

## Efficient storage and utilization of CO<sub>2</sub> in open raceway ponds for cultivation of microalgae

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**Abstract**—For efficient storage and utilization of CO<sub>2</sub> in open raceway ponds, the effects of cultural and operational parameters were studied. A 10 m<sup>2</sup> indoors raceway pond was operated to determine CO<sub>2</sub> storage capacity, average rate of absorbed CO<sub>2</sub> losses and mass transfer coefficient for CO<sub>2</sub> outgassing from various pH, salinity and alkalinity regimes of culture medium; mixing velocities and culture depths. Average rate of CO<sub>2</sub> outgassing for saltwater (35 ppt salinity) at 40 meq/L alkalinity was 40-fold higher than seawater (35 ppt salinity and 2.3 meq/L alkalinity) at pH 8. Operating at lower pHs or salinities aggravated CO<sub>2</sub> outgassing. An empirical equation for CO<sub>2</sub> outgassing average mass transfer coefficient,  $\bar{K}_L$ , was developed as a function of mixing velocity and depth. *Nannochloropsis* sp. PTCC6016 was cultivated in the pond for 14 days. Due to higher amount of outgassing, CO<sub>2</sub> utilization efficiency declined as the productivity in the pond decreased.

Keywords: CO<sub>2</sub>, Open Raceway Pond, Microalgae, Utilization Efficiency, Outgassing,  $\bar{K}_L$

### INTRODUCTION

Photosynthetic activity of most microalgal cultivation systems requires dissolved CO<sub>2</sub>, essential nutrients dissolved in the liquid medium and light [1-3]. Open ponds are common systems for mass cultivation of microalgae. The pond is designed in a raceway configuration, in which a paddlewheel circulates and mixes the cultivation medium containing algal cells and nutrients at the flow velocity of 15-30 cm/s. The depth of the cultures is generally 10 to 30 cm [4,5].

With a cellular carbon fraction of 0.5 and CO<sub>2</sub> being the only carbon source, a minimum of 1.83 kg CO<sub>2</sub> per kg of biomass must be provided, for oil rich microalgae can go up to 3 kg CO<sub>2</sub> per kg of biomass [1,6,7]. As pure air is not sufficient for CO<sub>2</sub> supply, carbon dioxide-enriched gas mixture should be introduced through the system. The cost of supplying sufficient CO<sub>2</sub> to large-scale cultures of microalgae is a major economic constraint [8,9]. CO<sub>2</sub> has a low solubility in water and unlike other microalgal nutrients must continually be replenished in a large-scale production pond [9].

Efficient delivery, storage and utilization of carbon dioxide in microalgal ponds are significant factors in the economic design of the pond and cultivation of microalgae. While simple design of counter-current carbonation sumps can provide up to 90% CO<sub>2</sub> injection efficiency [9], maximum storage of CO<sub>2</sub> in the pond and efficient utilization of CO<sub>2</sub> by microalgae are complicated issues in the operation of microalgal open raceway ponds. As the raceway ponds have a large surface area to volume ratio, absorbed CO<sub>2</sub> can easily escape

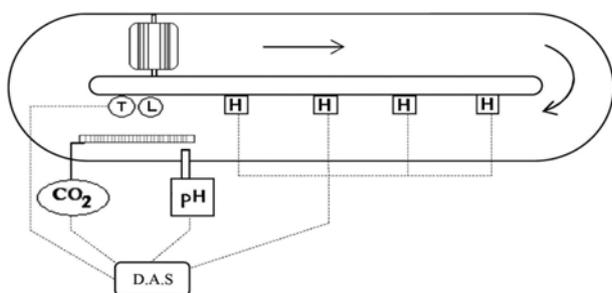
from the culture medium to the atmosphere, while the water tries to equilibrate with lower concentration of CO<sub>2</sub> in the air. The assimilation of CO<sub>2</sub> by rapidly growing algae and outgassing cause reduction in the free CO<sub>2</sub> level in the culture, thereby a disturbance of entire carbonate buffer system and a pH rise in the pond [6,10]. Thus, large-scale algal cultures are subjected to cycles of CO<sub>2</sub> and pH level between recarbonation events. These cycles depend on the pond size, hydrodynamics and the number of carbonation stations. In mass microalgal cultures, the pH of the pond must be maintained in the optimum range for cultivation of the desired species and to prevent the depletion of carbon in the culture medium [10]. Careful system design and operating considerations can reduce the frequency and amplitude of these cycles and, thus, lead to a better utilization of solar energy by microalgae. One problem of open systems is obtaining sufficient carbon storage with minimum amount of CO<sub>2</sub> outgassing. To evaluate the utilization efficiency of injected CO<sub>2</sub> in a pond, the losses of CO<sub>2</sub> must be estimated. Thus, determining the value of mass transfer coefficient for CO<sub>2</sub> outgassing,  $K_L$ , is necessary [11,12].

One of the most important aspects in economically viable production of biodiesel or other low value products from microalgae is to minimize the capital and nutrient costs by optimization of engineering and design parameters [4]. Although several published works have been devoted to the phenomenon of gas-liquid CO<sub>2</sub> exchange in different types of microalgal cultivation systems [7,13-15], our study was the first to comprehensively investigate the influence of various operational and cultural parameters on CO<sub>2</sub> outgassing and CO<sub>2</sub> storage capacity of culture medium in raceway pond type cultivation systems. This is a central issue in the operation of microalgal open pond systems as these parameters must be used to optimize for productivity and overall CO<sub>2</sub> utilization efficiency. An em-

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**Fig. 1. Schematic view of the 10 m<sup>2</sup> open raceway pond.**

H: heater  
 T: temperature sensor  
 L: level sensor  
 pH: pH sensor  
 CO<sub>2</sub>: carbonation station  
 D.A.S.: data acquisition system

pirical correlation has also been developed for  $K_L$ , based on data from operation of a raceway pond.

