

Microalgal removal of CO₂ from flue gases: CO₂ capture from a coal combustor

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Introduction

Emissions of carbon dioxide are predicted to increase this century (US DOE, 1997) 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. A large fraction of the anthropogenic emissions of carbon dioxide result from the combustion of fossil fuels for energy production (e.g., Kadam, 2002). 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 will require 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.

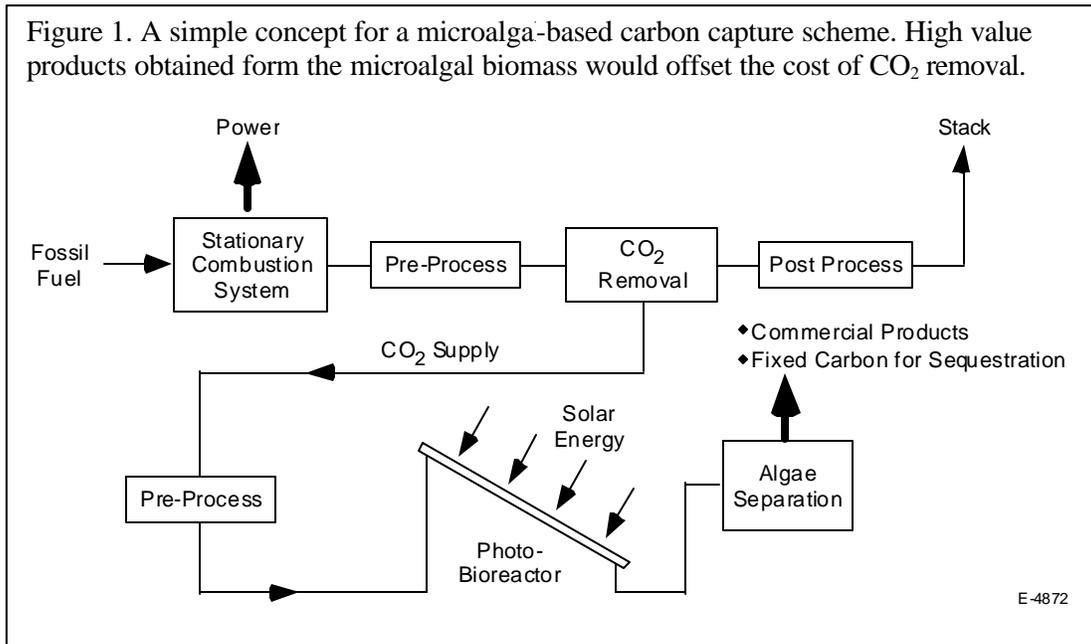
While chemical and physical means exist to capture CO₂ from smoke stack emissions, the cost of utilizing these technologies would result in a significant increase in the cost of power (IEA, 1998). For example, the cost of removing CO₂ from a conventional coal-fired power plant with flue gas desulfurization was estimated to be in the range of \$35 to \$264 per ton of CO₂. 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 capture anthropogenic carbon dioxide. Photosynthesis is the original process that created the fixed carbon present in today's fossil fuels. Aquatic microalgae are among the fastest growing photosynthetic organisms, having carbon fixation rates an order of magnitude higher than those of land plants. Microalgae utilize CO₂ as one of their main building blocks and we propose that algal photosynthesis may be a viable option for anthropogenic CO₂ capture and sequestration. While microalgal culturing is expensive, microalgae can also produce a variety of high value compounds that can be used to generate revenues (Borowitzka, 1995; Olaizola 2003a). Those revenues could pay for the cost of carbon capture and sequestration. Microalgal photosynthesis can also result in the precipitation of calcium carbonate, a potentially long-term sink of carbon (Mazzone et al., 2002)

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 utilize sunlight to photosynthetically convert the CO₂ into compounds of high commercial values or mineralized carbon for sequestration. The advantages of using a microalgal-based system are that

- High purity CO₂ gas is not required for algal culture. Flue gas containing varying amounts of CO₂ can be fed directly to the microalgal culture. This will simplify CO₂ separation from flue gas significantly.

