PSI-1356

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

Quarterly Technical Progress Report #10

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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 January to 31 March 2003 in which PSI, Aquasearch and University of Hawaii conducted their tasks. Based on the work during the previous reporting period, PSI conducted preparation work on direct feeding of coal combustion gas to microalgae and developed a design concept for photobioreactors for biofixation of CO_2 and photovoltaic power generation. Aquasearch continued their effort on characterization of microalgae suitable for CO_2 sequestration and preparation for pilot scale demonstration. University of Hawaii continued effort on system optimization of the CO_2 sequestration system.

Table of Contents

List of Figures

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:

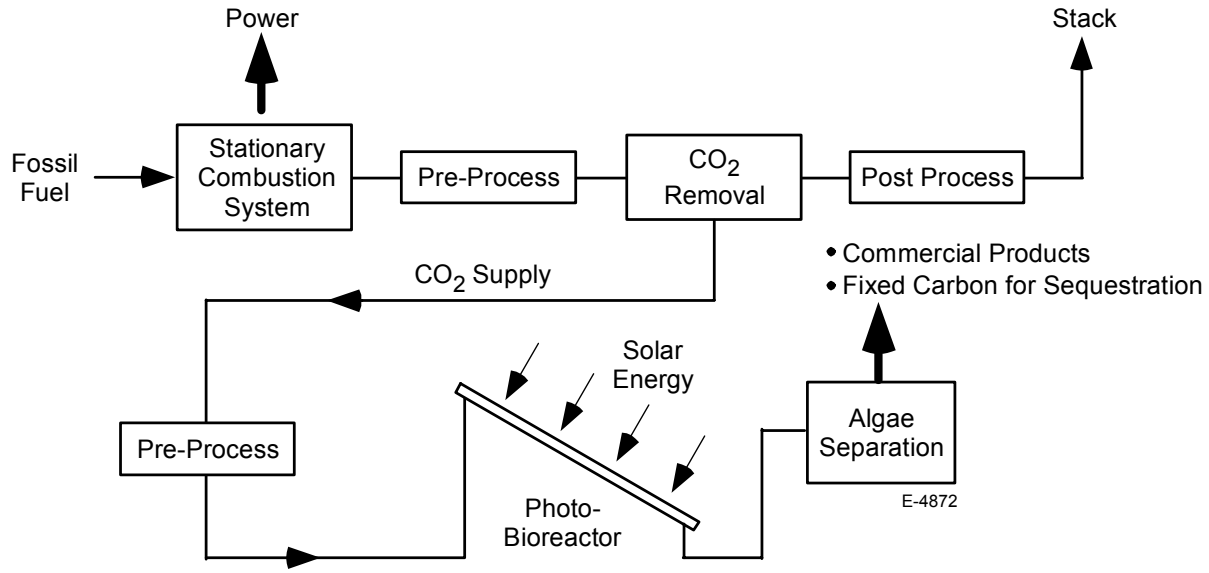

Figure 1. Recovery and sequestration of CO_2 from stationary combustion systems by photosynthesis of microalgae.

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.

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.;
- Conducted preparation of the PSI coal reactor to be used with the Aquasearch 2000 liter outdoor photobioreactor for direct feeding of coal combustion gas to microalgae;
- 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: CO_2 removal process; CO_2 injection device; photobioreactor; product algae separation process; and process control devices;
- Developed a photobioreactors 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 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 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.

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.
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	0%	Evaluation at 24,000 L industrial scale.
Subtask 3.3	Algae Separation and Final Product	15%	Evaluation of biomass separation.
Task 4.0	Carbon Sequestration System Design	50%	Incorporating new system concept.

Tasks	Title	% Complete	Milestone/Status Description
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 January to 31 March 2003.

3. Experimental

In this quarterly period we report on a second set of experiments carried out in open photobioreactors (open ponds as opposed to enclosed MGMs). This experiments were designed to test whether addition of $CaSO_4*2H_2O$, which we have shown in previous reports to enhance calcium carbonate precipitation might have deleterious effect on the productivity of the microalgal cultures. Open ponds were used simply for convenience.

The ponds were managed as per Mera's standard operating procedures.[3] Three open ponds were used for this experiment. All three were inoculated with 0.7 kg dry weight biomass into a total volume of 23,000 liters. The first pond was treated as the control, the pond had 5 kg of $NaHCO_3$ added for pH stability as per our standard operating procedures in the production of astaxanthin from *Haematococcus*. A second pond had 4.82 kg of $CaSO_4 * 2H_2O$ added (plus 5 kg of $NaHCO_3$) to help induce precipitation of $CaCO_3$ and a third pond had 4.82 kg of $CaSO_4 * 2H_2O$ (but no $NaHCO_3$) to test the effects of this mineral, if any, on the productivity of the system. The ponds were allowed to grow for 6 days. The pH was automatically controlled (at 7.5) by additions of CO_2 in response to changes in pH. At the end of the growth period, the ponds were harvested and the particulates (biomass and any precipitated carbonates) were centrifuged, dried and weighted.

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 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 CO_2 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 experimentation on culture conditions that favor CO_2 sequestration into minerals, such as carbonates, that offer the possibility of long term storage of carbon.

CO_2 Mineralization

The objectives of this project is develop microalgal cultures that not only sequester CO_2 into the biomass and produce high value products but also are able to mineralize CO_2 into carbon solids, such as carbonates, that can be disposed of for long term storage. Previously, we reported that altering cultures conditions (raising pH via photosynthetic CO_2 uptake by the microalgae) and addition of calcium sulfate (gypsum) to the culture medium induced the precipitation of $CaCO_3$, a stable form of carbon that could be used for long term sequestration, apparently independently of the microalga used.

In our previous report (Quarterly Technical Progress Report #09) we showed that:

- Photosynthesis by microalgae can produce dramatic increases in pH of the culture medium (up to 10.5 pH within a few hours),
- The increase in pH apparently is able to induce precipitation a significant fraction of the dissolved carbon in the culture medium (22% and 68% for two different experiments).

Also, in our previous quarter we considered the possible concern that addition of $CaSO_4*2H_2O$ to the cultures to help induce carbon precipitation might have a negative effect on the productivity of the system. In our last report we reported the results of our first test which

indicated that addition of $CaSO_4*2H_2O$ to the cultures did not negatively affect the viability nor the productivity of the cultures.

