

**RECOVERY AND SEQUESTRATION OF CO₂ FROM STATIONARY COMBUSTION
SYSTEMS BY PHOTOSYNTHESIS OF MICROALGAE**

Quarterly Progress Report #1

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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 from 1 October to 31 December 2000. During this period planning of chemostat experiments at Aquasearch was initiated. These experiments will be used to select microalgae for the photobioreactor demonstrations. An initial survey of techniques for removing CO₂ from coal-fired flue gas was begun. Chemical adsorption using MEA is the most mature technology and looks to be the most economically viable in the near future.

1. EXECUTIVE SUMMARY

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. 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 entails combining CO₂ from the fossil fuel combustion system and nutrients in a photobioreactor where microalgae photosynthetically convert the CO₂ into compounds for high commercial values or mineralized carbon for sequestration. The advantages of the proposed process include the following.

1. High purity CO₂ gas is not required for algae culture. It is possible that flue gas containing 2~5% CO₂ can be fed directly to the photobioreactor. This will simplify CO₂ separation from flue gas significantly.
2. Some combustion products such as NO_x or SO_x can be effectively used as nutrients for microalgae. This could simplify flue gas scrubbing for the combustion system.
3. Microalgae culturing yields high value commercial products that could offset the capital and the operation costs of the process. Products of the proposed process are:
(a) mineralized carbon for stable sequestration; and (b) compounds of high commercial value. By selecting algae species, either one or combination or two can be produced.
4. The proposed process is a renewable cycle with minimal negative impacts on environment.

The proposed program calls for development of key technologies pertaining to: (1) treatment of effluent gases from the fossil fuel combustion systems; (2) transferring the recovered CO₂ into aquatic media; and (3) converting CO₂ efficiently by photosynthetic reactions to materials to be re-used or sequestered. A description of the work plan for accomplishing these objectives is presented in Section 2.2 of this report.

The work discussed in this report covers the reporting period from 1 October 2000 to 31 December 2000. During that time an initial survey of techniques for removing CO₂ from coal-fired flue gas was begun. Application of these carbon dioxide separation processes to flue gas depends on the concentration of CO₂ in the stream, on the presence of impurities in the gas, and on the pressure of the flue gas stream. Chemical adsorption may be preferred for cases in which the concentration of CO₂ is low and the pressure is near atmospheric. Physical adsorption is favored for higher total pressure and concentration of CO₂. Chemical adsorption using MEA is the most mature technology and looks to be the most economically viable in the near future.

Planning of chemostat experiments at Aquasearch was initiated during this period. These experiments will be used to select microalgae for the photobioreactor demonstrations. Gas compositions were specified and equipment was ordered.

2. INTRODUCTION

Emissions of carbon dioxide are predicted to increase in the next 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 10-15 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.

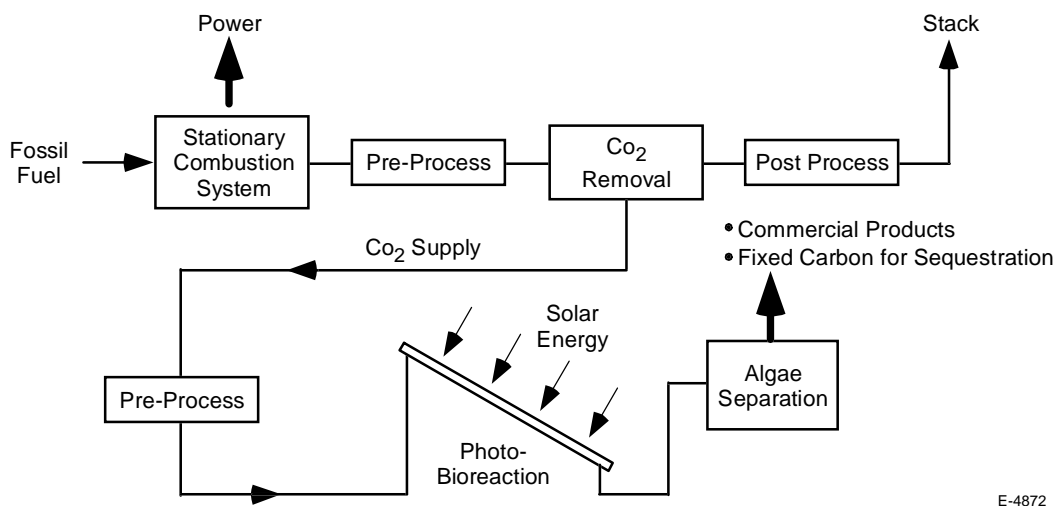


Figure 1. Recovery and sequestration of CO₂ from stationary combustion systems by photosynthesis of microalgae.