- 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.
- Microalgae culturing may yield high value commercial products. Sale of these high value products can offset the capital and the operation costs of the process.
- The envisioned process is a renewable cycle with minimal negative impacts on environment.



The concept of using microalgae to ameliorate CO_2 emissions from stationary combustion sources is not new (Kadam, 1997; Oswald and Golueke, 1968; Sheehan, et al., 1998). A number of studies have been carried out to determine the ability of microalgae to withstand the high CO_2 concentrations present in flue gas (Hanagata et al., 1992; Yun et al., 1997) as well as the potentially toxic accompanying SO_x and NO_x gases (Lee et al., 2002; Negoro et al., 1991). Thus, a number of efforts were carried out to isolate microalgal strains that are especially adept to this application such as those by the RITE program (Murakami and Ikenouchi, 1997) and others (Chang and Yang, 2003; Maeda et al., 1995; Sung et al., 1999).

We are working towards developing technologies for recovery and sequestration of CO_2 from stationary combustion systems by microalgal photosynthesis. Specifically, our aims are to quantify the efficacy of microalgae-based carbon sequestration at industrial scale and determine under which conditions carbon capture and sequestration by microalgal photosynthesis is economically attractive when compared with other means of carbon capture and sequestration. We are focusing our efforts on demonstrating the ability of selected species of microalgae to effectively fix carbon from typical power plant exhaust gases.

Here, we report on experiments conducted to estimate the effects of medium pH and flue gas composition (e.g., coal and propane combustion gases and other simulated gas mixtures) on the microalgal CO_2 capture efficiency. The results indicate that, medium pH is a key determinant of CO_2 capture efficiency while the effect of flue gas composition is negligible.

Methods

The experiments reported here were designed to test the carbon capture efficiency of microalgal cultures from the growth medium under several different culture conditions. Specifically, we compared the rate of photosynthetic carbon uptake versus the amount of carbon lost from the medium by degassing. This was done by measuring the changes in dissolved inorganic carbon (DIC) content of the culture medium, estimated from pH and alkalinity measurements (e.g., Eaton et al., 1995), over time (Figure 2). Estimates of DIC disappearance from the medium in the dark were assumed to be caused by degassing. By comparing the rates of DIC disappearance from the medium in the light versus dark, we estimated the rate of DIC disappearance caused by photosynthetic carbon uptake.

Figure 2. Calculate DIC concentration in a microalgal culture from pH and alkalinity measurements (left panel). The changes in DIC over time were used to estimate the rate of carbon disappearance from the medium (right panel).

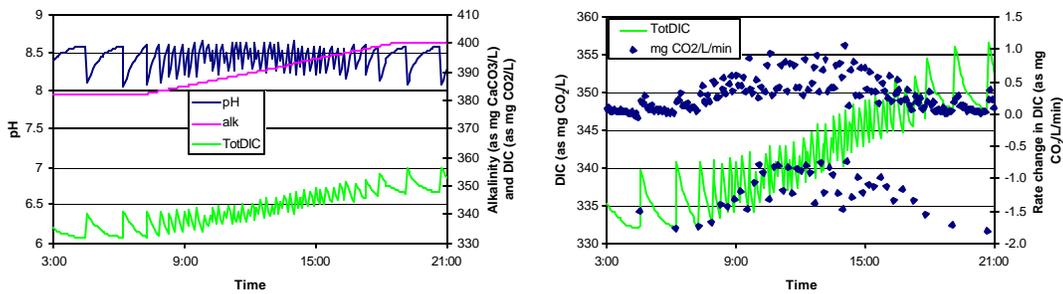
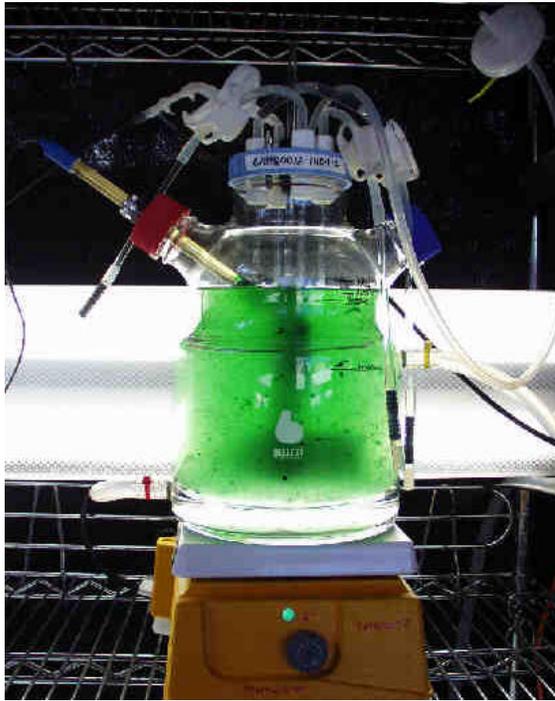