## MATERIALS AND METHODS

### 1. Raceway Pond Design

Experiments were carried out in a 10 m<sup>2</sup> pond of 1.2 m wide and 8.4 m long, divided by a central baffle to form a raceway. To minimize friction at the pond bottom and its effect on outgassing losses of CO<sub>2</sub>, as a consequence of change in hydrodynamic of the pond, the pond bottom was lined with polyethylene (PE) (Fig. 1). The pond was operated under sunlight radiation and indoors to exclude the effect of wind speed on CO<sub>2</sub> mass transfer. Required flow velocity was provided by an eight-blade paddle wheel. Data from all probes was captured by a data acquisition system, connected to a computer for on-line monitoring, logging and control.

### 2. Microorganism and Culture Conditions

The microalga used in the present study was *Nannochloropsis* sp. PTCC6016 with a high growth rate and oil content, isolated previously [16,17] from the Persian Gulf for our large-scale cultivation of microalgae. The required inoculum for cultivation of the strain in the 10 m<sup>2</sup> pond was grown indoors in a one m<sup>2</sup> Plexiglas pond, at pH 7.5 and 20 °C under fluorescent lamp illumination at 200 μmol/m<sup>2</sup>/s and using diurnal illumination of 12 h light/12 h dark (L/D) cycles. To prepare the culture medium, the following nutrients were added per liter of artificial seawater: 75 mg NaNO<sub>3</sub>, 5 mg NaH<sub>2</sub>PO<sub>4</sub>·H<sub>2</sub>O, 4.4 mg Na<sub>2</sub>EDTA·2H<sub>2</sub>O, 3.2 mg FeCl<sub>3</sub>·6H<sub>2</sub>O, 179 μg MnCl<sub>2</sub>·4H<sub>2</sub>O, 21.9 μg ZnSO<sub>4</sub>·7H<sub>2</sub>O, 9.95 μg CoCl<sub>2</sub>·6H<sub>2</sub>O, 9.76 μg CuSO<sub>4</sub>·5H<sub>2</sub>O, 6.18 μg Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, 100 μg vitamin B1, 0.5 μg Biotin, 0.5 μg vitamin B12 [18].

### 3. Measurements of Microalgal Productivity and Density

The productivity for the 10 m<sup>2</sup> pond was measured based on biomass dry weight. In every single day of cultivation, four 35 ml samples were collected from various locations of the pond. The samples were centrifuged at 15,000 g, washed with NaCl solution and distilled water to remove non-biological material, dried at 100 °C for 18 hr and weighed. Productivity was measured on a daily basis and reported as g/m<sup>2</sup>/d. Cell density was determined using optical density measurements of the absorbance at 590 nm with a spectrophotometer (Unicom UV-Vis spectrometry, China).

### 4. Measurements of Parameters

The temperature, pH and depth of culture medium were meas-

ured by sensors located in the liquid bulk as shown in Fig. 1. These parameters were controlled and monitored using a control system. Several electric heaters were used to maintain temperature for experiments. The salinity and alkalinity were measured by standard methods [19]. These two parameters were changed by addition of sodium chloride and sodium bicarbonate powder in the pond, respectively. NaHCO<sub>3</sub> increases the alkalinity level without affecting the pH significantly [20]. Average flow velocity was measured with an open channel flowmeter (Marsh-McBirney, Inc., model-2000, USA). Mapping of velocities has identified the best place for measuring average velocities to be approximately at 10 cm from the pond bottom, exactly before the bend, at the channel in which the paddle wheel was located [21]. At least ten flow velocity measurements were made and the average velocity was calculated. Input gas streams of pure CO<sub>2</sub> were delivered through mass flow controllers (Omega Engineering, Inc., FMA-A2121, USA) and for distribution of fine gas, CO<sub>2</sub> was introduced by means of 1.5 cm diameter and one m long porous diffuser, resting on the pond bottom.

### 5. Carbon Storage Capacity and Average Rate of Carbon Dioxide Outgassing

By measuring temperature, salinity, pH and alkalinity of liquid phase, dissolved carbon dioxide and total inorganic carbon (TIC) were determined from carbonate equilibrium equations according to previous studies [22-24]. CO<sub>2</sub> storage capacity of the pond was obtained by calculating the change in dissolved carbon dioxide in the liquid phase for the specified pH range of the pond.

For the liquid phase, the rate of CO<sub>2</sub> outgassing from surface of the pond is expressed as follows:

$$R_{CO_2} = K_L(C_{CO_2}^* - C_{CO_2})$$

where  $R_{CO_2}$  is the rate of CO<sub>2</sub> outgassing per unit surface area of the pond (mol/m<sup>2</sup>/s),  $K_L$  denotes the coefficient of mass transfer for CO<sub>2</sub> outgassing (m/s),  $C_{CO_2}^*$  denotes equilibrium CO<sub>2</sub> concentration with the air (mol/L) and  $C_{CO_2}$  is dissolved CO<sub>2</sub> concentration in the pond (mol/L).

For each condition of parameters, average rate of absorbed CO<sub>2</sub> losses was determined by measuring the decrease in total inorganic carbon per unit time and surface area, after sparging CO<sub>2</sub> in the non-inoculated liquid, traveling between recarbonation events. Three samples were collected for each analysis from the liquid phase mixed gently in front of the paddle wheel. As demonstrated by earlier experiments [25-27], the existence of algae has no significant effect on CO<sub>2</sub> transfer rate of culture medium. pH was monitored over the course of the experiments at 15 min intervals.