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.

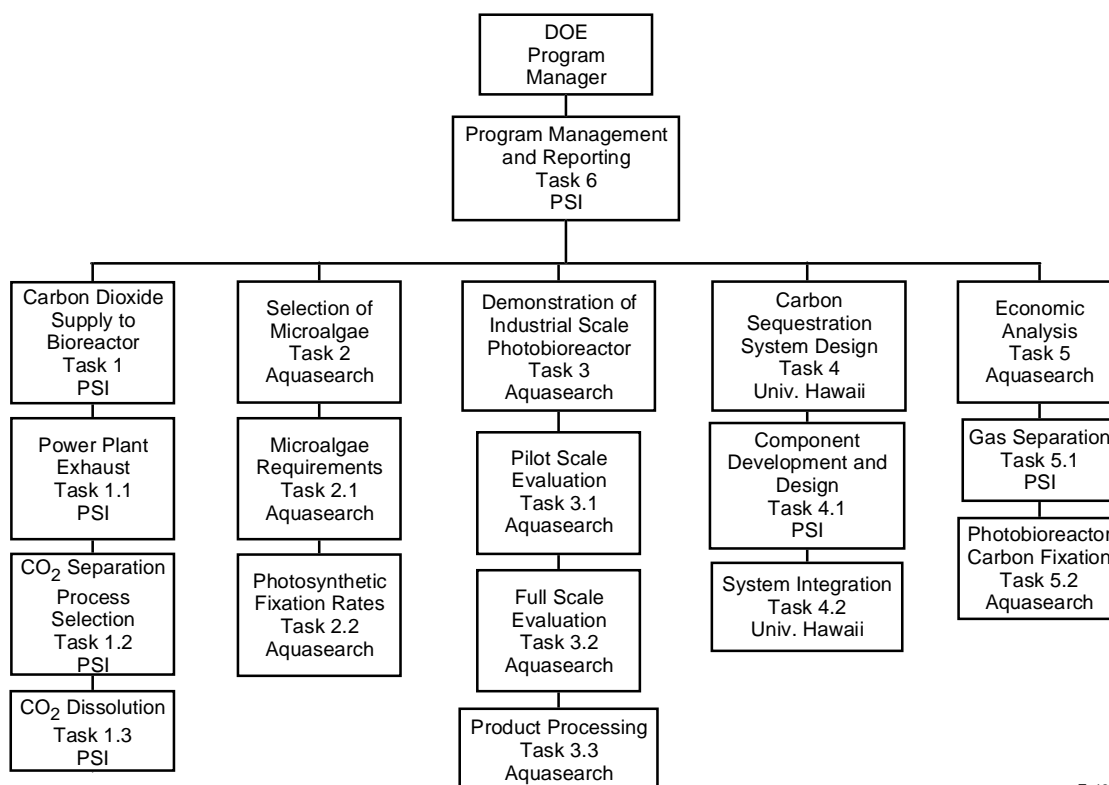
The research and experimentation we propose will examine and quantify the critical underlying processes. To our knowledge, the research we propose represents a radical departure from the large body of science and engineering in the area of gas separation. We believe the proposed research has significant potential to create scientific and engineering breakthroughs in controlled, high-throughput, photosynthetic carbon sequestration systems.

3. EXPERIMENTAL

The research program calls for development of key technologies pertaining to: (1) treatment of effluent gases from the fossil fuel combustion systems; (2) transferring the recovered CO₂ into aquatic media; and (3) converting CO₂ efficiently by photosynthetic reactions to materials to be re-used or sequestered.

The challenging nature of the proposed program requires a qualified multidisciplinary team. Aquasearch Inc., a U.S. company, has developed full-scale, operating photobioreactor technology with its own investment of more than \$13 million. Aquasearch photobioreactor technology now produces commercial quantities of high-value microalgae products. The University of Hawaii provides unique expertise in the understanding and analysis of carbon sequestration processes. PSI has extensive government program management experience and unique technical expertise in the areas of pollution control from stationary power systems and solar engineering.