Figure 3. 3.3 liter chemostat used for laboratory scale experiments.



The microalgal strains used for these experiments were selected from the Mera Pharmaceuticals Culture Collection (Olaizola, 2003b). The cultures were initially grown in computer controlled 3.3 liter chemostats (Figure 3) for pH and gas composition experiments at laboratory scale. For the first set of experiments, the chemostats were maintained at 3 different pH levels (6.5, 7.5 and 8.5, see Olaizola, 2003b for details) by injections of 100% CO₂ in response to increases in pH. The chemostats were kept at 25°C and on a 14:10 L:D cycle (fluorescent, 120 $\mu\text{E m}^{-2} \text{s}^{-1}$). The pH of the culture was constantly monitored and adjusted by a custom monitoring and control system designed and built in-house. For a second set of experiments, the pH of the chemostats was kept at 7.5 by injecting different mixtures of gases designed to mimic the flue gas composition that would be produced by combusting different fuels in different types of combustors (Table 1).

Table 1. Composition of gas mixtures used in the simulated flue gas experiments according to the combusted material. A sixth treatment was 100% CO₂.

Fuel type	A. Bituminous coal	B. Sub-bituminous coal	C. Natural gas	D. Natural gas	E. Fuel oil
Gas (wt)	Utility boilers			Gas Turb Comb	Diesel
CO ₂ (%)	18.1	24.0	13.1	5.7	6.2
O ₂ (%)	6.6	7.0	7.6	15.9	17.0
N ₂ (%)	71.9	68.1	79.3	78.4	76.7
SO ₂ (ppm)	3504.0	929.7	0.0	0.0	113.1
NO (ppm)	328.5	174.3	95.1	22.1	169.7
NO ₂ (ppm)	125.9	66.8	36.5	8.5	65.0

Experiments were also carried out under outdoor conditions in large tubular photobioreactors (Olaizola 2000, Figure 4). In these experiments, the photobioreactors (PBR) were maintained at 7.5 pH. This was accomplished by on-demand injections of 100% CO₂ or injections of flue gases produced by an actual coal combustor (Figure 5) in the case of 2,000 liter PBR or by a propane combustor (a commercial water heater) in the case of 25,000 liter PBR. For the large scale experiments, we used *Haematococcus pluvialis*, a green microalga (Chlorophyta) known to produce astaxanthin, a high value carotenoid pigment.

Figure 4. The 25,000 liter MGM photobioreactor.



Figure 5. The custom built coal reactor used to provide actual flue gases to the cultures in the photobioreactors.



