CARBON CAPTURE USING THE MICROALGAE CHLORELLA VULGARIS IN A PACKED BUBBLE COLUMN PHOTOBIOREACTOR

By

Kenneth Kofiga Zame

A Thesis Submitted

In Partial Fulfillment of the Requirements for the

Degree of Master of Science

In the Environmental Studies Program

YOUNGSTOWN STATE UNIVERSITY

August 2010
Carbon Dioxide Capture Using the Microalgae *Chlorella vulgaris* in a Packed Bubble Column Photobioreactor

Kenneth Kofiga Zame

I hereby release this thesis to the public. I understand that this thesis will be made available from the OhioLINK ETD Center and the Maag Library Circulation Desk for public access. I also authorize the University or other individuals to make copies of this thesis as needed for scholarly research.

Signature: 

*Kenneth Kofiga Zame, Student*

Approvals: 

*Douglas Price, Thesis Advisor*

*Felicia P. Armstrong, Committee Member*

*Gary Walker, Committee Member*

*Lauren Schroeder, Committee Member*

*Peter J. Kasvinsky, Dean of School of Graduate Studies & Research*
Acknowledgement

It is a pleasure to express my appreciation to those who made this thesis possible. I am thankful to my supervisor, Dr. Douglas Price, whose encouragement, guidance and support throughout my work on this thesis enabled me to successfully complete it. I would like to thank Dr. Gary Walker and Dr. Lauren Schroeder for their support and guidance as members of the thesis committee. Special thanks to Dr. Felicia Armstrong who is also a member of the committee for her assistance and support not only on this thesis but also on my work as a teaching assistant at the Geological and Environmental Science Department at Youngstown State University.

I would like to say thank you to Dr. Peter Norris (Interim Chair, Geological and Environmental Sciences Department), Dr. Isam Amin, Dr. Colleen McLean, Ms. Shari McKinney and all faculty members of the Department of Geological and Environmental Sciences at Youngstown State University for their support in diverse ways.

I am also grateful to my family and friends for their support and encouragement.

Finally, I say glory be to God for everything.
# Table of Contents

Acknowledgements ........................................................................................................... iii

List of Figures ................................................................................................................... vi

List of Tables .................................................................................................................... vii

Abstract ............................................................................................................................ viii

Chapter 1: Introduction ..................................................................................................... 1

  1.1 Greenhouse Gases and Global Warming ................................................................. 1

  1.2 Geological CO$_2$ Sequestration .............................................................................. 1

  1.3 Chemical CO$_2$ Capture ......................................................................................... 3

  1.4 Biological Carbon Sequestration ............................................................................ 3

    1.4.1 Forest Carbon Sequestration ........................................................................... 4

    1.4.2 Algae Carbon Capture ..................................................................................... 4

Chapter 2: Literature Review ............................................................................................ 6

  2.1 Systems for Algae CO$_2$ Sequestration ................................................................. 6

  2.2 Photobioreactors for Algae CO$_2$ Capture .......................................................... 6

  2.3 Concept in Mass Transfer ...................................................................................... 9

  2.4 Resistance to Mass Transfer in Bioreactors .......................................................... 11

  2.5 Requirements for Algal Photobioreactors ............................................................. 12

  2.6 Chlorella vulgaris for CO$_2$ Sequestration in a Photobioreactor ......................... 12

    2.7 Purpose of this Research ..................................................................................... 13

Chapter 3: Methods, Procedures and Materials ............................................................... 14

  3.1 Experimental Setup and Approach ....................................................................... 14

  3.2 Medium and Chemicals ......................................................................................... 16
Chapter 4: Results and Discussion

4.1 Material Balance on CO₂

4.2 Experimental Results

4.2.1 Gas flow rate versus Outlet CO₂ Concentration

4.2.2 Gas flow rate versus Moles of CO₂ Transferred

4.2.3 Gas flow rate versus Moles of CO₂ Transferred

4.3 Discussion of Results

Chapter 5: Conclusions and Recommendations

References
List of Figures

Fig. 1.1: Carbon Capture and Storage Options.................................................................2