In this quarter, we have continued this work including scale up of the cultures to 20 to 20,000 liter scale and have repeated the experiment in open-pond, 23,000 liter photobioreactors. As in the previous experiment, three open ponds were used for this experiment. All three were inoculated with 0.7 kg dry weight biomass into a total volume of 23,000 liters. The first pond was treated as the control, the pond had 5 kg of $NaHCO_3$ added for pH stability as per our standard operating procedures in the production of astaxanthin from *Haematococcus*. A second pond had 4.82 kg of $CaSO_4 * 2H_2O$ added (plus 5 kg of $NaHCO_3$) to help induce precipitation of $CaCO_3$ and a third pond had 4.82 kg of $CaSO_4 * 2H_2O$ (but no $NaHCO_3$) to test the effects of this mineral, if any, on the productivity of the system. The ponds were allowed to grow for 6 days. The pH was automatically controlled (at 7.5) by additions of CO_2 in response to changes in pH. At the end of the growth period, the ponds were harvested and the particulates (biomass and any precipitated carbonates) were centrifuged, dried and weighted.

The results of this experiment are summarized in Figure 2 along with the results from the previous experiment and show that the ponds receiving $CaSO_4*2H_20$ performed as well or better (more astaxanthin produced) than the control pond. This confirms that, at least for this process, addition of $CaSO_4*2H_20$ does not have any deleterious effects on high value chemical productivity. Also, the total mass of particulates harvested was higher in the ponds receiving the $CaSO_4*2H_20$ treatments in both experiments indicating, possibly, higher content of precipitated carbonates. We intend to continue testing the effects of $CaSO_4*2H_2O$ addition in the next quarter to eliminate reactor-to-reactor variability.

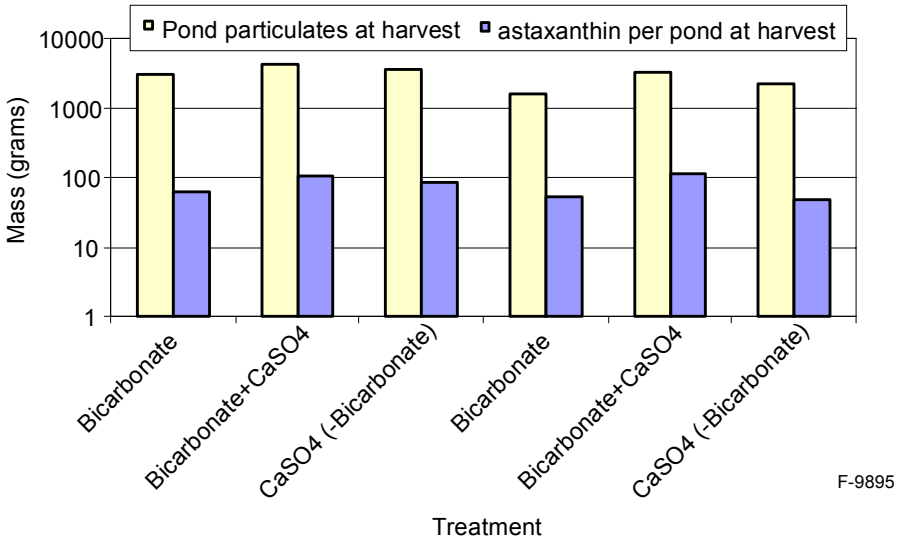

Figure 2. Results obtained in pilot scale outdoor pond experiments showing that addition of CaSO4*2H_2O to the medium did not result in a lowering of productivity (astaxanthin or total weight of mass harvested) for two experiments carried out so far.

Experiments with Pulverized Coal Combustion Gas

In preparation for the experiments with pulverized coal combustion, we have received a combustion-gases analyzer from PSI (IMR 5000 Gas Analyzer). After designing and constructing a stand and mounting the gas analyzer components (Figure 3) and after designing, fabricating and mounting the housings for the gas analyzing probes (Figure 4), a few challenges were encountered during startup of the unit.

Figure 3. IMR 5000 Gas Analyzer mounted on its rack next to a photobioreactor.

Figure 4. IMR 5000 Gas Analyzer mounted on its rack next to a photobioreactor showing the constructed housings set up to accommodate the stack probes.

Following is a short summary of the problems and challenges we encountered during the startup of the gas analyzer.

1. The output relays of the Red Lion controllers that were used in the IMR 5000 Gas Analyzer to report data from the gas analyzer were wired at the IMR factory with a 4 to 20 mA signal output signal. Our process control and data acquisition IO modules

require a 0 to 5 VDC signal input. Because of this requirement, it was necessary to re-wire the relay outputs of the controllers to match the input signal requirements of Mera's Process Control System.

2. After completing the rewire to the IMR gas analyzer, we installed the American Advantech control hardware (ADAM 5017) that enables us to collect and view real time data from the outputs of the IMR 5000 Gas Analyzer (Figure 5).

Figure 5. Detail wiring and location of the analog data acquisition module (ADAM 5017, American Advantech) control hardware, which enables us to collect and view real time data from the outputs of the IMR 5000 Gas Analyzer.

3. Then, upon initial startup of the IMR Gas Analyzer, the Red Lion Controllers supplied with the gas analyzer to display data did not accurately compute to zero. It became necessary to consult directly with Red Lion's tech department and IMR to understand how to accurately calibrate the controllers. This delay was in part due to the absence of critical information inadvertently omitted from IMR's installation and operation manual for the gas analyzer.
4. During the low-end (zero) calibration of the controllers, an electrical glitch in the IMR 5000 Gas Analyzer became apparent. While the gas analyzer was being trouble shot and before we could find this the source of this problem, the unfound electrical glitch caused the Programmable Logic Controller (PLC) in the gas analyzer to loose its entire program.
5. At this point, it was initially thought by us and by IMR that the quickest and least expensive solution would be for us to reinstall the lost program onto the PLC at Mera's facility in Hawaii. However, the program IMR sent by e-mail could not be opened and used without first purchasing additional software from the manufacturer of the PLC and then installing it on our computer.
6. At this point we decided the least expensive approach was to remove the PLC from the gas analyzer (Figure 6) and return it to IMR and have them install the program onto the PLC at their facility. IMR installed the program and returned the PLC to us.

Figure 6. Detail wiring and location of the PLC unit (large black component in the bottom half of the photograph).

