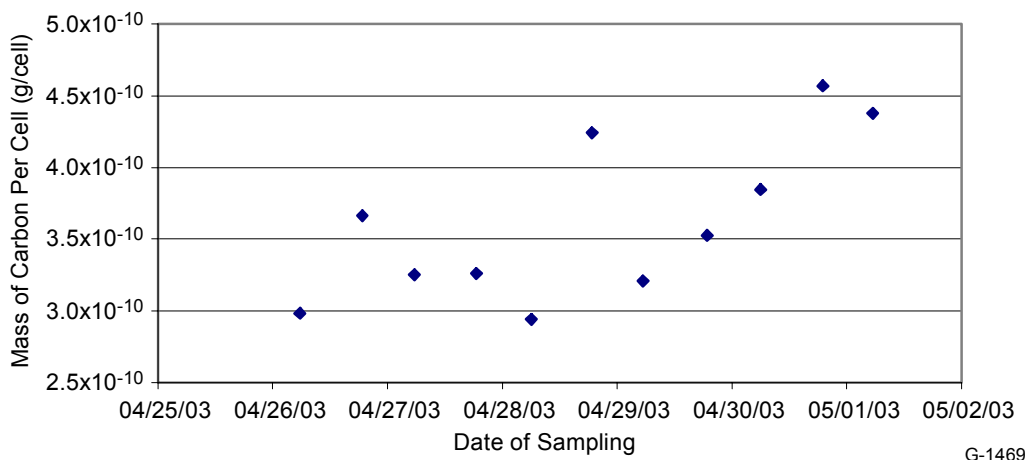


Figure 15. Mass of carbon per cell for second set of samples.

Total Inorganic Carbon

The total inorganic carbon can be computed from pH and alkalinity measurements that are based on the thermodynamics of the inorganic carbon system (Geider and Osborne, 1992). Assuming that equilibrium, the total inorganic carbon (TCO₂) is determined from the relationship

$$[\text{TCO}_2] = [\text{CA}] \frac{1 + K_2^1 / \text{H}^+ + \text{H}^+ / K_{L1}^1}{1 + 2K_2^1 / \text{H}^+} \quad (1)$$

where [TCO₂] is the total inorganic carbon concentration in mg/L, [CA] is the carbonate alkalinity in mg/L as CaCO₃, [H⁺] is the hydrogen ion activity (*i.e.*, 10^{-pH}), K_{L1}^1 is the first apparent dissociation constant for carbonic acid in water, and K_2^1 is the second apparent dissociation constant for carbonic acid in water. Values of the dissociation constants can be found in the literature (Geider and Osborne, 1992).

Photosynthetic CO₂ fixation can be used to estimate the quantity of carbon that was metabolized and bound in the cell biomass pool that is part of the carbon sequestration efficiency. Photosynthetic CO₂ fixation creates an increase in the pH of the media without changing the alkalinity. Therefore, changes in the pH of the media with an initial value of the carbonate alkalinity can be used to measure changes of net total inorganic carbon concentration using Eq. (1).

The procedure that will be employed to estimate photosynthetic CO₂ fixation consists of two steps. First, using the data provided from Mera Pharmaceuticals, Inc., the net total inorganic carbon concentration can be determined for each CO₂ injection period. Second, all net total inorganic carbon concentration between two sampling dates will be summed to determine photosynthetic CO₂ fixation over that period.

4.5 Task 5: Economic Analysis

Our aim in the economic analysis is to identify those components of the carbon sequestration process that have the greatest associated costs, given the design based on current data. Subsequent modeling will explore alternative technologies and procedures that might enable significant reduction in both capital and operating costs.

4.5.1 Task 5.1: Gas Separation Process

Much of work pertaining to this subtasks has been completed in the previous reporting periods. We will address this issues again after we complete Tasks 3 and 4.

4.5.2 Task 5.2: Photobioreactor Carbon Fixation Process

We have continued the development of an economic model for industrial scale algae facilities. The model includes over 500 variables that are used to calculate monthly cost of goods, capital equipment requirements, land requirements and cash flow and balance sheets for 15 years of operation. The model is in the form of an EXCEL workbook with 9 separate worksheets:

- CULTURE PARAMETERS,
- OPERATIONS PARAMETERS,
- UTILITIES CALC SHEET,
- LABOR CALC SHEET,
- CAPITAL COSTS,
- ECONOMIC MODEL,
- PROFIT AND LOSS,
- CASH FLOW, and
- BALANCE SHEET.

