TENNESSEE VALLEY AUTHORITY
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# *Chemical Fixation of $CO_2$ in Coal Combustion Products and Recycling Through Biosystems*

## Annual Technical Progress Report

DE-FC26-00NT40933

00RE6-266797

October 26, 2001

# Chemical Fixation of $CO_2$ in Coal Combustion Products and Recycling Through Biosystems

**Annual Technical Progress Report**

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# ABSTRACT

This Annual Technical Progress Report presents the principle results in enhanced growth of algae using coal combustion products as a catalyst to increase bicarbonate levels in solution. A co-current reactor is present that increases the gas phase to bicarbonate transfer rate by a factor of five to nine. The bicarbonate concentration at a given pH is approximately double that obtained using a control column of similar construction. Algae growth experiments were performed under laboratory conditions to obtain baseline production rates and to perfect experimental methods. The final product of this initial phase in algae production is presented.

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# 1.0 INTRODUCTION

## 1.1 Conversion of $CO_2$ to Bicarbonate Using Fly Ash as a Catalyst

The mass transfer rate of carbon dioxide gas to carbonate solution is the rate-limiting step in producing carbonate solutions. One of the objectives of the "Chemical Fixation of $CO_2$" project was to develop a method to increase the rate of transfer for $CO_2$ using coal combustion products (CCP). The data present here demonstrates that fly ash is able to provide the critical mechanism needed to increase the available $CO_2$ in solution above the limits that are achievable with the dissolved gas alone.

## 1.2 Algae Growth

The limiting factor of algae growth is usually the level of bicarbonate available for photosynthesis. Increased bicarbonate would most likely increase algal growth beyond what is normally attainable. This was tested with a number of experiments. A number of sampling and analysis issues had to be resolved before reproducible results could be obtained. The experiment presented here is the end product of this study.

# 2.0 EXPERIMENTAL

## 2.1 Conversion of $CO_2$ to Bicarbonate Using Fly Ash as a Catalyst

The mass transfer rate of carbon dioxide gas to carbonate solution is the rate-limiting step in producing carbonate solutions. A co-current reactor was developed that contained fly ash and was compared to a similar reactor containing 5-mm glass beads.

The reactor consisted of a transparent PVC column (3.8 cm (1.5") diameter x 18 cm (7") long) with fitting on each end to introduce liquid and gas and to collect the overflow liquid and gas. Lean liquid was introduced at the bottom along with a controlled flow of $CO_2$. Water flow was controlled with a constant displacement pump.

The setup for the control included the transparent PVC column (3.8 cm (1.5") diameter x 18 cm (7") long), packed with 5-mm glass beads, and using a re-circulated salt water solution to which $CO_2$ gas was introduced prior to column inlet.

The test setup consisted of a similar column packed with fly ash. Gas flow was adjusted so that all the $CO_2$ was reacted in the reactor column. In this experiment, gas flow was electronically controlled to about 3 cc/min with a 50 sccm/min Tylan FC260 mass flow controller (four equal streams were produced with a total flow of 12 sccm). The gas stream was split into four segments using 0.013 mm (0.0005") PEEK capillary tubes approximately 12.7 cm (5") long. The flow rates through each of the four tubes were individually checked using a bubble flow meter and matched to less than one percent.

The glass bead control was tested under the same conditions. In this and the previous test, the actual flow was monitored with a bubble flow meter.

In all the test inorganic carbon (IC) analysis were performed on samples taken from an open container in which the solution is being re-circulated. Sample vials were filled to the top and capped with zero head space.

## 2.2 Algae Growth

Three aquaria (19 liter (5 gal), 800 $cm^2$ top surface area), each containing a different species of phytoplankton (isochrysis, nannochloropsis, and tetraselmis) were used. Four liters of liquid culture from the previous experiment was used and diluted with 12 liters of Instant Ocean (mixed according to package instructions). Four liters of liquid culture was also retained and filtered to ascertain biomass content.