7. It was not until after installing the PLC back into the gas analyzer that we discovered all the V-memories in the PLC were now reset to the factory defaults.
8. Finally, after locating and resetting all V-memory functions of the PLC to the correct settings for our application, we were able to successfully calibrate the controllers and complete the interface with our process control and data acquisition system.

Due to the details mentioned above, considerably more time and labor than originally allotted for this portion of the project were required to complete the startup of the gas analyzer. However, all challenges were met and the gas analyzer is now up and running and is interfaced with Mera's process control and data acquisition system.

We have also added the software necessary to interface with the gas analyzer controller and acquire data to our main DOE process control application. The user interface includes a panel showing raw instantaneous data for CO_2, NO_X and SO_X gases as well as real time trends for those gases for both stack 1 and stack 2 (Figure 7). A series of interactive historical trends were also created allowing the user to select and plot up to 30 days of data right on the process control application screen (Figure 8). All tags corresponding to gas analyzer data were also added to the archive InSQL database.

A coal reactor is being readied by PSI for shipment to Hawaii. The reactor will be used to burn three different types of coal the gases of which will be introduced into active photobioreactors to test the effectiveness of microalgae to take up the CO_2 thus produced.

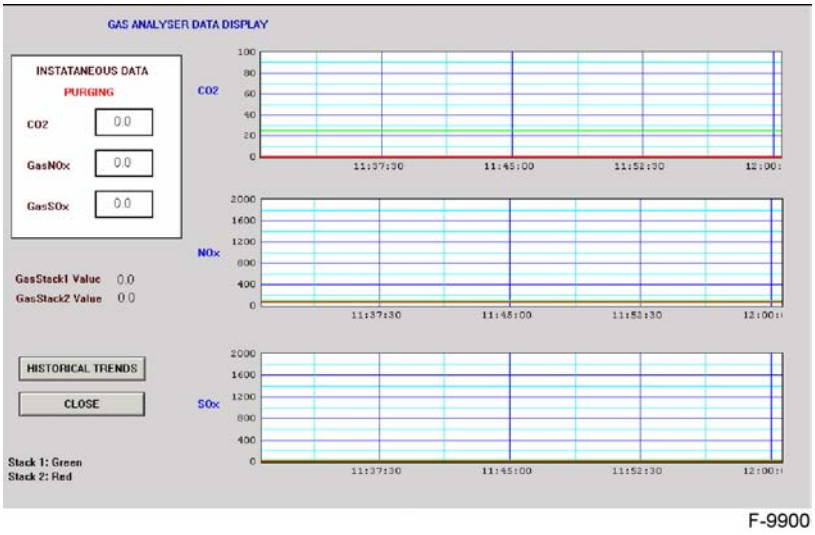

Figure 7. Screen capture from our user interface showing raw instantaneous data and real-time trends for CO_2, NO_X and SO_X gases (at this point this is only test data).

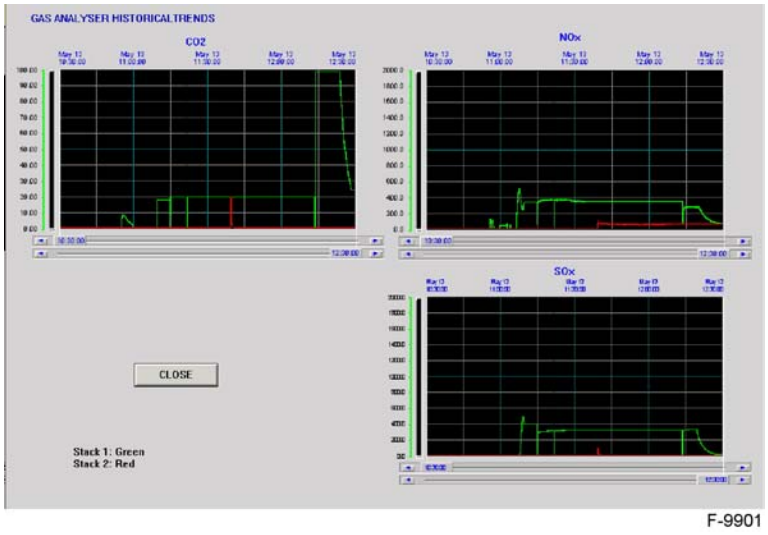

Figure 8. Screen capture from our user interface showing interactive historical trends which have also been created allowing the user to select and plot up to 30 days of data right on the process control application screen for CO_2, NO_X and SO_X gases for both stack 1 and stack 2 (at this point this is only test data).

4.3.2 Task 3.2: Full Scale Production Run

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 a propane combustor to the photobioreactors. Based

on the results of Task 1.3, we will optimize the gas injection system for maximum dissolution of CO_2. Each species will be run at this scale for 6-10 weeks, allowing for optimization.

Our focus here is on optimizing the performance of existing photobioreactors, rather than on making significant modifications to photobioreactor design. Mera has already invested approximately $10 million in engineering and development of the MGM, and has supported numerous quantitative studies in support of that effort. This is not to say that further improvements are undesirable, but we believe they are outside the scope of this project. Many of the significant possible improvements can be better understood by first incorporating these into our economic model (Task 5). At the 25,000-L scale, many improvements in carbon fixation rates can be achieved by careful alteration and testing of key variables. Our experiments will focus on the following: turbulence and light intensity, nutrient medium, temperature, and pH.

A propane combustion system is being designed (in house) to produce flue gases that will be similarly used in the photobioreactors.

4.3.3 Task 3.3: Algae Separation and Final Product

During this quarter we have not carried out any measurements on algal biomass separations. We will continue conducting harvest experiments on the 2000 L MGM pilot scale cultures during the following quarters.

4.4 Task 4: Carbon Sequestration System Design

To evaluate the potential for application of photosynthetic sequestration of CO_2 to industrial-scale combustion systems, we 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 CO_2. Key components to be designed include: CO_2 removal process; CO_2 injection device; photobioreactor; product algae separation process; and process control devices. As the proposed system depends on the solar energy to photosynthetically convert CO_2 to products compounds, optimization of the photobioreactor is an important part of this task. In the reporting period, PSI focused its effort on developing a design

concept for a large scale photobioreactor which accomplish sequestration of CO_2 and**,** at the same time, accomplish photovoltaic (PV) electric power generation.