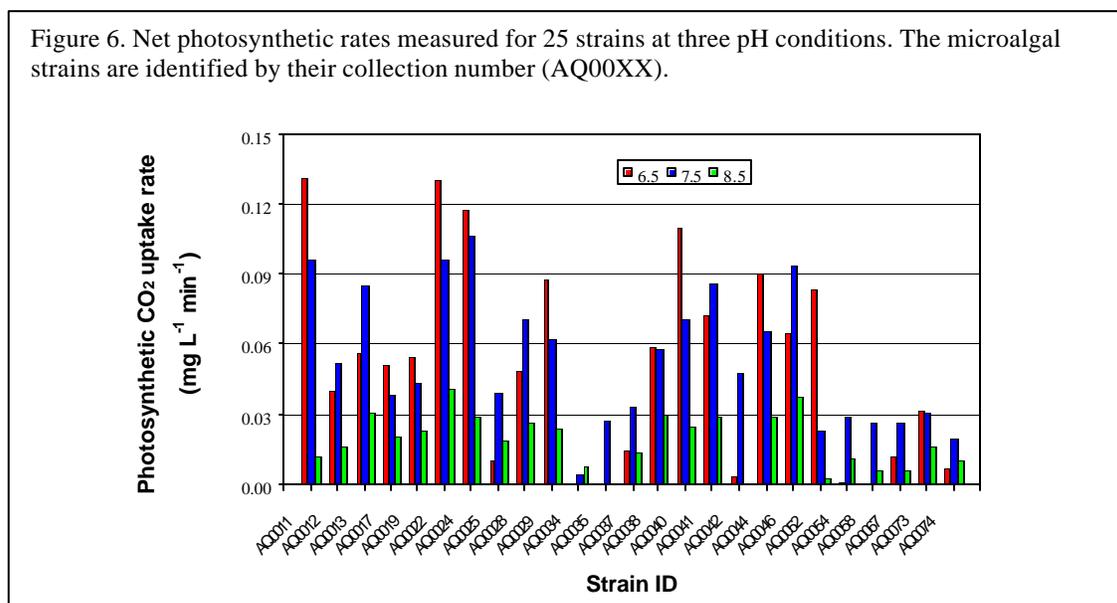
For these experiments we used a gas analyzer consisting of a IMR400 gas dryer and a IMR5000 analyzer to measure the concentration of NO_x, SO_x and CO₂ in the gas stream from the coal and propane combustors before and after the gas was introduced into the photobioreactor. From these values, we have estimated the relative capture efficiency of the microalgal culture for these gases. The gas analyzer was programmed to alternate between analyzing gases from the combustor smoke stack for a period of 20 minutes, switch to a purge period for five minutes, switch to the photobioreactor exhaust for 30 minutes and again to a five minute purge period. Then, the cycle repeated itself.

Results

Achieved CO₂ rates at laboratory scale. Effects of pH.

We used the changes in DIC in the cultures to estimate the relative importance of pathways that affect the concentration of DIC in the culture medium under different pH conditions. First, we considered the rate of DIC loss from the medium measured during the dark periods, for all strains, at three different pH levels. This “dark” rate represents net losses of DIC from the medium (degassing – respiration). The individual dark rate values measured for each strain ranged from less than 0.01 to 0.03, 0.02 to 0.08, and 0.20 to 0.49 at pH 8.5, 7.5 and 6.5 respectively. Thus, at lower culture pH the DIC loss rates from the medium are, on average, much larger than at higher medium pH.