Carbon dioxide gas was bubbled into the aquaria each morning. The pH was monitored to keep the pH above the low (pH = 6) levels seen in previous experiments. The low pH apparently shocked the algae and prevented growth until the pH was high enough. Dissolved oxygen, pH, chlorophyll, salinity, specific conductance, ORP, and temperature were monitored by unattended programmable sondes, and daily measurements were taken with the hand-held sonde to check the data.

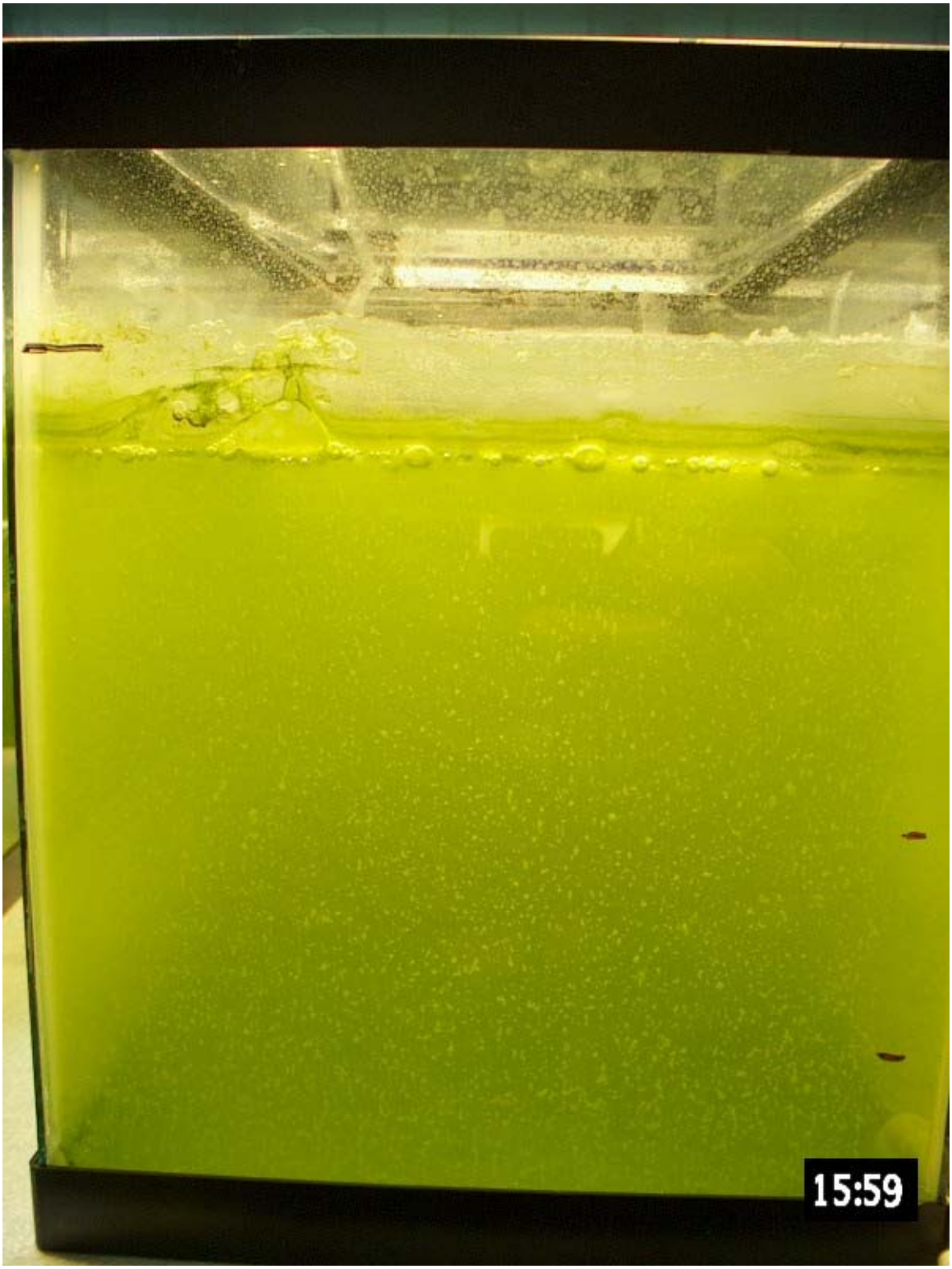
Biomass samples were taken of the water column twice daily (morning and afternoon). Prior to each sampling, the liquid culture was stirred to distribute settled biomass. Water column sampling used a 22-mm ID glass tube, approximately 25 cm long. A number four rubber stopper on the end of a 8-mm glass rod, approximately 60 cm long was used to seal the end of the sample tube. Sampling was accomplished by placing the stopper rod on the bottom of the aquarium and slowly lowering the sampling tube over the rod down through the water column. The lower end was sealed with the stopper and the sample removed.