Photobioreactor for CO_2 Sequestration and PV Power Generation

One of the important requirements for bio-fixation of CO_2 is to reduce the cost of the process. Aquasearch Inc. came up with producing high commercial value byproducts (pigments, diet supplements) to offset the sequestration cost. In a past quarterly report (Quarterly Technical Progress report #4) we discussed a method of utilizing the photosynthetically active radiation (PAR) for microalgae and non-PAR for photovoltaic electric power generation. The objective of the concept discussed in this report is to generate electric power utilizing the non-PAR spectra not useful for microalgae. By this method, biofixation of CO_2 is not disturbed by PV power generation. We will be using the solar spectra, which would otherwise be wasted, for useful purpose.

The photosynthesis reaction of microorganisms utilizes solar spectra between 400 and 700 nm, although the absorbance characteristic of species may vary. Figure 9 shows absorbance spectra of three species of planktonic algae.[4] These spectra, called photosynthetically active radiation (PAR), are only a portion of the incident solar energy on earth. Figure 10 shows the AM1.5 solar spectra, a typical terrestrial solar spectra reference used in the U.S. The solar spectra between 400 and 700 nm comprise about 44% of the total solar flux intensity. The solar spectra with wavelengths shorter than 400 nm comprise about 5%, while the spectra with wavelengths longer than 700 nm comprise 51% of the total solar flux.

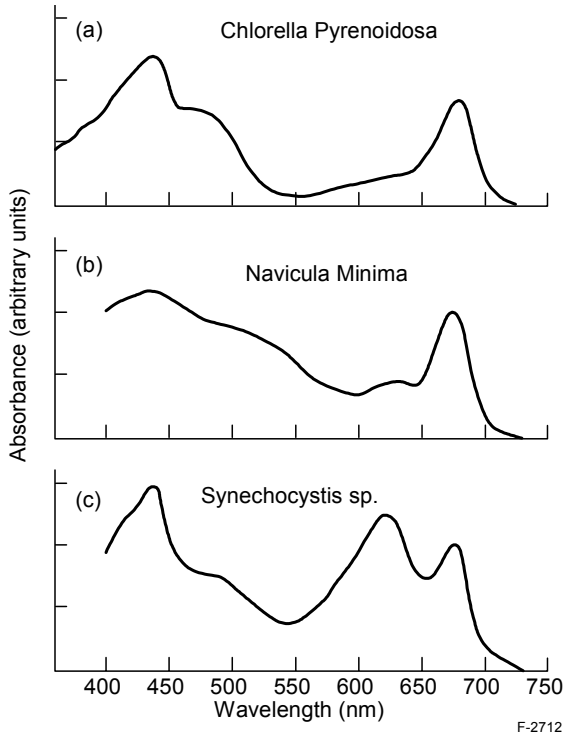

Figure 9. Absorbance spectra of three species of planktonic algae.

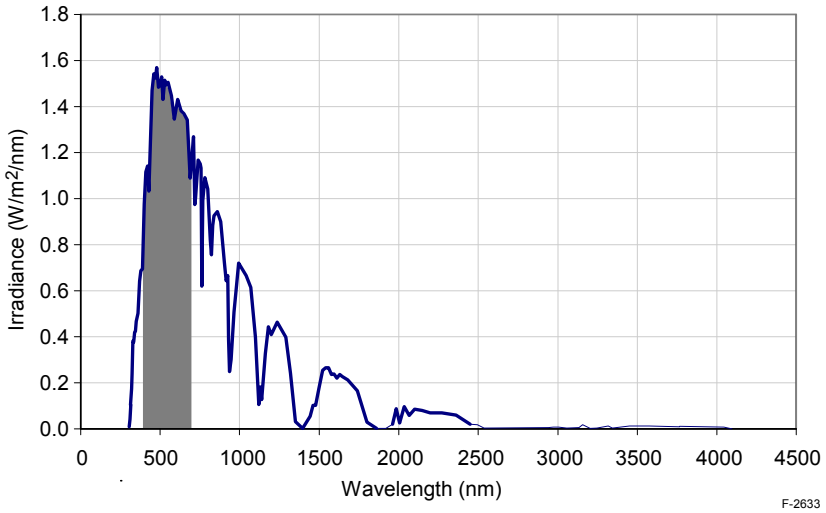

Figure 10. Air mass 1.5 (AM1.5) solar spectra with PAR portion marked in gray.

PSI has demonstrated separation of PAR from solar spectra using dichroic optics (cold mirror). Figure 11 shows the decomposed AM1.5 spectra.[5]

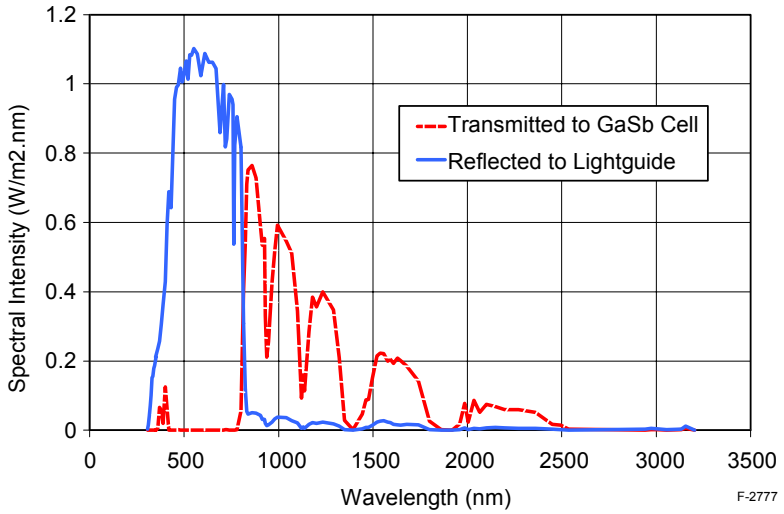

Figure 11. AM1.5 Solar Spectra (direct) separated by the Cold Mirror (Coherent 35-6907).