The 3-year program consists of the following tasks; (1) recovery of CO₂ from power plant flue gas to photobioreactor; (2) selection of microalgae best suited for the proposed process; (3) optimization and demonstration of industrial scale photobioreactor; (4) carbon sequestration system design; and (5) economic analysis. Figure 2 shows the organization of the program with five main tasks. The tasks are explained in more detail below.



E-4877

Figure 2. Program organization.

3.1 Task 1.0 - Supply of CO₂ from Power Plant Flue Gas to Photobioreactor

Subtask 1.1 - Power Plant Exhaust Characterization

The issue of supplying CO₂ from power plant flue gas to the photobioreactor system entails that the team reproduce representative types of industrial flue gas and test their ability to support microalgal carbon fixation. In this Subtask, we will first undertake to reproduce a variety of flue gas types at a scale sufficient only for laboratory experiments with microalgae. For the laboratory scale experiments in microalgae growth and carbon fixed to be carried out in Task 2, small amounts of simulated flue gas are needed and can be mixed using bottled gases. The results of the laboratory experiments (Task 2) will guide the selection of appropriate flue gas generation for large-scale demonstration (Task 3). At the larger scale (2,000 and 25,000 liter bioreactors), the flue gas will be generated using exhaust from the existing propane-fired boiler at the Aquasearch facility.

Subtask 1.2 - Selection of CO₂ Separation and Clean-Up Technologies

There are several technologies currently available to separate and capture CO₂ from fossil-fueled power plants including absorption from gas streams by contact with amine-based solvents, cold methanol or sorbents and passing the gas stream through special membranes. The optimum process for capturing CO₂ is largely influenced by the concentration or partial pressure of CO₂ in the flue gas; this depends, in turn, on the characteristics of the fuel and combustion system. The results of the laboratory screening experiments with microalgae will dictate the type and degree to which separation and clean up technologies may be necessary. Ideally, the no such procedures would be necessary. However, this will be dependent on the tolerance of the microalgae to certain components of the gas mixtures. Such tolerance will likely depend not only on the nature of the constituent compounds, but also on their concentration. Therefore, in this Subtask, we will characterize the effluents and processing conditions of processes applicable to separation of CO₂ from flue gas.

Subtask 1.3 - Carbon Dioxide Dissolution Method

In the small, laboratory scale reactors used in Task 2, any introduced gases are effectively mixed instantaneously throughout the culture medium. This is not so in larger scale reactors (particularly the 25,000 L AGM), due to the physical configuration of the photobioreactor. In this task, we will undertake theoretical and experimental investigations of the optimum method for dissolving CO₂ from the flue gas mixtures into the aqueous environment of the bioreactors. The results of this investigation will be implemented in Task 3 in the 25,000-L AGM.

3.2 Task 2.0 - Selection of Microalgae

Subtask 2.1 - Characterization of Physiology, Metabolism and Requirements of Microalgae

A preliminary set of laboratory experiments will be conducted using approximately 20 species of microalgae and 5 different, representative flue gases. We seek to use species that grow optimally at high temperatures, since this can yield order-of-magnitude increases in

photosynthesis, and those whose size, physiology and behavioral characteristics may favor reduced final processing costs. Finally, carbon-mineralizing species tend to be more effective at high pH, and can withstand significantly higher concentrations of dissolved inorganic carbon. The first level of cultivation will be carried out in 60-ml Erlenmeyer flasks, with the goal of determining temperature optima of the strains we have selected. Each strain will be cultured for a period of approximately 2 to 3 weeks at temperatures of 15, 20, 25, and 30°C in separate temperature-controlled incubation chambers. In each temperature range, we will adjust the pH of the medium to 7.0, 7.5, 8.0, and 8.5. All other variables will be kept constant.