These samples were vacuum filtered through a tared 0.4μ ?filter to collect the algal biomass. Sample sizes for filtering were between 25 and 50 ml. Larger samples could not be easily filtered. Filters were dried in a 65ºC oven and placed in a desiccator prior to obtaining a constant weight. Samples were also taken for inorganic carbon analysis before and after $CO_2$ was added and in the afternoons to determine how much IC was depleted in the course of a day. Sampling was performed over four consecutive days.

The three aquaria were exposed to artificial sunlight produced by "grow lights" with photosynthetically active radiation of 130 $W/m^2$ (600 $\mu E/m^2/sec$). This is approximately a third of solar light available on a clear day. The lights were operated on a simulated day of 14 hours on (6:00 a.m.—8:00 p.m.) and 10 hours off (8:00 p.m.—6:00 a.m.). The experiment was conducted during four consecutive days.

**Figure 1**

Typical Algae Tank at Beginning of an Experiment



# 3.0 RESULTS AND DISCUSSION

## 3.1 Conversion of $CO_2$ to Bicarbonate Using Fly Ash as a Catalyst

Table 1 shows that uptake of $CO_2$ in the fly ash column is five to nine times the rate in the glass bead column. At 1.5 hours the fly ash column pH was 6.5, while the glass bead column pH was 5.6. This indicates the fly ash has a capacity to buffer the solution. The pH of the fly ash column is more suitable for biological systems than the glass bead column.

**Table 1**

**Glass Beads v. Fly Ash @ 3 cc/min**

| Time | Glass Beads | | Fly Ash | |
|---|---|---|---|---|
| h:min | IC Conc (ppm) | pH | IC Conc (ppm) | pH |
| 0:00 | 19.52 | 10.08 | 12.25 | 9.22 |
| 0:05 | 27.11 | 9.26 | 55.92 | 7.78 |
| 0:10 | 33.28 | 8.72 | 63.59 | 7.14 |
| 0:15 | 37.65 | 7.47 | 68.55 | 6.89 |
| 0:30 | 44.68 | 6.59 | 84.01 | 6.61 |
| 0:45 | 50.81 | 6.34 | 97.20 | 6.53 |
| 1:00 | 54.16 | 6.22 | 105.60 | 6.49 |
| 1:30 | 63.73 | 6.06 | 128.80 | 6.48 |

## 3.2 Algae Growth

Table 2 and Figure 2 show the total biomass per aquarium for each of the algae species of phytoplankton (isochrysis, nannochloropsis, and tetraselmis) used in this experiment. The general characteristics of the growth curves are a moderate increase in biomass for two or three days followed by a significant increase on the next day. Afterwards there was a slow decrease in biomass indicating the onset of respiration metabolism for algae near the bottom of the aquaria. The average biomass increase to the maximum for isochrysis was 30 grams/$m^2$/day, for nannochloropsis was 54 grams/$m^2$/day, and tetraselmis was 29 grams/$m^2$/day. The final biomass values obtained in three days are approximately double those obtained in nine days in previous experiments. The previous experiments had only a single addition of carbon dioxide at the beginning.