### 6. Determination of Average Surface Mass Transfer Coefficient for CO<sub>2</sub> Outgassing

This experiment was performed by supplying CO<sub>2</sub> into water of fixed alkalinity and allowing the pH to rise as a consequence of CO<sub>2</sub> losses from the surface of the pond. Dissolved CO<sub>2</sub> concentration and decrease of total inorganic carbon concentration were calculated from the observed pH change, using equilibrium constants corrected for temperature and salinity [24,28,29]. The average mass transfer coefficient for CO<sub>2</sub> outgassing was then determined by linear regression of the calculated average CO<sub>2</sub> driving force with the rate of change in total dissolved inorganic carbon per unit surface area of the pond. Henry's law was used to calculate the equilibrium CO<sub>2</sub> level with the air, corrected for temperature and ionic strength [28,

29].

### 7. CO<sub>2</sub> Injection Efficiency and Utilization Efficiency

The CO<sub>2</sub> injection efficiency was determined as the ratio of the increase in total inorganic carbon level in the liquid phase after injection of CO<sub>2</sub>, to the total amount of CO<sub>2</sub> injected into the pond, measured by mass flow controller. The utilization efficiency was estimated by dividing the amount of CO<sub>2</sub> fixed in the biomass by the total CO<sub>2</sub> injected into the pond.

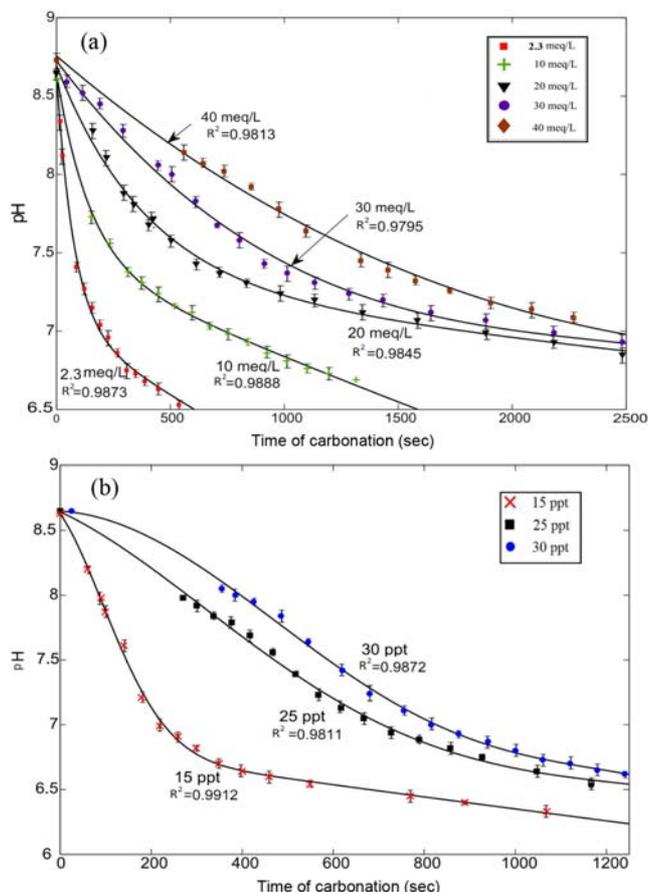
## RESULTS AND DISCUSSION

### 1. CO<sub>2</sub> Storage Capacity of the Pond

As a consequence of CO<sub>2</sub> outgassing and microalgae utilization, CO<sub>2</sub> concentration decreases and pH rises in the pond. Hence, to prevent that variations in CO<sub>2</sub> and pH at critical level limit the photosynthesis, a carbonation cycle is devised in the pond. In this cycle the culture medium travels from carbonation station after a specified period of time. In the flow of raceway ponds, adequate amounts of CO<sub>2</sub> must be injected into the carbonation stations, and subsequently be stored in water to meet the carbon demand of microalgae and compensate any outgassing of CO<sub>2</sub>, as the water travels between recarbonations (resupply events). In an optimized cultivation system, CO<sub>2</sub> content in the medium before reaching the carbonation station should not be lower than the critical amount of CO<sub>2</sub> required for unlimited photosynthesis [6,11,31]. Depending on the size of the pond, this injection can be continuous (sizes more than 0.5 hectare) or intermittent, with one or more carbonation systems along the pond [6].

Table 1 presents the calculated carbon storage capacity at different alkalinities and depths of two water resources with different ionic strengths. The pH in the water resources was considered to range within 6.5 to 8.7, which is the common pH range for outdoor cultivation of most microalgae [6,9]. The results show that the amount of CO<sub>2</sub> stored in the pond for fixed pH range of operation is directly proportional to alkalinity and depth of water in the pond. Table 1 also indicates that CO<sub>2</sub> storage capacity of high salinity waters is less than that of freshwater due to its effects on carbonate equilibrium constants.