Conversion of the non-PAR solar spectra to electric power can be accomplished by using low bandgap photovoltaic cells. Candidate photovoltaic cells include crystalline Si (cr-Si λ_{bg} =1.11 µm), crystalline Ge (cr-Ge λ_{bg} =1.9 µm), crystalline InGaAs (cr-InGaAs λ_{bg}= 1.55 µm), and crystalline GaSb (cr-GaSb λ_{bg} =1.8 µm), and thin film copper-indium-gallium-diselenide (CIGS λ_{bg} =1.8 µm). Table 2 shows a list of the five listed PV cells, with effective wavelengths given in the second row. For the cr-Si cell, the solar spectra $\lambda < 400$ nm or the spectra 700 nm $< \lambda <$ 1.11 µm can be utilized for electric power generation. The cr-InGaAs cell has an effective wavelength up to 1.55 µm and can utilize a broader solar wavelength regime ($\lambda <$ 400 nm and 700 nm $< \lambda <$ 1.55 µm). The cr-GaSb cell has an even broader regime,

Table 2. Characteristics of Low-Bandgap Photovoltaic Cells

	cr-Si	cr-InGaAs	cr-GaSb	cr-Ge	CIGS
Bandgap Energy Eq (eV)	1.12	0.8	0.72	0.66	1.10
Effective Wavelength (μm)	<1.11	<1.55	<1.8	<1.9	<1.14

converting solar spectra up to 1.8 μm ($\lambda < 400$ nm and 700 nm $< \lambda <$ 1.8 μm), and cr-Ge even broader ($\lambda < 400$ nm and 700 nm $< \lambda <$ 1.9 μm). The thin film CIGS cell has a spectral range close to that of cr-Si, but this amorphous material is more economical.

Large Scale Photobioreactor

The photobioreactor with PV cells to be used for the CO_2 sequestration must be in a large scale and low cost. A photobioreactor design concept is shown in Figure 12. In this design, microalgae flows in the transparent tube placed at the focal point of the cylindrical reflector. The reflector is aligned in the east-west direction so that the focus of the sun is always on the photobioreactor tube.

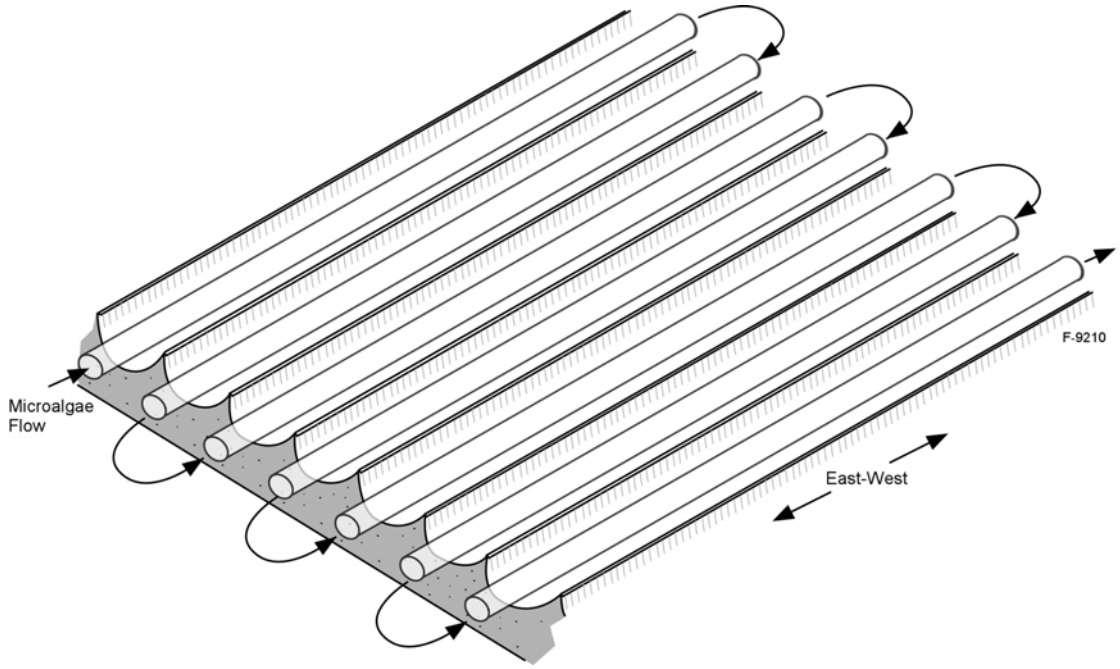

Figure 12. Large scale photobioreactor for CO_2 sequestration and PV power generation.

Construction of Photobioreactor and PV Cells

Construction of the photobioreactor is described in Figure 13. The cylindrical reflector is mould on the ground, likely to be made of concrete. PV cell panel (made of thin film amorphous silicon, for example) is placed on the cylindrical reflector surface. The PV cell panel is covered with a transparent membrane which has dichroic coating. The coating characteristic is the same

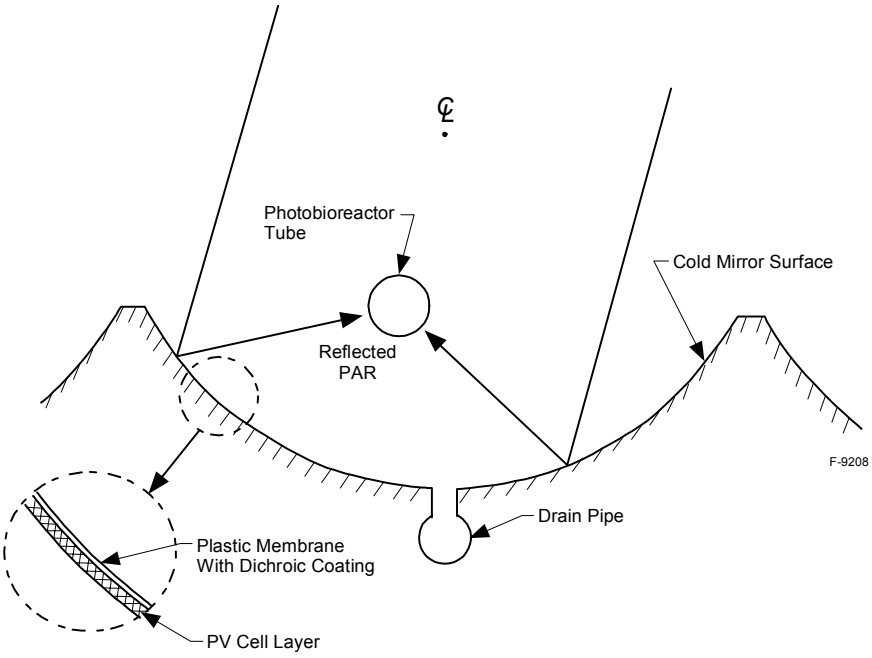

Figure 13. Construction of the cylindrical reflector and the photobioreactor tube.

as the "cold mirror" we have used in our previous solar spectra splitting experiment. The dichroic membrane reflects the PAR spectra to the photobioreactor tube, while the non-PAR spectra reaches the PV cell panel.