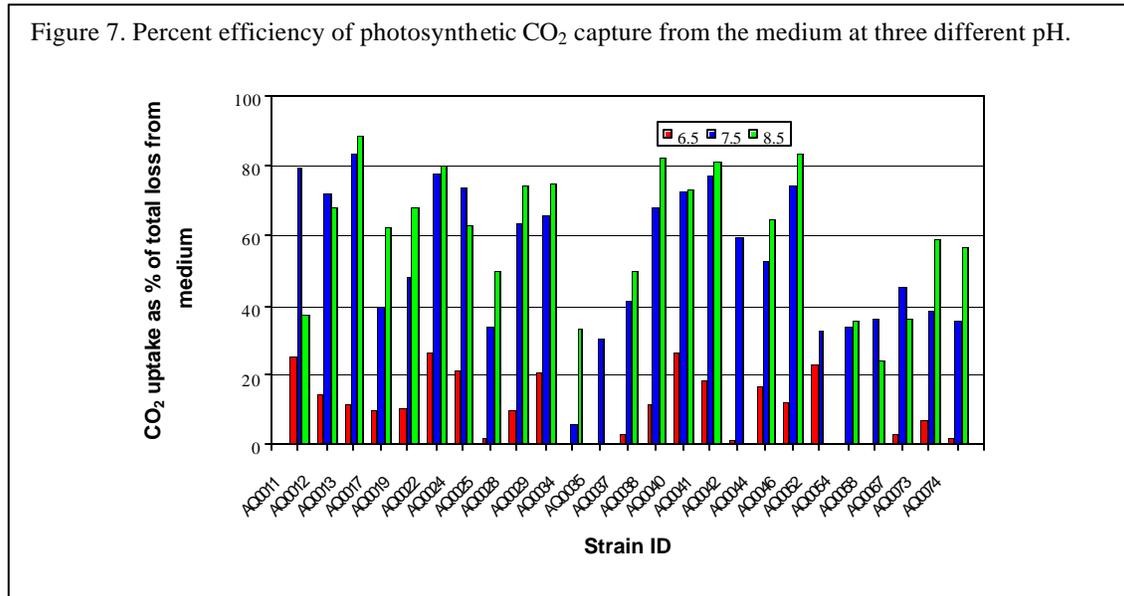
Second, we considered the rates of DIC loss during the light periods. These values represent the net loss of DIC from the medium (degassing + photosynthesis – respiration). We assume that, barring large changes in respiration between dark and light periods, the difference between the “light” and “dark” rates correspond to net photosynthesis. The results are summarized in Figure 6. The highest net photosynthetic rate was 0.13 mg CO₂ l⁻¹ min⁻¹.



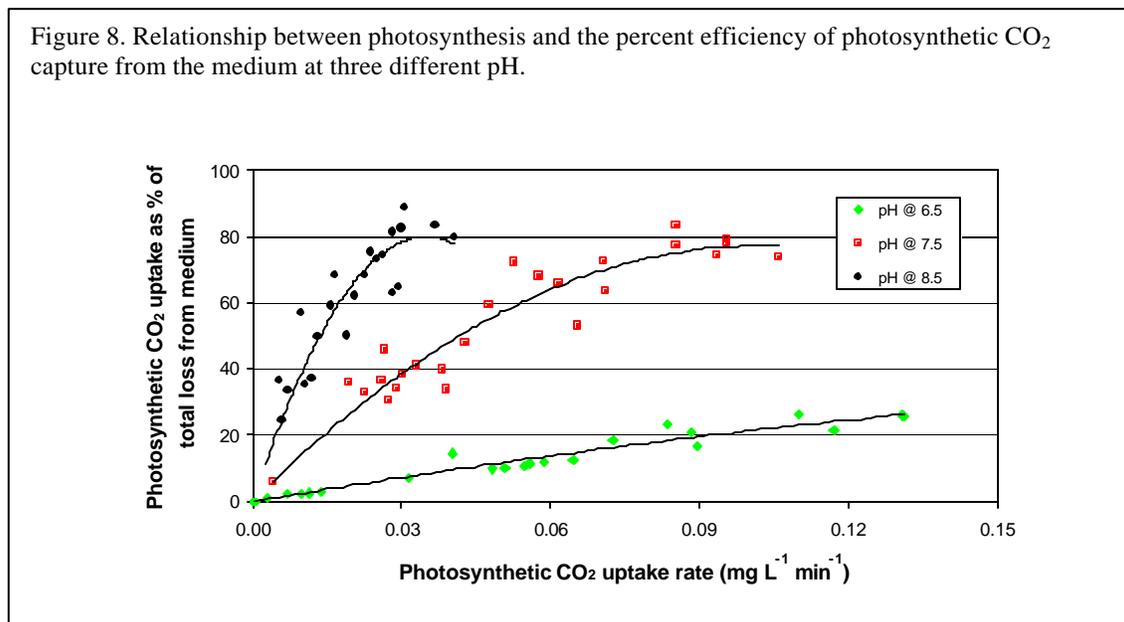
Achieved CO₂ capture efficiency at laboratory scale. Effects of pH.