Full details for labor, utilities, and other operational costs are listed as well as capital costs. Furthermore, it includes a table compiling various microalgae products along with the corresponding microalgae's growth parameters, expected market price and estimated cost of sales parameters.

The first five worksheets are used to update, by the user, the processes and associated costs for the different aspects of microalgal production. For example, the user may consider changing the parameters in the LABOR CALC SHEET and UTILITIES CALC SHEET depending on where the microalgal plant would be sited. The input is used in the ECONOMIC MODEL worksheet to estimate the total costs associated with the different aspects of the production of microalgal biomass in photobioreactors, including production of inoculum as well as harvesting, drying and processing costs. Finally, the last three sheets use the costs generated in the ECONOMIC MODEL worksheet plus information on the expected value of the microalgal biomass to generate Profit and Loss, Cash Flow, and Balance Sheet statements.

Model output includes expected monthly expenses depending on the user's input with respect to desired product and quantity to be produced. Land requirements and initial capital costs are calculated. The number of years over which capital costs are depreciated is also a variable. Monthly expenses include direct supplies, utilities such as electricity, freshwater, saltwater, and CO₂, maintenance, direct labor as well as fringe benefits and overhead. Finally, outsourced activities such as extraction and encapsulation of high-value microalgal products are also listed under monthly expenses. These monthly expenses are then used to create a yearly cash flow sheet after determining revenues based on expected sales and cost of sales in the profit and loss sheet. Finally, a balance sheet valid for the first 15 years of operation is generated based on projections.

We have run the model for three different types of products as an example. In these model runs we assume that capital expenses are depreciated over 10 years, that the microalgal plant starts production in 2004 and that sales reach 100% of production within 3 years.

Example 1. Biomass from *Spirulina* for the nutraceutical market.

We assume that *Spirulina* biomass represents 100% of the produced biomass (by weight),

Spirulina will be sold into the high end nutraceutical market (\$200/kg), and “cost of sales” represent 20, 15 and 10% of sales for years 1, 2, and 3.

Example 2. Astaxanthin from *Haematococcus* biomass for the nutraceutical market. Our basic assumptions are Astaxanthin represents 3% of the produced biomass (by weight),

astaxanthin will be sold into the nutraceutical retail market (\$70,000/kg), higher costs will be incurred by extraction, encapsulation and bottling of the astaxanthin, and

higher “cost of sales” would be incurred over the first two years since this represents a new product unknown to the consumer.

Example 3. Astaxanthin from *Haematococcus* biomass for the feed market.

Our assumptions are Astaxanthin represents 3% of the produced biomass (by weight),

astaxanthin will be sold into the bulk feed ingredient market (\$2,000/kg), lower costs will be incurred since there is no need for extraction, encapsulation and bottling of the astaxanthin, and lower “cost of sales” would be incurred over the first two years since this represents a product already known to the consumer.

The resulting Net Sales, Total Expenses, Net Cash Flow and Cumulative Cash Flow for the first 15 years of operation are shown in Figure 16 for the three scenarios. It is clear from those results that the model reflects changes in the assumptions in each case such as, for example, lowered production costs for *Spirulina* biomass and Feed astaxanthin and higher selling price for Nutraceutical astaxanthin.