Figure 3, Figure 4, and Figure 5 show pH and dissolved oxygen along with biomass. Note the sharp increase in pH in the region of maximum growth. This indicates a sharp decrease in bicarbonate level. The dissolved oxygen measurement is an indicator of photosynthetic activity. Note the decrease in dissolved oxygen at the maximum pH values, corresponding to a decrease in photosynthetic activity. Other experiments have indicated very little photosynthetic activity below pH of six.

**Table 2**

Algae Biomass in Aquarium

| Date/Time | Iso | Nanno | Tetra |
|---|---|---|---|
| 04/03 13:30 | 3.36 | 3.01 | 2.66 |
| 04/03 19:00 | 2.99 | 3.73 | 2.48 |
| 04/04 09:00 | 3.84 | 4.44 | 3.09 |
| 04/04 16:00 | 3.74 | 4.98 | 4.62 |
| 04/05 08:30 | 6.78 | 9.50 | 5.44 |
| 04/05 16:00 | 8.13 | 7.81 | 7.26 |
| 04/06 09:00 | 6.02 | 6.21 | 5.44 |
| 04/06 15:00 | 5.57 | 7.07 | 5.76 |

**Figure 2**

Algae Biomass in Aquarium

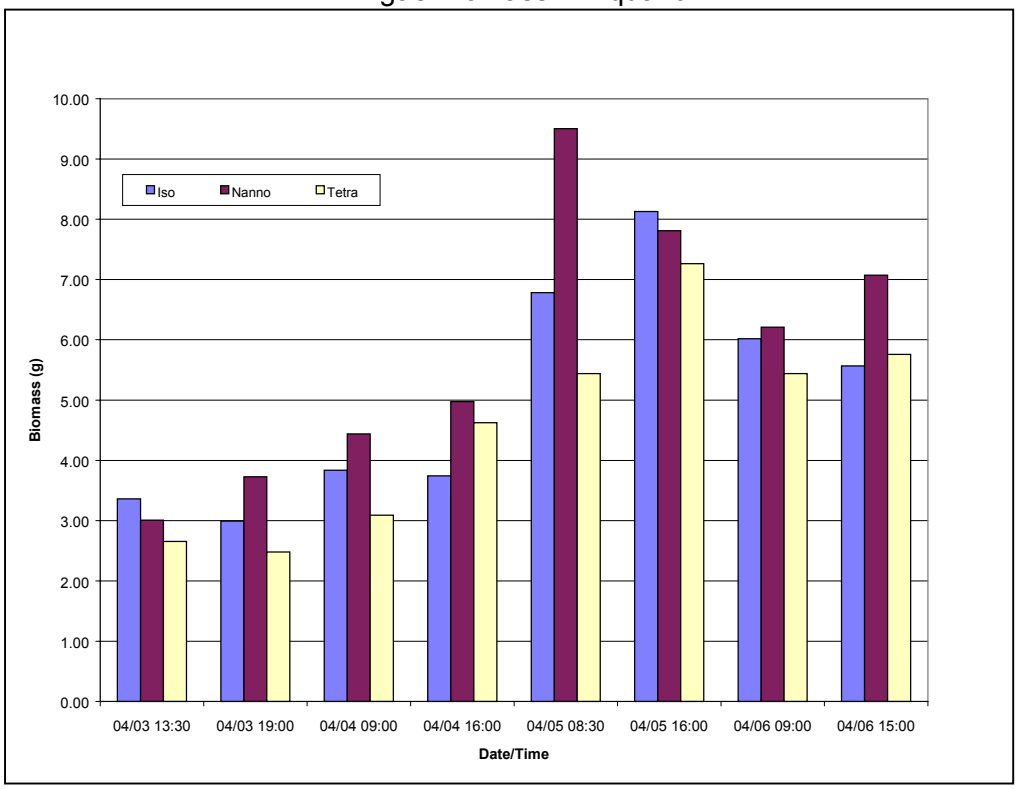


**Figure 3**

Sonde Data for Isochrysis

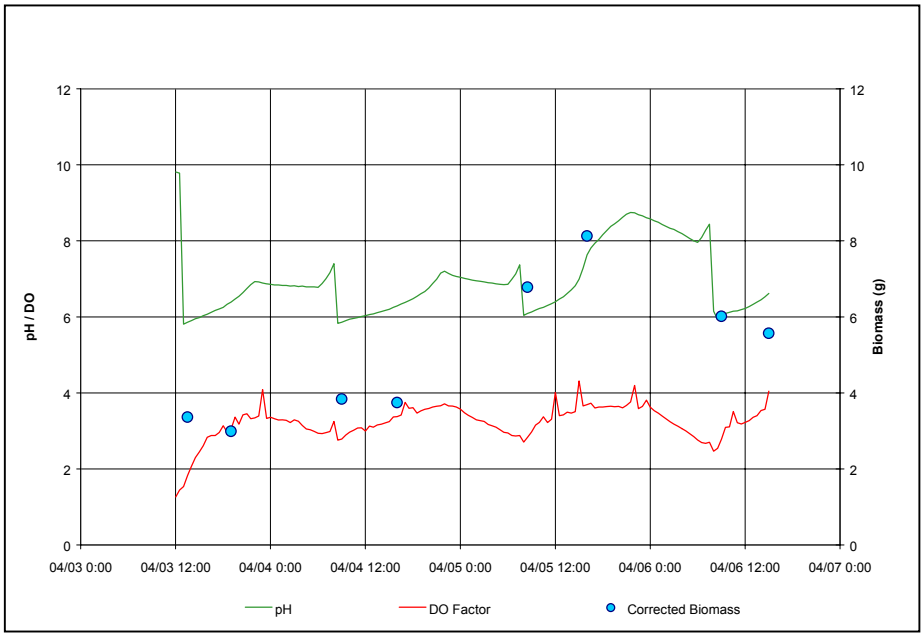



**Figure 4**

Sonde Data for Nannochloropsis

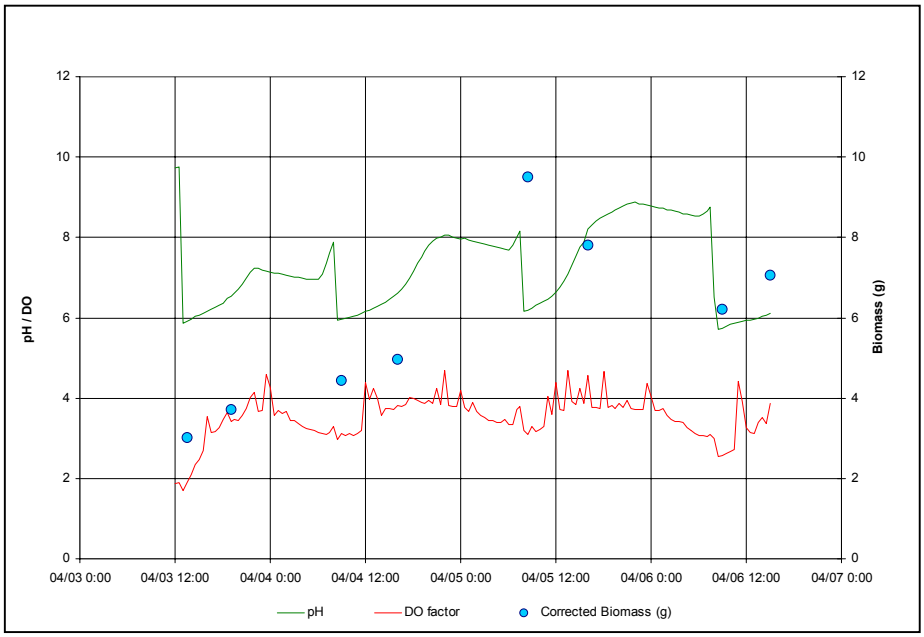
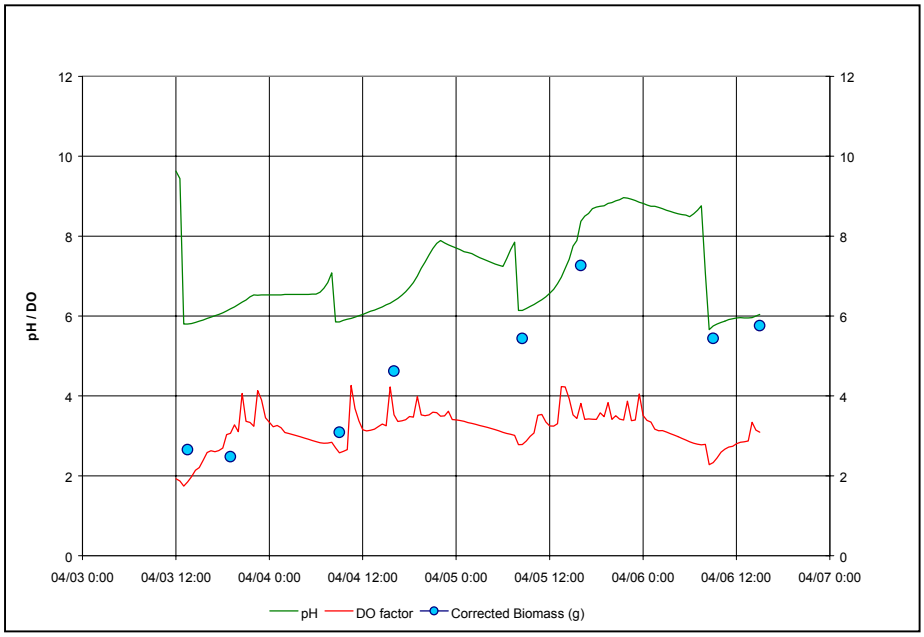