We then calculated the efficiency with which microalgae captured CO₂ from the medium by normalizing the calculated photosynthetic rates (above) to the “light” rates and multiplying the number by 100 (%). That number is the percentage of DIC lost from the medium caused by photosynthesis. The results indicate that, on average, the efficiency of photosynthetic CO₂ capture is higher at higher medium pH values, i.e., the probability for CO₂ to be lost from the medium

back to the gas phase is less at high pH (Figure 7), although there is substantial variability from strain to strain.



Finally, we consider the relationship between photosynthetic rates and CO₂ capture efficiency. Figure 8 shows three different relationships between calculated photosynthetic rates and the efficiency of photosynthetic CO₂ capture. It is clear that the efficiency of photosynthetic CO₂ capture is, first, dependent on the actual photosynthetic rates accomplished by the cultures (the three different lines in the figure) but, two, also dependent on the pH of the culture (i.e., the difference between the three lines).

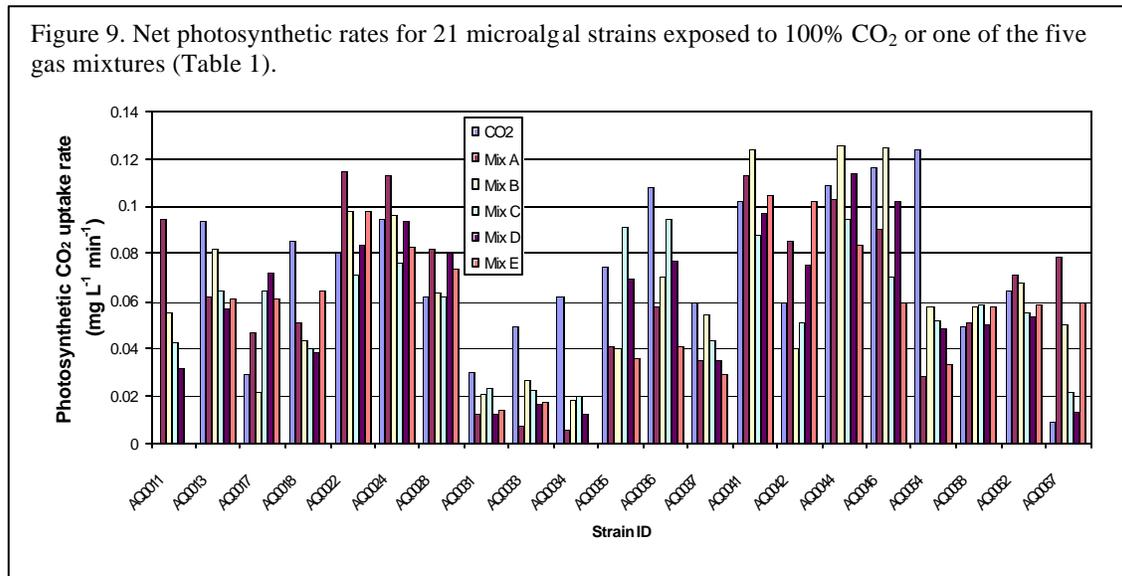


Achieved CO₂ rates at laboratory scale. Effects of gas composition.

We used the same approach as described for the pH experiments (above) to analyze the data from the flue gas experiments. If we consider the rate of DIC loss from the medium measured during the dark periods for all strains grown with 100% CO₂ and the five experimental gas mixtures we