As the cylindrical reflector is aligned in the east-west direction, it does not require daily solar tracking. However, it does require seasonal adjustment. This can be achieved by moving the photobioreactor tube as shown in Figure 14. In this figure adjustment of the photobioreactor tube for Hawaii (20 deg north) location is depicted. At Summer Solstice, the Sun is almost directly above (93.5 deg), while at Winter Solstice, the Sun is at 46.5 deg. The photobioreactor tube must be moved between the two extreme locations. However, this seasonal movement of the photobioreactor tube can be made with a simple mechanical device at a minimum power requirement. Note that moving the photobioreactor tube, rather than tilting the cylindrical reflector, is cost effective method for a large scale photobioreactor plant.

In the following quarters, we will evaluate the concept discussed above 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 CO_2 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

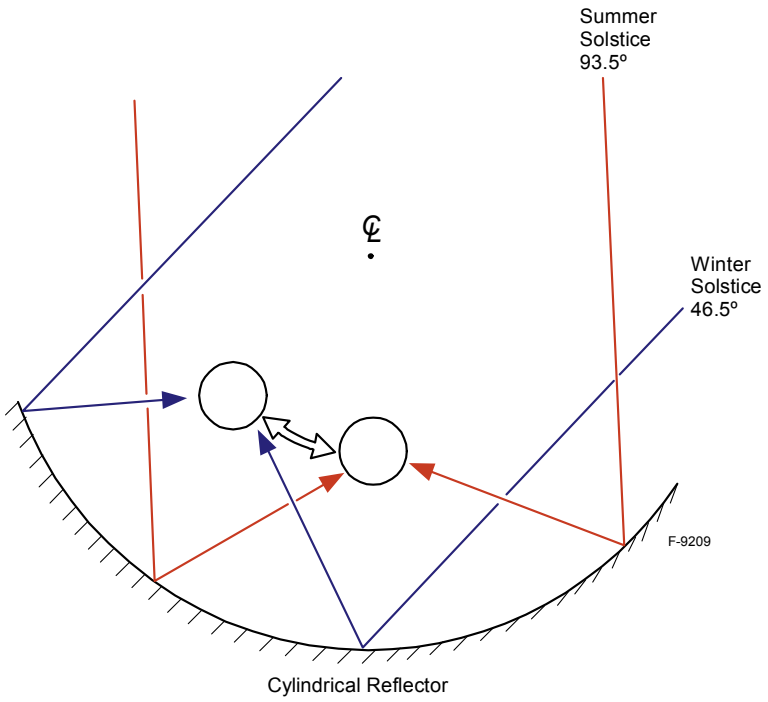

Figure 14. Seasonal adjustment of the photobioreactor tube.

on the data obtained since the visit. A description of technical activities conducted by UH during this reporting period is provided below.

CO_2 Injections

As mentioned in the previous Quarterly Report, we have been employing information provided by Mera Pharmaceuticals to conduct carbon balances and to estimated CO_2 sequestration efficiencies. An issue that required clarification was whether there was significant outgassing of injected CO_2 from the media in the Mera Growth Modules (MGM). During this reporting period an analysis was conducted to compare the solubility of CO_2 in the media with the daily amount of CO_2 injected. When the amount of injected CO_2 exceeds the solubility of the gas in the liquid media, then there is an expectation that outgassing will occur. The converse (solubility greater than the amount of injected CO_2), however, does not guarantee that CO_2 is retained in the liquid, since phase transfer effects (i.e., injected gas residence time and transfer rates between the gas phase and liquid media) must also be considered.

Assuming that water was a reasonable approximation of the MGM media, CO_2 solubility was determined by standard formulations. Data collected from photobioreactors identified as M13A-020317, M13A-020421, and M13A-020603 indicated an average media temperature of 17°C. At 17°C and 1 atmosphere pressure, CO_2 solubility in pure water is 0.1845 g CO_2 per 100 g water. The average volume of media in the MGM is 20,879 L. This indicates that 38.52 kg of CO_2 can be dissolved before the solution is saturated. Review of the Mera data indicated that the maximum daily volume of CO_2 injected into the media was 5.50 m^3 or

10.18 kg. The maximum mass of CO_2 injected into the media on any day was therefore about 26% of the mass of CO_2 that could be dissolved. More detailed analyses of the media carbon chemistry is being conducted.

Sample Analysis

As mentioned in the previous Quarterly Report, total organic carbon content analysis of dried samples of *Haematococcus pluvialis* collected from the MGM have been initiated. During the present reporting period, we submitted a request for additional samples from Mera Pharmaceuticals. These samples need to be collected following a particular sampling protocol. The first sample should be collected immediately after seeding of the photobioreactor. If the seeding occurs during the day, then the next sample will be taken after sunset that seeding day. If seeding occurs during the night, then the next samples will be taken before sunrise and after sunset of the next day. The samples to follow will be taken before sunrise and after sunset every day until the first harvest. The last sample will be taken before the first harvest. These samples will be analyzed to obtain a more complete documentation of the variation in the percentage of total organic carbon during the day and night.

Graduate Research Assistant (GRA) Thesis Proposal

The GRA working on this project prepared his M.S. thesis proposal during the present reporting period. The proposed effort will focus on the development of a systems model that can be used to optimize the harvesting of *Haematococcus pluvialis* for astaxanthin production. The Executive Summary of this thesis proposal follows.