Subtask 2.2 - Achievable Photosynthetic Rates

The performance of each species will be quantitatively evaluated with regard to photosynthetic carbon fixation. The comparative results of these laboratory experiments will be used to select a much smaller number of species for demonstration scale experiments in commercial photobioreactor systems. The goal of these experiments is to quantify the response of selected microalgae to differences in the nature of representative flue gases. We will use experimental mixtures of simulated industrial gases both (a) as the primary carbon source and (b) as a means of controlling pH of the cultures. Gas composition will be formulated and controlled as described in Task 1. Standard laboratory methods for continuous cultures will be followed. Laboratory cultures will be inoculated and maintained in 2-L chemostats (laboratory-scale photobioreactors). Nutrient media will be sterilized. Light will be provided by full-spectrum fluorescent lighting at an incident intensity in the range of 100 to 150 $\mu\text{E cm}^{-2} \text{ sec}^{-1}$. For each species, this experiment will be carried out only at the temperature indicated by the optimum temperature from the preliminary experiments in 60-ml flasks. We will use a standard method for maintaining homogeneous suspensions of cells: cultures will be agitated by bubbling with filtered, ambient air. Experimental gases will be administered on an as-needed basis as determined by the pH of the medium. All cultures will be equipped with a calibrated pH electrode, connected to the Aquasearch process-control system. When the photosynthetic utilization of dissolved inorganic carbon causes the pH to move above the upper-limit set point, the experimental gas stream will be automatically turned on. When the concentration of inorganic carbon in the medium attains the lower-limit set point, the experimental gas stream will automatically be turned off. We will initiate each chemostat culture by using the purest form of CO_2 possible. This initial phase will act as a control. With pure CO_2 we expect to obtain the highest possible rates of cell division and carbon fixation. We will use the common practice in chemostat cultivation for determining maximum sustainable rate of production. This is done by administering nutrient medium at ever-increasing rates during the initial phase of the experiment. As the dilution rate of the culture increases, so does total productivity - up to some optimum point where it begins to decrease again as the culture is washed out. Once the maximum productivity of the cultures is established using pure CO_2 , we can proceed to administer simulated flue gas. All cultures will be connected to the same experimental gas source at the same time. The experimental gas line will be joined to the ambient air line. The rate of providing gas will be determined, as indicated above, by the pH of the medium which, at high and low set points, *will* activate a solenoid valve that open or shuts to control the flow of gas. We plan to test approximately half a dozen simulated flue gases. This approach allows us to determine relative rates of maximum productivity for each species, and to maintain each culture under reasonably favorable growing conditions for a long enough time to observe the effects of

each flue gas in a quantitative manner. Measurement of the amount of carbon supplied to each culture will be based on a calculation from the following information: (1) the known concentration of carbon in the source gas, either as pure CO₂ or as CO₂ present in any simulated flue gas; (2) the flow rate of the gas to the culture when the solenoid valve is open and (3) the amount of time that the solenoid valve is open, as recorded by the Aquasearch process control system. Thus we will be able to estimate the rate at which carbon was supplied to any culture for any selected period of time during the experiment. The analysis of laboratory experiments will yield the following specific, quantitative information for both mineralizing and high-value species:

- Comparative carbon fixation rates and
- Carbon utilization efficiency as a function of type of industrial flue gas and
- Standard variables of microalgal growth, including temperature, pH, and composition of the nutrient medium.

Based upon the quantitative outcome of these measurements, we will reduce the number of candidate species to no more than three species from each category (i.e., carbon-mineralizing or high-value). We may also choose, as a result, to focus only on certain types of representative flue gases for large-scale demonstration.

3.3 Task 3.0 - Optimization and Demonstration of Industrial Scale Photobioreactor

Subtask 3.1 - Pilot Evaluation

The main goal of these experiments is to quantify carbon fixation rates and utilization efficiencies in AGM 2,000-L photobioreactor. There are two significant differences between laboratory chemostats and the AGM that could influence carbon utilization at this scale. These differences concern (1) light intensity and (2) the mixing, dissolution and distribution of gases. Each experiment will involve cultivating a single species in six separate 2,000-L photobioreactors. One reactor will employ pure CO₂, serving as a control to benchmark the maximum-C fixation rate. All gas sources, whether pure CO₂ or flue gas, will serve as both the inorganic carbon source and the means of controlling pH. The method of carbon supply will be as in chemostat experiments, with the gas source automatically turned on and off as dictated by the pH set points. All photobioreactors will be run under the same conditions, so that the only variable is the type of flue gas. We plan to run each experiment for approximately 30 days. With standard methods used by Aquasearch, 2,000-L photobioreactors need 7 to 10 days after inoculation to come to steady-state condition (depending upon growth rate). This leaves 20 days of steady-state operation to provide a time-series of data for analysis. The 20-day period is important because it allows averaging of the effects of day-to-day variability in incident solar radiation, and also provides for sufficient replicate measurements in all variables, which will be measured daily. Data analysis will be as for chemostat cultures (Task 2). The purpose of the AGM experiments is precisely to examine scale-related effects. The measured variables will, however, be identical. Results should allow us to make realistic estimates of carbon fixation rates and utilization efficiencies in large scale photobioreactors, as a function of the inorganic carbon source.