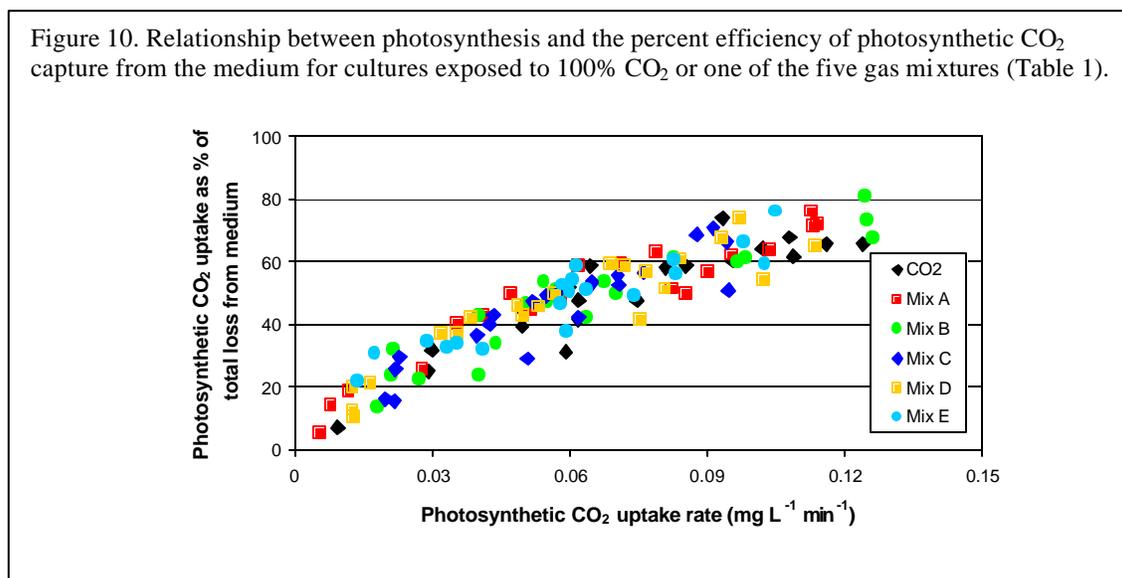
find virtually no differences. The values ranged between 0.033-0.131, 0.035-0.097, 0.029-0.127, 0.037-0.123, 0.035-0.114, and 0.033-0.098 mg CO₂ l⁻¹ min⁻¹ for 100% CO₂ and gas mixes A, B, C, D, and E respectively (Table 1).

The rates of DIC loss during the light periods represent the net loss of DIC from the medium (degassing + photosynthesis – respiration). We again assume that, barring large changes in respiration between dark and light periods, the difference between the “light” and “dark” rates correspond to net photosynthesis. The photosynthetic values thus obtained are summarized in Figure 9 and they indicate large differences among strains.



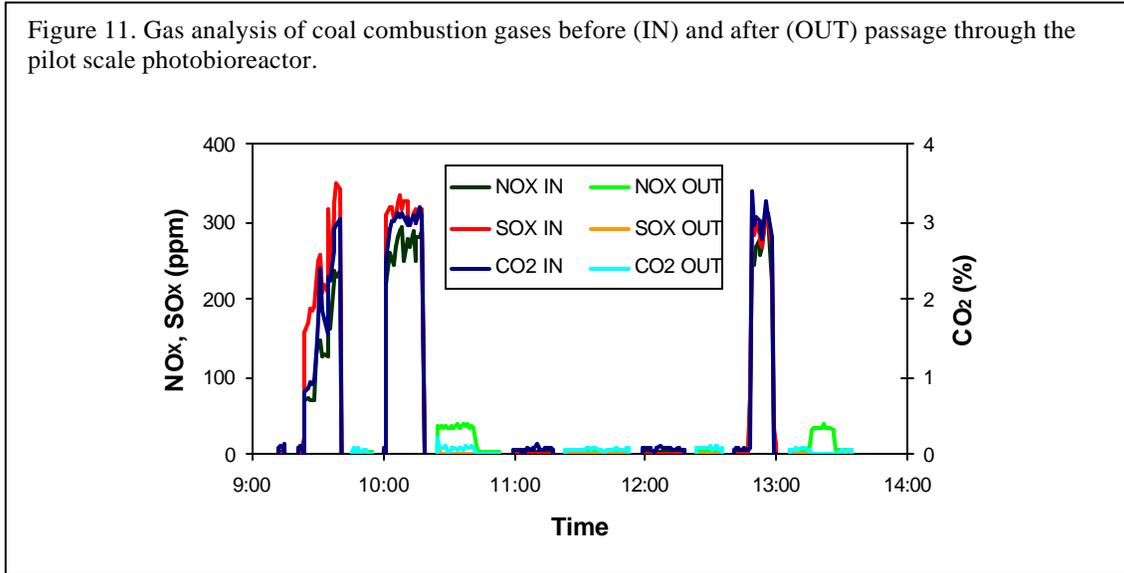
Achieved CO₂ capture efficiency at laboratory scale. Effects of gas composition.