The duration of carbonation required to decrease pH from 8.7 at different alkalinities and salinities of water resources was measured,



**Fig. 2.** Duration of carbonation required to introduce CO<sub>2</sub> (at 25 slpm) into the 10 m<sup>2</sup> raceway pond of 20 cm depth by carbonation system, at different alkalinity of freshwater (a) and at different salinity of liquid phase (2.3 meq/L alkalinity) (b).

as CO<sub>2</sub> was introduced through mass flow controller at 25 slpm (standard liters per minute) flow rate to the 10 m<sup>2</sup> pond at 20 cm depth (Fig. 2(a) and 2(b)). Injection efficiency of carbonation system was 57-69%, depending on the alkalinity of the liquid phase. Liquid height and gas flow rate had no significant effect on injection efficiency [9]. The measurements were done after a short period of paddle wheel

**Table 1.** Carbon storage capacity and duration of carbonation required to introduce CO<sub>2</sub> (at 25 slpm), for the 10 m<sup>2</sup> pond at various alkalinities, depths and salinities during pH change from 8.7 to 6.5 and 57-69% carbonation injection efficiency

|                    |            | Freshwater (salinity=0 ppt)                   |                         | Saltwater (salinity=35 ppt)                   |                         |
|--------------------|------------|---|-------------------------|---|-------------------------|
| Alkalinity (meq/L) | Depth (cm) | Carbon storage capacity (mol/m <sup>3</sup> ) | Time of carbonation (s) | Carbon storage capacity (mol/m <sup>3</sup> ) | Time of carbonation (s) |
| 2.3                | 15         | 0.03  | 165                     | 0.0591  | 85                      |
|                    | 20         | 0.04  | 215                     | 0.0788  | 110                     |
|                    | 25         | 0.05  | 270                     | 0.0985  | 135                     |
| 10                 | 15         | 0.1503  | 540                     | 0.2955  | 275                     |
|                    | 20         | 0.2004  | 720                     | 0.3940  | 365                     |
|                    | 25         | 0.2505  | 900                     | 0.4925  | 460                     |
| 30                 | 15         | 0.4510  | 1440                    | 0.8866  | 735                     |
|                    | 20         | 0.6013  | 1920                    | 1.1821  | 975                     |
|                    | 25         | 0.7516  | 2400                    | 1.4776  | 1220                    |

mixing.

The duration of carbonation did not show any significant difference at various mixing velocities in the range of 15 cm/s to 35 cm/s. For example, it took 910 seconds for pH to change from 8.7 to 7, for freshwater at 30 meq/L alkalinity and 20 cm depth in a pond with 15 cm/s mixing velocity, and 890 seconds for the same condition in a pond with 35 cm/s mixing velocity. The results show that at high alkalinity levels, large amounts of CO<sub>2</sub> must be injected so that a small change in pH can be observed. When the carbon dioxide is dissolved in the liquid phase, it is stored in the inorganic carbon pool in three forms of H<sub>2</sub>CO<sub>3</sub> (CO<sub>2</sub>), HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup>, depending on pH of liquid phase (Fig. 3). It is evident from Figs. 2(a) and 2(b) that the required time for carbonation increases significantly at lower

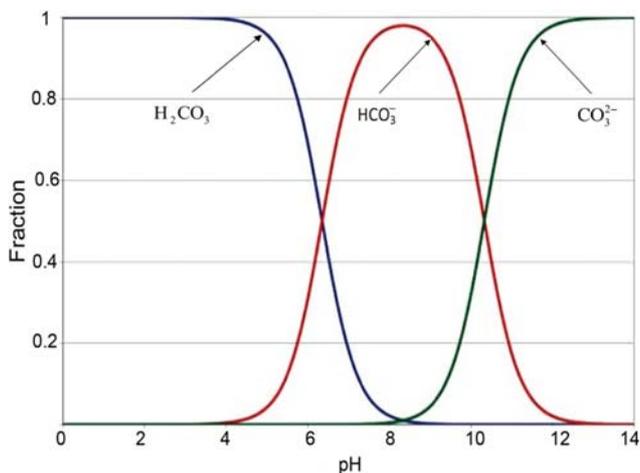


Fig. 3. Relative fraction of H<sub>2</sub>CO<sub>3</sub> (CO<sub>2</sub>), HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> in a liquid phase at 35 ppt salinity and 2.3 meq/L alkalinity as a function of pH [6].

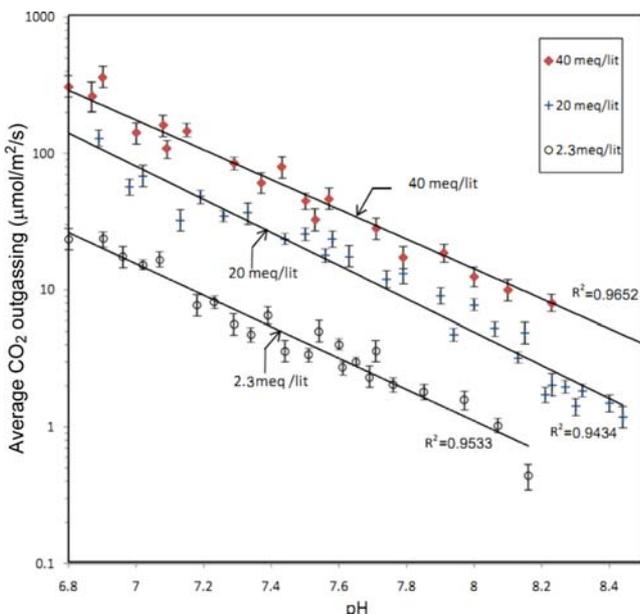


Fig. 4. Rate of CO<sub>2</sub> outgassing during operation of the 10 m<sup>2</sup> pond at various alkalinities of saltwater (35 ppt salinity). In each case, pond depth and mixing velocity are 20 cm and 25 cm/s, respectively.

operating pHs. In the narrower operating pH range the pond shows less CO<sub>2</sub> storage capacity; therefore, to maintain the level of productivity, the number of carbonation stations (for large ponds) must be increased, which corresponds to a decreased time between recarbonation events (for small ponds).