**Figure 5**

Sonde Data for Tetraselmis



# 4.0 CONCLUSION

## 4.1 Conversion of $CO_2$ to Bicarbonate Using Fly Ash as a Catalyst

The rate of uptake of $CO_2$ in a fly ash column is five to nine times the rate of uptake in the control column containing glass beads. At 1.5 hours the fly ash column pH was 6.5, while the glass bead column pH was 5.6. This indicates the fly ash has a capacity to buffer the solution. At a pH of 6.5, the bicarbonate using the fly ash column was double that of the glass beads. The pH and higher bicarbonate levels from the fly ash column are more suitable for biological systems than the glass bead column.

## 4.2 Algae Growth

Significant increases in biomass production can be obtained by supplementing the algae growth medium with additional bicarbonate. The annual production of biomass from an algae facility could be in excess of 150 metric tons per hectare (74 metric tons per acre).

## 5.0 REFERENCES

There are no references.

# APPENDIX

# Conversion of Carbon Dioxide Gas to Carbonate Solution Using Fly Ash as a Catalyst

# Conversion of Carbon Dioxide Gas to Carbonate Solution using Fly Ash as a Catalyst

**By**
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**December 18, 2000**

## 1. Introduction

The mass transfer rate of carbon dioxide gas to carbonate solution is the rate-limiting step in producing carbonate solutions. One of the objectives of the "Chemical Fixation of $CO_2$" project was to develop a method to increase the rate of transfer using coal combustion products (CCP). It was felt that fly ash or scrubber gypsum could provide the critical mechanism needed to increase the available $CO_2$ in solution above the limits that are achievable with the dissolved gas alone.

This would most likely increase algal growth beyond what is normally attainable. Carbon in the algal biomass can then be extracted and converted to hydrogen gas with a gasifier or converted to liquid $CO_2$. An anaerobic digestor in the system may be used to convert the biomass into methane for on-site use in a gas turbine generator. The solid biomass residue from the digestor may be re-cycled as additional fuel stock for the gasifier. The liquid residue from the digestor may be re-cycled to provide nutrients to perpetuate the algal biosystem. The system provides for continued cycling of sequestered carbon within the system.