Subtask 3.2 - Full Scale Production Runs

The goal of the 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 AGMs, the commercial reactors on which current economic models are based. Flue gas will be supplied by a slipstream from the existing propane combustor that 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, the goal of this task will be to optimize the gas injection system for maximum dissolution of CO₂. We will conduct experiments in the 25,000-L AGM using propane combustion product flue gas supplied by the system developed and using only the 5-6 species of microalgae selected for large-scale experiments. Each species will be run at this scale for 6-10 weeks, allowing for optimization. The focus here is on optimizing the performance of existing photobioreactors, rather than on making significant modifications to photobioreactor design. Many of the significant possible improvements can be better understood by first incorporating these into the 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. The experiments will focus on the following: turbulence and light intensity, nutrient medium, temperature, and pH.

Subtask 3.3 - Algae Separation and Final Product

We plan to carry out studies on separation and final processing sufficient to parameterize economic models. Processing costs may vary over a broad range, depending primarily on the equipment and manpower required. The goal of this portion of the work will be to identify the type of equipment and manpower needed for each of the final five to six species used demonstrated at the 25,000-L photobioreactor scale. We plan to carry out experimental processing methods for each of the five to six final microalgae species. Aquasearch does have a wide array of commercial scale processing equipment, including centrifuges and dryers. Experiments using this equipment, supplemented where necessary by laboratory-scale measurements (e.g., sedimentation rates of whole cells), will be adequate to estimate procedures and costs of large-scale processing.

3.4 Task 4.0 - Carbon Sequestration System Design

Subtask 4.1 - Component Design and Development

In this sub-task we will 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. We are aware of the vast amount of work conducted in solar energy R&D programs sponsored by DOE and other agencies. Results of those programs will be utilized to optimize the design concept of the industrial scale field deployable photobioreactor.

Laboratory scale experiments will be conducted at PSI and at Aquasearch to determine the optimum design concept for the photobioreactor.

Subtask 4.2 - System Integration

Based on the results of Task 4.1, we will develop a process model of the integrated system and conduct parametric studies. These studies will provide quantitative insight into process performance; identify potential problems and limitations of the system; and facilitate design optimization. Results from Tasks 1 through 4.1 will be utilized to develop the operational profiles of the flue gas production module (i.e., power station combustor); the gas treatment module comprising cooling, cleanup, and CO₂ separation components; and the photobioreactor module. The modular nature of the Aquasearch photobioreactor minimizes uncertainties related to scale-up. These simulation modules and applicable property and performance databases will be integrated into a system utilizing the ASPEN PLUS process simulation software by the University of Hawaii. Process simulations will be performed for conventional coal-fired and gas turbine power stations and natural gas boilers. These scenarios represent a broad range of gas compositions, for both CO₂ and pollutant species. Flue gas production rates will be varied over at least an order of magnitude. We will vary the concentrations of particulates and gas phase contaminants within limits established by Task 1. The parametric simulations will be analyzed to assess the suitability of photosynthetic sequestration to a range of industrial fossil fuel combustors and operating scenarios (such as variations in output in response to changes in load). System performance penalties associated with increased exhaust back-pressure, parasitic loads, etc. arising from the CO₂ clean-up components will be quantified. These results will be applied to optimize component and system design.

3.5 Task 5.0 - Economic Analysis

Subtask 5.1 - Gas Separation Process

In this task, we will survey the current state of costs for carbon separation technology as applied to stationary combustion systems. The currently favored approach for removing CO₂ from flue gases is to scrub the flue gas using MEA. It is a proven technology with low technical risk. Several other processes have been proposed for carbon separation from flue gas. Each will be evaluated technically - in terms of the processing conditions and composition of the effluent stream - and economically.