**2. Average Rate of Absorbed CO<sub>2</sub> Outgassing**

The average rate of absorbed CO<sub>2</sub> outgassing was determined experimentally for the 10 m<sup>2</sup> pond at 25 cm/s average mixing velocity, 20 cm depth and constant 20 °C temperature. The results of CO<sub>2</sub> outgassing rate are shown in Fig. 4 at different alkalinities of saltwater as pH change in the pond. The average rate of absorbed CO<sub>2</sub> losses increased at higher alkalinities. Due to larger total carbon storage capacity in a liquid phase with higher alkalinity (Table 1), the driving force for outgassing increases. Outgassing for saltwater with 35 ppt salinity and 40 meq/L alkalinity was 40-fold higher than seawater with the same salinity and 2.3 meq/L alkalinity at pH=8, but, it took more time for pH to change in the pond with higher alkalinity. For example, it took 450 min at 40 meq/L alkalinity and 250 min at 2.3 meq/L alkalinity for pH to change from 7 to 8 (Fig. 5).

As shown in Fig. 4, average rate of absorbed CO<sub>2</sub> losses increased at lower pHs, which is critical in particular at high alkalinity levels. At lower pHs, dissolved CO<sub>2</sub> concentration and consequently driving force for outgassing increased. Outgassing steeply increased below pH 8 for seawater at 35 ppt salinity and 2.3 meq/L alkalinity. This loss can be minimized by maintaining pH at higher levels. Thus, to minimize CO<sub>2</sub> losses from the pond without a significant productivity reduction, it is favorable in open ponds to have a low alkalinity when the desired species require a low pH for optimal growth and a high pH if the medium has a high alkalinity. The upper limit of operating pH range in a raceway pond is set by the growth and productivity response of the algae to high pHs as well as low CO<sub>2</sub> concentrations and calcium carbonate precipitation [32]. The latter is especially acute when the alkalinity is low, as in the seawater (10.3 mM Ca<sup>+2</sup> concentration and 2.3 meq/L alkalinity). This precipitation results in low carbon storage capacity, due to loss of alkalinity. In seawater, CaCO<sub>3</sub> is precipitated considerably at pHs

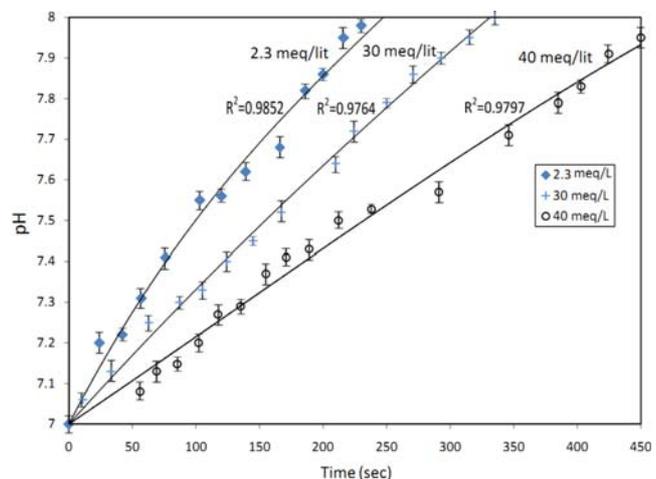


Fig. 5. Time dependent variation of pH in the 10 m<sup>2</sup> pond due to CO<sub>2</sub> outgassing, at different alkalinities of saltwater at 35 ppt salinity. In each case, pond depth and mixing velocity are 20 cm and 25 cm/s, respectively.

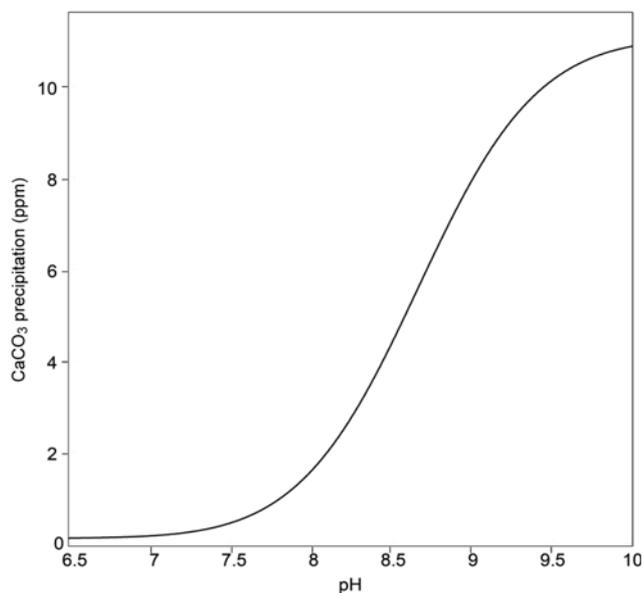


Fig. 6. CaCO<sub>3</sub> precipitation at various pH of seawater [32].

above 8 (Fig. 6). In the high alkalinity cases, growth and productivity response of microalgae dictate the upper limit of pH. The effects of low CO<sub>2</sub> concentration (25 μM) and high pH (9-10) (the economic conditions for operation of open ponds), on productivity of several species has been investigated [9]. At low CO<sub>2</sub> concentration and high pH cultures, the productivity was 10-15% lower than in control cultures, which is not significant in a practical sense.