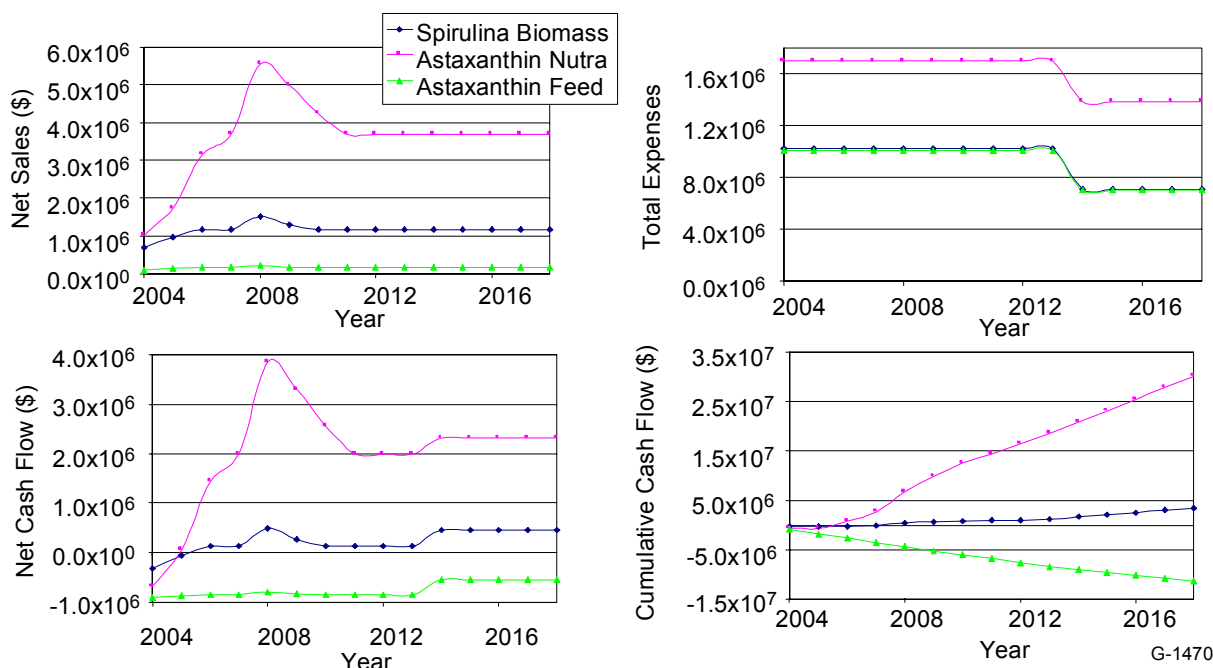


Figure 16. Resulting Net Sales, Total Expenses, Net Cash Flow and Cumulative Cash Flow for the first 15 years of operation for three microalgal scenarios: *Spirulina* biomass, nutraceutical astaxanthin and feed astaxanthin.

We will continue to fine-tune our modeling efforts as the results from Task 2 and 3 are incorporated for a larger number of microalgal species and microalgal products.

5. Conclusion and Future Plans

5.1 Task 3: Optimization and Demonstration of Industrial Scale Photobioreactor

In this quarter we have continued preparations for our large scale photobioreactor experiments where we will use combustion gases from coal and propane to produce microalgal biomass and sequester carbon. Conclusions and future plans are summarized below.

- The coal and propane combustors were installed and are now nearly operational.
- Results from our bench-top centrifugation experiments show large differences in harvesting efficiencies for different microalgal strains. This is expected to significantly affect final costs of carbon sequestration. In general, the larger the cells or colonies the more efficient (i.e., cheaper) the centrifugation harvest will be.

Within the next quarter we expect to

- Start the first experiments with microalgal strains fed carbon exclusively from either coal or propane combustion.
- Continue bench-top centrifugation experiments.

5.2 Task 4: Carbon Sequestration System Design

- Identified design concept for a large scale photobioreactor with photovoltaic electric power generation.
- Continued carbon balance analyses and estimation of CO₂ sequestration efficiency for the Aquasearch facility.
- Continued total organic carbon content analysis of *Haematococcus pluvialis* samples. A sampling protocol was developed and submitted to Mera Pharmaceuticals, Inc. along with a request for additional samples.

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

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

5.3 Task 5: Economic Analysis

In this quarter we have continued the development of an economic model for industrial scale algae facilities. The current version of the model allows us to reflect the different costs associated with microalgal production of different strains in the resulting cash-flow statement of a production facility. Within the next quarter we expect to

- Continue development of 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.

6. **References**

1. McCabe, W.L. and Smith, J.C., Unit Operations of Chemical Engineering (McGraw-Hill, New York, 1976), pp. 697-700.
2. Perry, R.H. and Chilton, C.H., Chemical Engineer's Handbook (McGraw-Hill, New York, 1973).