Subtask 5.2 - Photobioreactor Carbon Fixation Process

Aquasearch employs several different models to assess the economic performance of photobioreactor technology. The economic models are all driven by scientific/technical variables (e.g., microalgal growth rate), and can therefore be easily applied to a variety of product scenarios. At present, the models are designed for facility sizes in the range of 10 to 100 acres, and may be changed for application to the larger facilities contemplated by 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 Aquasearch economic models are currently based on historical data for actual costs incurred. One of the 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.

4. RESULTS AND DISCUSSION

4.1 Supply of CO₂ from Power Plant Flue Gas to Photobioreactor

4.1.1 Power Plant Exhaust Characterization

The issue of supplying CO₂ from power plant flue gas to the photobioreactor system entails that the team reproduce representative types of industrial flue gas and test their ability to support microalgal carbon fixation.

In the United States coal and natural gas are the primary fuels used for power generation, although fuel oil is important in some regions. Conventional boilers (as opposed to gas turbine combustors) employ modest amounts of excess air for combustion. The CO₂ content of flue gas from boilers used for power generation ranges from 7 to 15 vol% (Table 1). Stationary diesel combustors and gas turbines fired with natural gas, also used for power generation, use much higher amounts of excess air and have, therefore, much lower CO₂ content, on the order of 3 vol%.

Table 1. Typical Flue Gas Compositions for Different Fuels and Combustion Systems

		Utility Boilers				GTCC	Diesel
	Bituminous Coal	Sub-bituminous Coal	Fuel Oil	Biomass	Natural Gas	Natural Gas	Fuel Oil
CO ₂	12%	15%	12.0%	19%	7.5%	3.5%	4%
H ₂ O	7%	12%	8%	13%	15.0%	7%	3.5%
O ₂	6%	6.0%	6%	6%	6.0%	13.5%	15.0%
N ₂	75%	67%	74%	62%	71.5%	76.0%	77.5%
SO ₂ [ppm]	1600	400	300	200	0	0	50
NO _x [ppm]	400	200	400	200	100	25	200

Concentrations of the trace acid gas species such as NO_x and SO₂ depend on the composition of the fuel and on the pollution control system employed. Natural gas-fired combustors have virtually no SO₂ in the flue gas, while coal-fired systems can have an SO₂ content in the range of 50 ppmv up to 600 ppmv; the lower end of the range represents systems with FGD systems, about 25% of the boilers in the United States. The range of NO_x emissions given in Table 1 reflect the use of low NO_x burners, selective catalytic reduction or selective non-catalytic reduction to achieve the lower end of the range.

For the small (Chemostat) experiments to be carried out in Task 2, a gas mixing system is being designed. This system will deliver up to 3 liters per minute of different gas mixtures.

4.1.2 Selection of CO₂ Separation and Clean-Up Technologies

According to recent reports^{2,3} the most likely options currently available for CO₂ separation from combustion flue gas include: gas adsorption (both physical and chemical), cryogenic separation, and membrane separation. Some of the major commercial applications of these processes are given in Table 2.

Table 2. Examples of Commercial Applications of CO₂ Removal by Gas Adsorption

Process	Owner	Uses	Comments
Sulfinol	Shell Oil Company	Natural gas, refinery gas, and synthesis gas	180 commercial units in operation or under construction in 1996
Selexol	UOP	Natural gas, refinery gas, and synthesis gas	53 commercial units installed by 1992
Rectisol	Lurgi GmbH and Linde AG	Heavy oil partial oxidation process of Shell and Texaco, also Lurgi gasification	More than 100 commercial units in operation or under construction in 1996
Purisol	Lurgi GmbH	Natural gas, hydrogen, and synthesis gas	Seven commercial units in operation or under construction in 1996
Catacarb	Eickmeyer & Associates	Any gaseous stream	
Benfield	UOP	Synthesis gas, hydrogen, natural gas, town gas	600 commercial plants had been installed by 1992
Alkanolamines	No specific owner	Any gaseous stream	Chemicals produced and supplied by Dow, DuPont, Union Carbide; they do not supply process equipment

In gas adsorption systems, CO₂ reacts with a liquid solvent in which it is soluble. Both physical and chemical solvents have been used. Physical solvents take up CO₂, but do not react with it, whereas chemical solvents cause the formation of an intermediate compound with CO₂.