CO<sub>2</sub> outgassing was determined for different ionic strengths of liquid phase (Fig. 7). As a consequence of the effects of ionic strength on the carbonate equilibrium constants and the amount of carbon storage capacity, CO<sub>2</sub> outgassing was higher in freshwater mediums

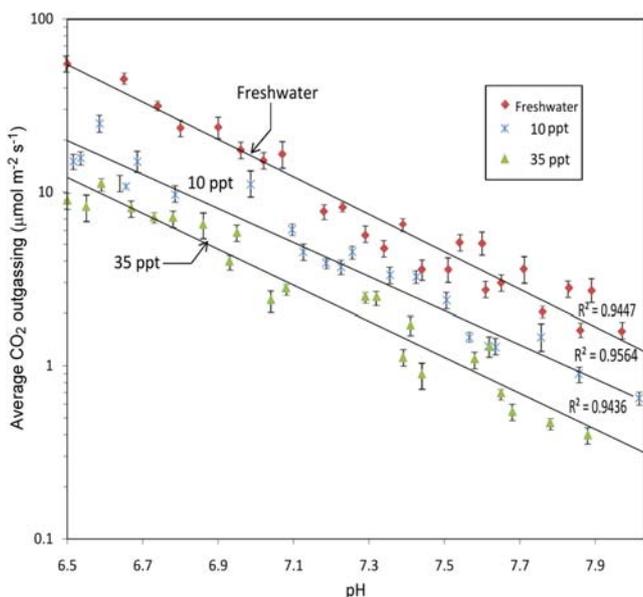


Fig. 7. Rate of CO<sub>2</sub> losses during operation of the 10 m<sup>2</sup> raceway pond at various salinities of liquid phase. For each case, pond depth, mixing velocity and alkalinity are 20 cm, 25 cm/s and 2.3 meq/L, respectively.

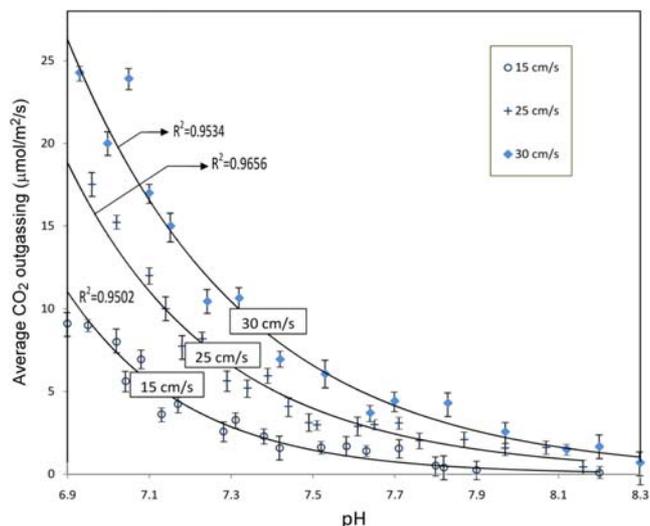


Fig. 8. Effects of mixing velocity in the pond at 20 cm depth on the CO<sub>2</sub> outgassing rate of liquid phase at 2.3 meq/L alkalinity and 35 ppt salinity.

than in saltwater ones.

The results (Fig. 8) show that doubling mixing velocity elevates the average rate of absorbed CO<sub>2</sub> outgassing about 1.5 times due to the higher rate of surface renewal and hence mass transfer coefficient for outgassing. On the other hand, for large-scale cultivation systems, increase in mixing velocity can decrease the time intervals between recarbonations and subsequently pH range experienced in the pond. Therefore, mixing velocity must be optimized for these two conflicting effects. Decreases in volume of liquid per unit surface area acted to aggravate CO<sub>2</sub> outgassing and decreased carbon storage capacity (Fig. 9 and Table 1). Hence, the depth of liquid must be increased up to the extent that not to limit productivity due to reduction in light availability for photosynthesis.

To determine the pond size with fixed number of carbonation stations, the number of carbonation stations required (or the frequency of carbonation in small ponds) and the CO<sub>2</sub> transfer stations

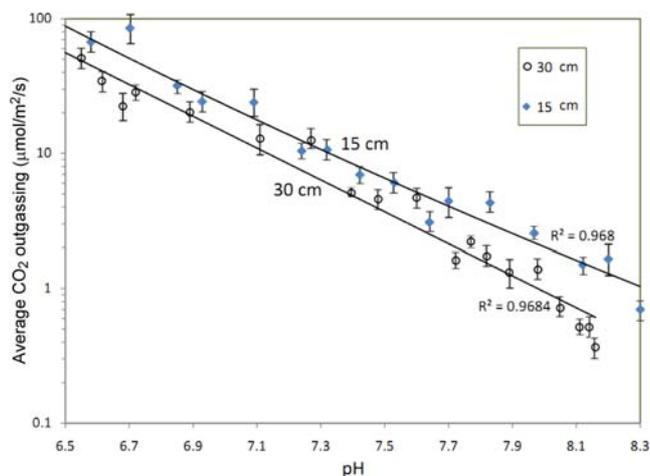


Fig. 9. Rate of CO<sub>2</sub> outgassing from the 10 m<sup>2</sup> pond at two different depths of liquid phase (35 ppt salinity and 2.3 alkalinity), 15 cm and 30 cm, and 25 cm/s mixing velocities.

spacing, first, the optimized pH range experienced in the pond should be specified with the consideration of CO<sub>2</sub> outgassing and productivity. pH range, depth and alkalinity will determine the total carbon storage capacity of the pond. As the required CO<sub>2</sub> for photosynthesis and outgassing in distance between carbonation stations must be equal to (or exceed) that stored in the pond in this distance, an adequate frequency of recarbonation should be determined. The frequency and the optimized mixing velocity values are used to determine the distance between carbonation stations, and thereby the pond size.