M.S. Thesis Proposal Executive Summary

One method for reducing the atmospheric concentration of carbon dioxide, a greenhouse gas that may play a role in global warming, is to capture and sequester carbon dioxide from stationary combustion systems by photosynthetic microalgal species such as *Haematococcus pluvialis*. Under adverse environmental conditions, *Haematococcus pluvialis* produces a high-value compound called astaxanthin, a carotenoid pigment that provides health benefits to humans. Mera Pharmaceuticals, Inc. has an industrial-scale astaxanthin production process. As part of this process, biomass production occurs in a Mera Growth Module (MGM) and astaxanthin accumulation occurs in the ponds. A harvesting strategy is used in the large-scale astaxanthin production process when transferring the cells from the MGM to the ponds. However, the harvesting strategy is not optimized. An optimal harvesting strategy can be used to maximize profit, and in such a strategy, knowledge about the biological, physical, and economical elements in the production process are crucial. In this study, a model of the harvesting strategy that includes *Haematococcus pluvialis* population dynamics will be developed to maximize profit for astaxanthin production. An economic analysis will be derived from the model. Also, the carbon sequestration efficiency will be determined from the population dynamics. After developing the model, it will be checked to verify that it is working properly. Different scenarios will be simulated using the model to determine the combination of harvesting quantities and the number of days between harvests that provide for maximum profit.

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

During this quarter, we have continued to put together the economic modeling effort that will result in predicted costs for a microalgal-based carbon sequestration plant. The economic models are driven by scientific/technical variables (e.g., microalgal growth rate) and can be applied to a variety of product scenarios. At present, the models are designed for facility sizes of 5 to 50 ha, and may be changed for application to larger facilities as contemplated in this proposal.

The models also treat a detailed breakdown of operating expenses, capital costs, and human resources, each of which is analyzed with regard to functional subsystems (e.g., water pretreatment, media formulation, photobioreactor operation, product processing, quality control). Finally, the models also include detailed analysis of area requirements, utility usage, and product flows within the production system.

Costs in the Mera/Aquasearch economic models are currently based on historical data for actual costs incurred. One of our key activities in this project will be to research the costs of equipment and supplies at significantly larger scales. All model assumptions will be clearly stated in detail and, where applicable, all model results will comply with international GAAP (Generally Accepted Accounting Principles) standards.

Microalgal plant design

On our last report we presented the basic assumptions that would go into the design of non-optimized microalgal plant that would utilize combustion gases as its source of CO_2. The design parameters for this plant are:

Total plant surface area:	12 ha
Culture surface area:	7 ha
Support systems:	5 ha

And it assumed the following parameters:

Productivity:	8 g C m^{-2} d^{-1}
Efficiency of CO_2 utilization:	12%
Percent of culture area under cultivation:	81.6%

We also presented a sketch of such a plant and the materials mass flows that reflect the needs to run Mera's actual microalgal plant in Kona, Hawaii. The plant under consideration is, however, significantly larger (about 30x more capacity) and an updated mass flow diagram will be generated and presented in future reports. It should be noted that this plant's characteristics are specific to the production of a high value product, astaxanthin, from *Haematococcus*. Thus, the plant utilizes both enclosed photobioreactors (MGM) and open pond systems. As we continue work on this design, we will also generate alternate designs for similar sized plants to produce other types of materials which might utilize only open pond reactors (e.g., *Spirulina*) or only enclosed photobioreactors (e.g., *Nanochloropsis* for lutein production).

Capital and recurring costs of microalgal plant

In this quarter we have started to put together the capital and recurring costs of a microalgal plant producing astaxanthin from *Haematococcus pluvialis.* As a first step we have begun tabulating (e.g., Table 3) all the capital costs (e.g., equipment), recurring costs (materials and supplies), labor costs, utilities, etc. Furthermore, we will carry out similar cost analysis for microalgal plants that produce other products such as *Spirulina* biomass and lutein from *Nanochloropsis*.

Calculation of "economies of scale" factors in microalgal plant engineering

We expect that as the size (scale) of the microalgal facility increases, the costs per unit biomass produced/costs per unit CO_2 sequestered will decrease. We intend to model this ESF (economy of scale factor) as follows. First, we will determine the costs associated with what we consider, based on our experience and economic models at Mera's microalgal plant, to be the smallest size microalgal plant that is economically viable (smallest economical unit or SEU). Based on the capacity of the different units of material handling equipment used in these processes we will determine at what scale (e.g., 2x, 5x, 20x, 200x capacity of the smallest size plant) the change in ESF becomes 0 (zero). We will then determine the costs for two or more microalgal plants of intermediate size. Using our calculated cost results we will formulate an equation that will relate microalgal plant scale to ESF.

In Figure 15, we show a number of possible scenarios. The different results are caused by assuming differences in the rate at which savings can be affected as plant size increases. We have also assumed that the maximum ESF that can be attained is 50% for this exercise. The equation's factors that ultimately fit our scale up cost estimates will be used in conjunction with our economic models to determine the actual costs of any plant that may be size limited by, for example, land area available near a fuel combustion gases source (e.g., a power plant).

Table 3. Partial List of Infrastructure Equipment in Mera's Kona Microalgal Plant Shown as an Example of the Large Database that We Have Put Together to Use as Input into Our Economic Models