Physical adsorption processes are more suitable for mixed gas streams that are under high pressure because the solubility of CO₂ increases with increasing gas pressure. Physical adsorption can be carried out in a solvent according to Henry's law; regeneration is accomplished using heat or pressure reduction. Solvents used for physical adsorption include dimethylether of polyethylene glycol (Selexol process) or cold methanol (Rectisol process). Physical adsorption processes are more economical if the CO₂ partial pressure is above 200 psia. At low CO₂ partial pressure, chemical adsorption processes are favored.

Chemical solvents (for example, monoethanolamine (MEA), dimethanolamine (DEA), ammonia, or hot potassium carbonate) form an intermediate compound that can be broken down by heating to give the original solvent and CO₂. These processes can be used at low partial pressure of CO₂, but the flue gas must be free of SO₂, hydrocarbons, and particulate matter. In particular, SO₂ must be reduced to below 5 to 10 ppmv for MEA adsorption.

Pressure-swing adsorption (PSA) or temperature-swing adsorption (TSA) are used in chemical process streams and have also been proposed for removal of CO₂ from flue gas. A combination of chemical and physical adsorption is used with beds of solid sorbents, for example, of alumina, zeolite, or activated carbon.

Gas adsorption or gas separation membranes have the potential to remove CO₂ from flue gas. Gas separation membranes employ a membrane that is selective for transport of CO₂ and high pressure on the flue gas side to concentrate CO₂ on the low pressure side of the membrane. Gas adsorption membranes employ a liquid on the other side of the membrane instead of a gas stream.

Application of these carbon dioxide separation processes to flue gas depends on the concentration of CO₂ in the stream, on the presence of impurities in the gas, and on the pressure of the flue gas stream. Chemical adsorption may be preferred for cases in which the concentration of CO₂ is low and the pressure is near atmospheric. Physical adsorption is favored for higher total pressure and concentration of CO₂.

Chemical adsorption using MEA is the most mature technology and looks to be the most economically viable in the near future. An example of an MEA system applied to flue gas is given here, taken from a DOE report.⁴

Figure 3 shows a process flow diagram for an MEA absorption process as applied to flue gas from a coal-fired power plant. In this implementation, gas leaves the flue gas desulfurization (FGD) unit at 56°C and is drawn into a fan and the pressure is boosted to 19.7 psia. The gas stream is cooled slightly and then enters the absorber where it contacts the lean MEA stream flowing countercurrently. The lean MEA stream contains 30 wt% MEA and absorbs more than 90% of the CO₂ in the flue gas (which can now be discharged to the atmosphere). The rich MEA solution is pumped from the bottom of the absorber to a stripper in which water vapor (produced in the reboiler) is used to strip CO₂ from the solution. The CO₂ and water vapor go to a condenser and gas/liquid separator. The condensed water is recovered and the CO₂ can be further processed downstream.