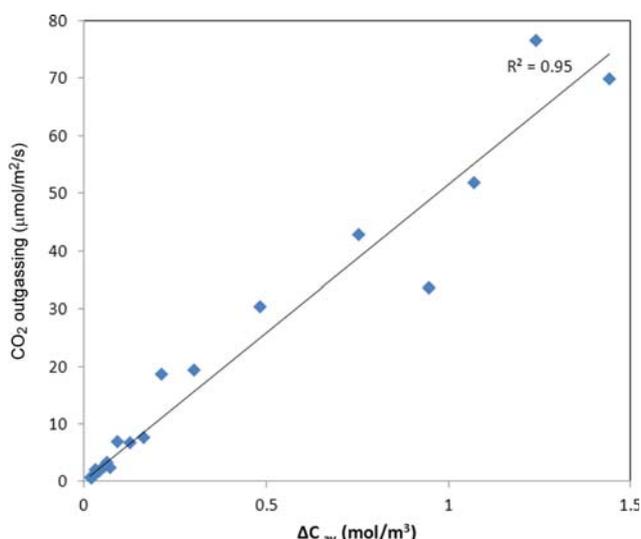
### 3. Average Mass Transfer Coefficient for Absorbed CO<sub>2</sub> Outgassing

Experimental and theoretical correlations developed for outgassing mass transfer coefficient of CO<sub>2</sub>,  $K_L$ , for lakes, estuaries [33, 34], aquaculture ponds [35] and open ponds with different configurations [36,37] are not suitable for open raceway ponds, where irregular surface deformations occur due to its special design. They provide only approximate estimate for  $K_L$ ; therefore, the accurate

**Table 2. Mass transfer coefficient for CO<sub>2</sub> outgassing,  $K_L$ , at different average linear velocities and depths of culture medium in the 10 m<sup>2</sup> raceway pond**

| Depth (cm) | Velocity (cm/s) | $K_L$ (m/s)                            |
|------------|-----------------|--|
| 15         | 15              | $1.43 \times 10^{-5}$ ( $R^2=0.963$ )* |
|            | 25              | $2.6 \times 10^{-5}$ ( $R^2=0.942$ )   |
|            | 30              | $3.31 \times 10^{-5}$ ( $R^2=0.955$ )  |
| 20         | 15              | $1.28 \times 10^{-5}$ ( $R^2=0.932$ )  |
|            | 25              | $2.3 \times 10^{-5}$ ( $R^2=0.966$ )   |
|            | 30              | $2.8 \times 10^{-5}$ ( $R^2=0.953$ )   |
| 25         | 15              | $1.1 \times 10^{-5}$ ( $R^2=0.971$ )   |
|            | 25              | $2 \times 10^{-5}$ ( $R^2=0.944$ )     |
|            | 30              | $2.5 \times 10^{-5}$ ( $R^2=0.955$ )   |

\*Coefficient of determination ( $R^2$ )



**Fig. 10. Rate of CO<sub>2</sub> outgassing vs. average CO<sub>2</sub> driving force, for operation of the 10 m<sup>2</sup> pond at an average mixing velocity of 30 cm/s and 20 cm depth. The slope of the line corresponds to a  $K_L$  value of  $2.5 \times 10^{-5}$  m/s.**

amount must be derived empirically from prototypes and pilots.

Mass transfer coefficient for CO<sub>2</sub> outgassing mainly depends on hydrodynamics of the pond [36,37]. It was determined for common operational velocity range (15-35 cm/s) and depth range (10-30 cm) in open raceway ponds for cultivation of microalgae (Table 2). Fig. 10 shows an example of experimental data and fitted line used for determining  $\bar{K}_L$  at 30 cm/s mixing velocity and 20 cm depth. The following empirical equation was obtained from a regression analysis:

$$\bar{K}_L = 2.79 \times 10^{-6} d^{-0.46} v^{1.09} \quad R^2 = 0.93$$

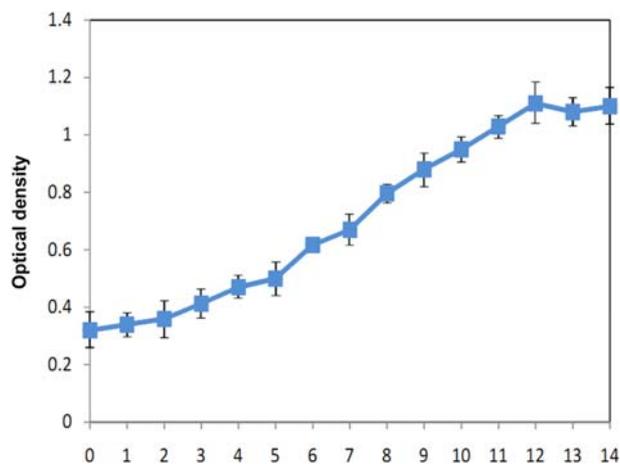
where  $\bar{K}_L$  is average mass transfer coefficient for absorbed CO<sub>2</sub> outgassing (m/s),  $d$  is the height of medium in the pond (cm) and  $v$  is the mixing velocity (cm/s). In the range of pH 6.5 to 8.7, the mass transfer coefficient did not vary. Benemann et al. [37] measured the same  $\bar{K}_L$  value of  $3.4 \times 10^{-5}$  m/s for a 1.2 m<sup>2</sup> pond at 15 cm depth and 30 cm/s velocity over two pH ranges 6.77 to 7.09 and 7.17 to 7.59. In an alkaline medium, CO<sub>2</sub> is present in an uncatalyzed reaction path, i.e., hydration of CO<sub>2</sub> and subsequent acid-base reaction to form carbonate ion.