## 2. Method and Materials

A co-current reactor was developed that contained fly ash and was compared to a similar reactor containing 5-mm glass beads. Using PEEK capillary tubes and a mass flow controller, a method was developed to deliver a controlled stream of $CO_2$ gas that was introduced at the bottom of the reactor. Water flow was controlled with a constant displacement pump.

The reactor consisted of a transparent PVC column (1.5" d x 7" l) with a fitting on each end to introduce liquid and gas and to collect the overflow liquid and gas. Lean liquid was introduced at the bottom along with a controlled flow of $CO_2$.

The initial set up for the control included the transparent PVC column (1.5" d x 7 1/2" l), packed with 5-mm glass beads, and using a re-circulated salt water solution to which $CO_2$ gas was introduced prior to column inlet. The gas flow rate was approximately 10 cc/min. It was maintained by adjustment of a needle valve and by observing flow rate of gas using a bubble flow meter. Data is reported in Fig. 2 under "Glass Beads."

Next, a similar column packed with fly ash was tested. Gas flow was adjusted so that all the $CO_2$ was reacted in the reactor column. In this experiment, gas flow was electronically controlled to about 3 cc/min with a

50 sccm/min Tylan FC260 mass flow controller. The gas stream was split into four segments using 0.0005 PEEK capillary tubes approximately 5" long. The flow rates through each of the 4 tubes were individually checked using a bubble flow meter and matched to less than 1%. Data is reported in Fig. 1 and Fig 2 under "Fly Ash."

Finally, the glass bead control was tested under the same conditions. In this and the previous test, the actual flow was monitored with a bubble flow meter. Data is reported in Fig. 1 under "Glass Beads."

All the test inorganic carbon (IC) analysis were performed on samples taken from an open container in which the solution is being re-circulated. Sample vials were filled to the top and capped with zero head space.

## 2. Conclusions

It is clear, from the table below (Fig 1), that uptake of $CO_2$ in the fly ash column is 5 to 9 times the rate in the glass bead column. At 1.5 hours the fly ash column pH was 6.5, while the glass bead column pH was 5.6. This indicates the fly ash has a capacity to buffer the solution. The pH of the fly ash column is more suitable for biological systems than the glass bead column.

**Fig 1. Glass Beads v. Fly Ash @ 3 cc/min**

| Time | Glass Beads | | Fly Ash | |
|---|---|---|---|---|
| h:min | IC Conc (ppm) | pH | IC Conc (ppm) | pH |
| 0:00 | 19.52 | 10.08 | 12.25 | 9.22 |
| 0:05 | 27.11 | 9.26 | 55.92 | 7.78 |
| 0:10 | 33.28 | 8.72 | 63.59 | 7.14 |
| 0:15 | 37.65 | 7.47 | 68.55 | 6.89 |
| 0:30 | 44.68 | 6.59 | 84.01 | 6.61 |
| 0:45 | 50.81 | 6.34 | 97.20 | 6.53 |
| 1:00 | 54.16 | 6.22 | 105.60 | 6.49 |
| 1:30 | 63.73 | 6.06 | 128.80 | 6.48 |

The table below (Fig 2) further confirms this phenomena. Note that with glass beads, 3 times the gas flow is required to achieve carbonate concentrations approximately equal to that with fly ash.

**Fig 2. Fly ash column @3cc/min v. Glass bead column @10cc/min**

| Time | Fly Ash | | Glass Beads | |
|---|---|---|---|---|
| h:min | IC Conc (ppm) | pH | IC Conc (ppm) | pH |
| 0:05 | 55.92 | 7.78 | 34.75 | 9.51 |
| 0:10 | 63.59 | 7.14 | 50.61 | 8.81 |
| 0:15 | 68.55 | 6.89 | 63.70 | 8.12 |
| 0:30 | 84.01 | 6.61 | 83.90 | 6.23 |
| 1:00 | 105.6 | 6.49 | 127.50 | 5.83 |
| 1:30 | 128.8 | 6.48 | 145.90 | 5.71 |