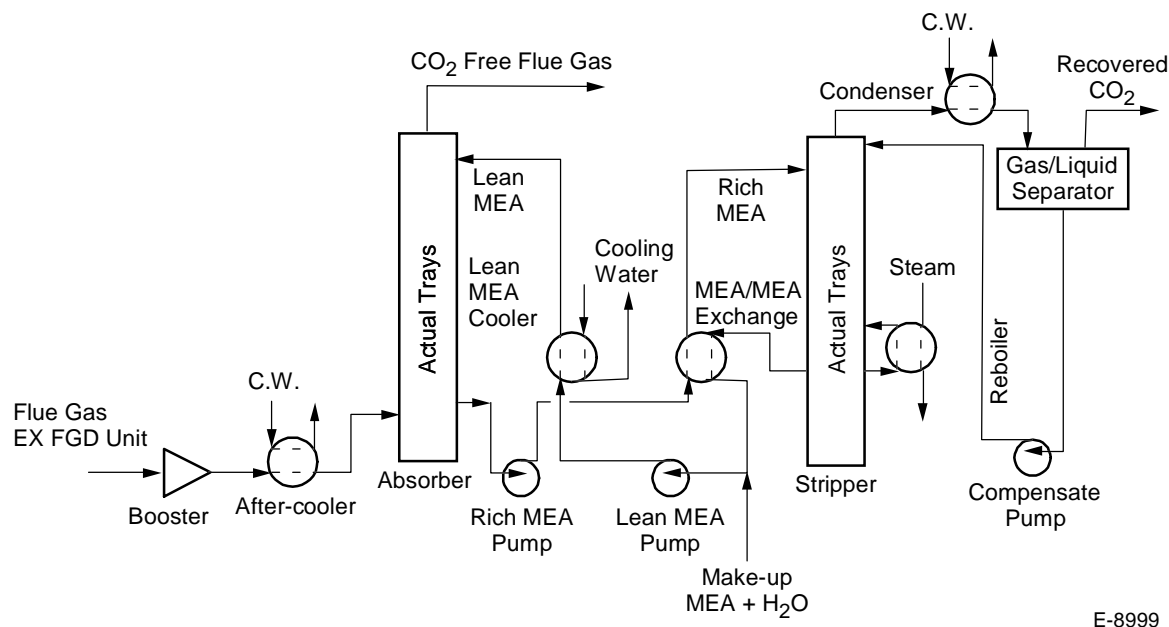


Figure 3. Process flow diagram for MEA absorber unit for removal of CO₂ from coal-fired flue gas (Source: Reference 4).

A unit sized for a 25 MWe plant burning a bituminous coal would process 235,000 lb/hr of flue gas and produce 42,000 lb/hr of CO₂. Table 3 lists the major equipment and costs. The total major equipment cost is approximately \$5M (1999 dollars). The total capital cost is on the order of \$11M.

Table 3. Cost for Major Equipment in MEA Absorber (Source: Reference 4)

Equipment	Quantity	Cost, in 1999 Dollars
Absorber	1	210,000
Stripper	1	17,000
MEA Make Up Tank	1	29,000
After Cooler	1	127,000
MEA Cooler	1	344,000
MEA/MEA Exchanger	1	481,000
Condenser	1	1,921,000
Reboiler	1	1,324,000
Booster	1	601,000
Rich-MEA Pump	2	34,000
Lean-MEA Pump	2	31,000
Condensate Pump	2	6,000
Total		5,125,00

4.2 Characterization of Physiology, Metabolism and Requirements of Microalgae

We will conduct a preliminary set of laboratory experiments using approximately 20 species of microalgae and 5 different, representative flue gases. We will use species that grow optimally at high temperatures, since this can yield order-of-magnitude increases in photosynthesis. We also seek species whose size, physiology and behavioral characteristics may favor reduced final processing costs. Finally, carbon-mineralizing species tend to be more effective at high pH, and can withstand significantly higher concentrations of dissolved inorganic carbon.

During the time from the kick-off meeting in November 2000 and the end of December 2000, Aquasearch designed the laboratory space for the small-scale (chemostat) experiments and set up microalgal strain collection and database for this project. Local sources of microalgal strains are being considered. In addition, the process for obtaining import permits for for *Dunaliella* strains was also initiated.

5. SUMMARY AND FUTURE PLANS

An initial survey of techniques for removing CO₂ from coal-fired flue gas was begun. Application of these carbon dioxide separation processes to flue gas depends on the concentration of CO₂ in the stream, on the presence of impurities in the gas, and on the pressure of the flue gas stream. Chemical adsorption may be preferred for cases in which the concentration of CO₂ is low and the pressure is near atmospheric. Physical adsorption is favored for higher total pressure and concentration of CO₂. Chemical adsorption using MEA is the most mature technology and looks to be the most economically viable in the near future.

Planning of chemostat experiments at Aquasearch was initiated during this period. These experiments will be used to select microalgae for the photobioreactor demonstrations. Gas compositions were specified and equipment was ordered.

Although final economic analysis of the separation process is tightly coupled to that of photo-bioreactor carbon fixation, PSI will attempt to delineate cost boundary of the preferred gas separation method in the next reporting period. More detailed engineering analyses will be conducted on CO₂ separation method, leading to selection of the preferred separation method. In the next reporting period, work will begin on the CO₂ dissolution method. Aquasearch will set up the experimental apparatus for the chemostat experiments.

6. REFERENCES

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