For common operational pH and alkalinity range in microalgal ponds, the effect of this reaction on CO<sub>2</sub> transfer coefficient is negligible compared with hydrodynamic effects [38]. We measured the same  $K_L$  value, even for alkalinities of up to 30 meq/L.

### 4. CO<sub>2</sub> Utilization in Large-scale Cultivated Open Raceway Pond

To evaluate the utilization of CO<sub>2</sub> in a production pond, strain *Nannochloropsis* sp. PTCC6016 was cultivated in the 10 m<sup>2</sup> raceway pond for 14 days [17]. The pond was operated at 30 cm/s mixing velocity and 20 cm depth. Variation of cell density in the production pond is illustrated in Fig. 11. A portion of stored CO<sub>2</sub> in the pond for an operating pH range, fixed in the biomass and the remaining outgassed during travelling of liquid phase in the pond. For each microalgal productivity in the pond, the mass of carbon fixed in the biomass during the cultivation period was estimated to be 1.83-fold of the biomass produced (dry weight) [1,6] and subsequently, CO<sub>2</sub> lost to the atmosphere through outgassing was esti-



**Fig. 11. Cell density in the 10 m<sup>2</sup> pond during 14 day cultivation for *Nannochloropsis* sp.**

**Table 3. Carbon utilization efficiency in the production pond, at operating pH range of 6.5 to 8.26, 2.3 meq/L alkalinity and 35 ppt salinity of culture medium**

| Day of cultivation | Productivity <sup>a</sup> (g/m <sup>2</sup> /d) | Biomass (g/m <sup>2</sup> ) | Outgassed (g/m <sup>2</sup> ) | Utilization efficiency (%) |
|--------------------|---|-----------------------------|-------------------------------|----------------------------|
| 2                  | 4.7   | 4.22                        | 5.04                          | 31                         |
| 7                  | 20.4  | 6.84                        | 2.42                          | 49                         |
| 9                  | 17.5  | 6.45                        | 2.81                          | 46                         |
| 12                 | 8.5   | 5.49                        | 3.77                          | 39                         |

<sup>a</sup>Based on constant productivity over 10 hr day

mated from a preliminary mass balance for CO<sub>2</sub>. The results are shown in Table 3 for operating pH range of 6.5 to 8.26 at 2.3 meq/L alkalinity and 35 ppt salinity of culture medium. At the pH 8.26, there is no driving force for outgassing, but pH of culture media could rise to 10 as a result of CO<sub>2</sub> utilization by microalgae. The data is based on the assumption that the productivity is constant during 10-hr-daylight period. The samples for productivity analysis were taken in the morning and the evening, so no nightly respiration occurred in between. The amount of CO<sub>2</sub> outgassed increased as the pond was operated at lower productivities, and, as a consequence, CO<sub>2</sub> utilization efficiency declined. At the productivity of 20.4 g/m<sup>2</sup>/d, 26% of the CO<sub>2</sub> absorbed in the pond was lost to the atmosphere through the pond surface. Operation of the pond at the lower productivity 4.7 g/m<sup>2</sup>/d increased CO<sub>2</sub> losses to more than 54%. At the maximum productivity of 20.4 g/m<sup>2</sup>/d, the low CO<sub>2</sub> utilization efficiency, 49%, was mainly caused by low injection efficiency of carbonation system, 57%. In this case, selection of a carbonation system with 95% injection efficiency [9] could increase CO<sub>2</sub> utilization efficiency in the pond up to 70%. Each condition of the parameters in the pond reducing CO<sub>2</sub> outgassing rate can increase CO<sub>2</sub> utilization efficiency.

### CONCLUSION

The influence of various operational and cultural parameters on an optimized storage and utilization of CO<sub>2</sub> in open raceway ponds was investigated. For economic CO<sub>2</sub> supply into the pond, especially to produce low value products, design parameters should be selected accurately.

CO<sub>2</sub> outgassing from the pond increased as the pond was operated at lower pHs (especially less than 8 for seawater at 2.3 meq/L alkalinity and 35 ppt salinity), and higher alkalinities, the conditions at which the carbon storage capacity of the pond was increased. Because the pond should have a large carbon storage capacity, and on the other hand, CO<sub>2</sub> outgassing must be minimized, an optimized value of pH and alkalinity for operation of the pond must be selected. In the higher alkalinity cases, more time for CO<sub>2</sub> injection was required to adjust the pH of the pond. Furthermore; it took more time for pH to increase as the pond was operated at the higher alkalinities. CO<sub>2</sub> outgassing was 4.5-fold higher in freshwater at 2.3 meq/L alkalinity than in seawater at the same alkalinity and 35 ppt salinity at pH=7. An empirical correlation for  $\bar{K}_L$  was developed, where  $\bar{K}_L$  is a function of depth and mixing velocity. Variation of mixing velocity had more effect on the rate of outgassing than the height of medium in the pond. Evaluation of a production pond for

cultivation of *Nannochloropsis* sp. showed that higher productivity in the pond results in more efficient utilization of CO<sub>2</sub>, due to lower amount of CO<sub>2</sub> outgassing from the pond. At maximum productivity in the pond, low CO<sub>2</sub> utilization efficiency (49%) was mainly due to low injection efficiency (57%).

Accurate setting of the mentioned parameters is important, as they determine the pond size and the number of carbonation stations for cultivation of known species, and as a result, capital costs for carbonators. Another aspect in efficient carbonation of large-scale raceway ponds is to select the best engineering design for supply and transfer systems, in order to maximize injection efficiency, which is the topic of ongoing research.

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