Part Number	Manufacturer	Type of Part	Number of parts in Kona	Purchase Price	Total Cost
2A147	AMETEK	Pressure Gauge	8	$4.66	$37.28
5HK69	Ametek	Pressure Gauge	3	$8.15	$24.45
38-06-61-010	AMIAD	Turboclean Filter	1	$1,539.30	$1,539.30
6KK47	APOLO	Isolation Valve	1	$7.92	$7.92
1113060	Asahi	Butterfly valve	1	$179.20	$179.20
1070005	ASAHI	Isolation valve	6	$11.30	$67.80
1101020	ASAHI/AMERICA	Isolation Valve	1	$157.00	$157.00
CHII-N1-2FE	CHALLENGER	transfer pump	1	$548.00	$548.00
TN4885JP	Chem-Tainer, Inc.	Chemical Storage Tank	4	$951.00	$3,804.00
TN7285JP	Chem-Tainer, Inc.	Chemical Storage Tank	3	$1,606.00	$4,818.00
TC8086CC	Chem-Tainer, Inc.	Storage Tank	1	$12,199.00	$12,199.00
OS	CLA-VAL	Pressure Regulator	1	$652.00	$652.00
250W	CLOW	Isolation Valve	2	$282.00	$564.00
38471	EG&G Rotron	Blower, air, low pressure	4	$2,918.00	$11,672.00
FEBCO 825Y RP	FEBCO	Isolation Valve	2	$40.05	$80.10
KC 1130	FINISH THOMPSON	Pump	1	$1,753.00	$1,753.00
VTPVS20V-B	FIP	3-way valve	2	$269.87	$539.74
VFXV105	FIP	Ball valve	11	$17.40	$191.40
VXPVS05E-B	FIP	Control valve, FIP type	2	$34.78	$69.56
1011-10	FLO CONTROL	Backflow Valve	1	$11.17	$11.17
1011-20	FLO CONTROL	Spring Check Valve	8	$15.53	$124.24
3/4 DN 20	FN	Isolation Valve	1	$11.74	$11.74
2" DN 50	FNW	Isolation valve	2	$40.05	$80.10
69050D331141	Gemu	valve, Gemu pneumatic	17	$426.00	$7,242.00
69080D301141	GEMU	Valve, Gemu pneumatic	2	$963.00	$1,926.00
HUR-170-HP	Harmsco	Filter	4	$2,500.00	$10,000.00
1078002	HARRINGTON	Labcock Valve	4	$11.40	$45.60
HCTB1200SACTV	Hayward	Ball valve	48	$250.40	$12,019.20
HCTB1200SACTV-4	Hayward	Ball valve	5	$602.40	$3,012.00
HCTB1100SACTV	HAYWARD	Isolation valve	3	$267.00	$801.00
2475N7.5	Ingersol Rand	Compressor, air	1	$2,273.00	$2,273.00
MP0101	Inland Machinery	portable S.S. tank	2	$3,600.00	$7,200.00
L423-44	LMI, Milton Roy	Metering Pump	4	$2,983.50	$11,934.00
U-07553-70	MASTERFLEX	Tubing Pump	1	$495.00	$495.00
11200-0100	NORTON	storage tank	2	$472.90	$945.80
CKM050V-PF	PLAST-O-MATIC	Backflow Valve	5	$82.10	$410.50
PRH300B-PV	Plast-O-Matic, Inc.	Pressure Regulator	1	$1,623.16	$1,623.16
3-2536-P0	Signet	Flow sensor	11	$224.40	$2,468.40
SS4P4T1	Swagelock	Pecock Valve	4	$45.90	$183.60
A/SA182	TAH Industries, Inc.	Static mixer	1	$450.00	$450.00
MBV200VST-PV	TRUE BLUE	Control valve	17	$77.38	$1,315.46
RF45	Water King	Water Softener	1	$1,582.00	$1,582.00
A88E1013	WATTS	Backflow Valve	2	$134.34	$268.68
25AUB-Z3	WATTS	Pressure Regulator	2	$85.30	$170.60

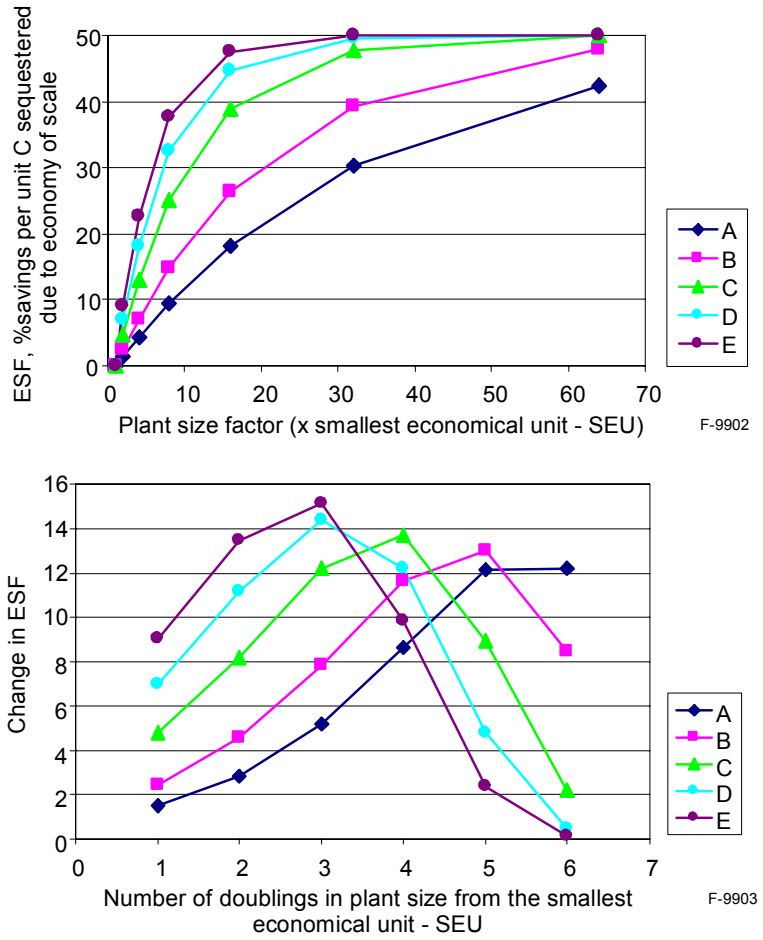

Figure 15. Possible ESF results based on 5 different scenarios reflecting differences in the assumed rate at which savings can be effected (A→E = faster) as plant scale increases (top panel) and the resulting changes in ESF as plant size doubles (bottom panel). In this case, we have assumed that maximum attainable ESF is 50%.

5. Conclusion and Future Plans

5.1 Task 3: Optimization and Demonstration of Industrial Scale Photobioreactor

In this quarter we have continued with our scale up efforts, including describing conditions that favor formation of carbonates at larger scale. Conclusion and future plans are summarized below.

- Based on the scale-up and open pond experiments we concluded that addition of $CaSO_4*2H_2O$ to the medium did not result in a lowering of productivity (astaxanthin or total weight of mass harvested) .
- Prepared instrumentation for gas analyzer for pilot scale and full scale production run.

- Installed gas analyzer in preparation for pilot scale and full scale production tests.
- Prepared and readied PSI coal reactor to be shipped to Aquasearch in Kona, Hawaii.

Within the next quarter we expect to

- Continue scaling up of promising strains to the 2000 L outdoor photobioreactor scale,
- Continue testing gas measuring equipment,
- Install a coal combusting unit (provided by Physical Sciences Inc.) to supply coal combustion waste gases to the MGM cultures, and
- Design and install a propane combustion system to provide propane combustion gases to the MGM cultures.

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 CO_2 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

- Put together the economic modeling effort that will result in predicted costs for a microalgal-based carbon sequestration plant.

6. References

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