Finally, we also consider the relationship between photosynthetic rates and CO₂ capture efficiency for the cultures grown under 100% CO₂ and the five gas mixtures. For this set of experiments, the relationships between photosynthetic rate and CO₂ capture efficiency are indistinguishable for the 5 gas mixtures and the 100% CO₂ treatment (Figure 10).

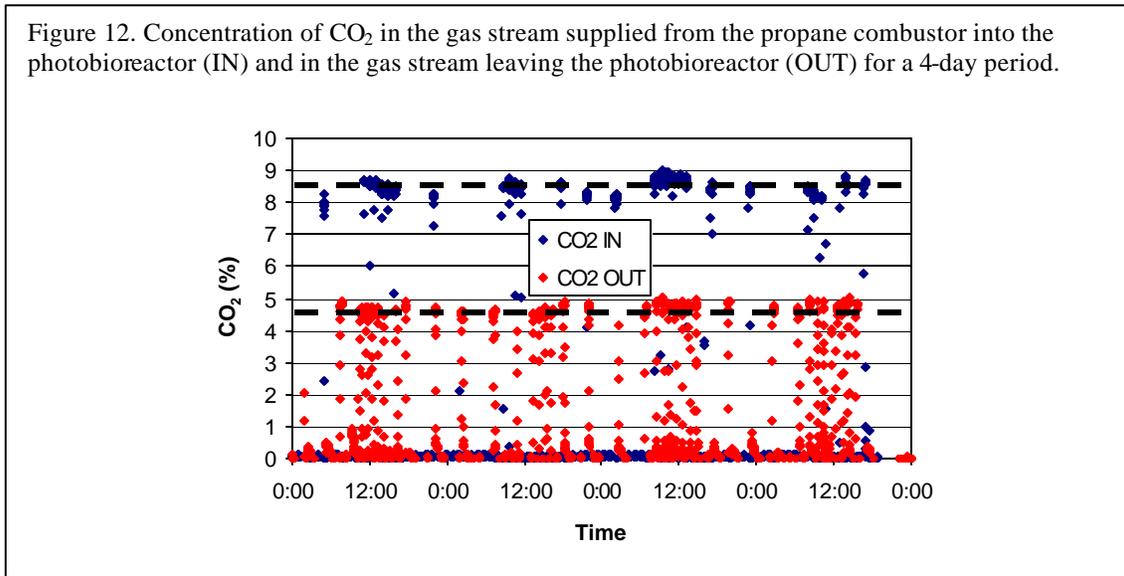


Achieved CO₂ capture rates at pilot and industrial scale.

Typical composition of coal combustion flue gases, before and after entering the pilot scale PBR (2,000 liter) microalgal photobioreactor, are shown in Figure 11. On average, our mass calculations indicate that the microalgal culture was able to capture nearly 70% of the available CO₂ when the culture was maintained at pH 7.5.



Typical CO₂ composition of propane combustion flue gases, before and after entering the full scale PBR (25,000 liter) microalgal photobioreactor, are shown in Figure 12. On average, our mass calculations indicate that the microalgal culture was able to capture about 45% of the available CO₂ when the culture was maintained at pH 7.5.



Summary

In this report we show that

- microalgae are able to capture anthropogenic CO₂ from a wide variety of simulated flue gases and from actual coal and propane combustion gases,
- microalgae are able to capture anthropogenic CO₂ under a wide variety of pH and gas concentrations
- the efficiency of CO₂ capture by microalgae is directly dependent on the pH of the culture but is not affected by differences in gas composition,
- the process is scalable to industrially significant scales.

Future work

We are now continuing our work on carbon capture and sequestration by microalgae using actual flue gases from the coal and propane combustors. Among other things, we will test whether significant changes in capture efficiency are realized when the culture conditions (such as pH) change at industrial scale. Such results will have a significant impact, for example, on the design of a microalgal facility designed to remove CO₂ from the flue gases produced by an actual stationary combustion system such as a power plant.

Acknowledgements

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