Fig. 2.1 Open ponds for Algae CO₂ Sequestration.............................................................6

Fig. 2.2: Vertical Column Photobioreactor........................................................................8

Fig. 2.3: Horizontal Column Photobioreactor.................................................................8

Fig. 2.4: Plate Photobioreactor.......................................................................................8

Fig. 2.5: Typical Gas-Liquid interface.............................................................................9

Fig. 2.6: Counter-current gas-liquid interface.................................................................10

Fig. 3.1: Schematic of Packed Bubble Column...............................................................15

Fig. 3.2: Packed Bubble Column equipment for Experiment........................................15

Fig. 3.3: Packed Bubble Column Photobioreactor system for Experiment.......................16

Fig 4.1: Molar CO₂ flow rate effect on outlet CO₂ concentration at different alga

Culture Concentrations and CO₂ inlet compositions.................................................22

Fig 4.2: Gas flow rate effect on outlet CO₂ concentration at different

CO₂ inlet concentrations............................................................................................23

Fig 4.3: Gas flow rate effect on outlet CO₂ concentration at different

Algal culture concentrations at 5% CO₂ composition..............................................24

Fig 4.4: Molar Gas flow rate effect on % of CO₂ transferred at different

Algal culture concentrations..................................................................................25
List of Tables

Table 2.1: Prospects and limitations of various algae photobioreactor systems ........7
Table 3.1: Chemical Components of Bold 3N Medium.................................17
Table 3.2: Chemical Components of P-IV Metal Solution............................18
Table 3.3: Chemical Components of Soilwater.........................................19
Table 3.4: Chemical Components of Vitamin B₁₂ .....................................19
Table 4.1: Result of varying inlet CO₂ gas flow rate and corresponding
          Outlet CO₂ gas concentration at algal concentration of 0.21g/l and
          Flow rate of 200 mL/min...............................................................21
Table 4.2: Result of varying inlet CO₂ gas flow rate and corresponding
          Outlet CO₂ gas concentration at algal concentration of 0.35g/l and
          Flow rate of 200 mL/min...............................................................21
Table 4.3: Result of varying inlet gas flow rate at algal Concentration of
          0.21 g/L and inlet CO₂ concentration of 5.0 mol% ..........................22
Table 4.4: Result of varying inlet gas flow rate at algal Concentration of
          0.21 g/L and inlet CO₂ concentration of 5.0 mol%............................23
Abstract

In response to increasing pressure to reduce carbon emissions, algae photobioreactors have become central to finding environmentally-sustainable mitigation strategies for carbon capture. Although a good number of photobioreactors have been proposed, only a few of them can be practically used for large-scale algal CO$_2$ sequestration and for that matter mass production of algae. One of the major factors that limit their practical application with algal mass cultures is mass transfer. Against this background, the purpose of this research was to test a scalable bench scale photobioreactor with a capacity to enhance the mass transfer of CO$_2$ (gas) into a fresh water *Chlorella vulgaris* algal culture (liquid) phase. To achieve this, a packed vertical column being referred to as a Packed Bubble Column Photobioreactor (PBCP) was used to increase gas-liquid contacting surface area enhancing the mass transfer of the gas into the liquid phase.

The dynamics of the PBCP showed more moles of CO$_2$ were transferred with higher composition of inlet CO$_2$ at same algal culture composition. Higher algal culture concentration showed lower composition of CO$_2$ in the outlet gas from of the reactor. CO$_2$ increased in outlet gas composition with increasing rate of moles of CO$_2$ into the reactor. During 45 minutes of steady state semi-continuous experimental test runs with 350 mL of algal culture at 0.21 and 0.35 g/L and CO$_2$ (of 5.0 – 9.5% composition at flow rate of 25.0 mL/min to 112 mL/min); CO$_2$ transferred into the algal culture phase was typically in the range of 10 to 30%. These results have shown that the PBCP is able to significantly enhance the transfer of CO$_2$, and reductions of carbon dioxide greater than 30% are achievable with higher algal cultures and CO$_2$ composition in the reactor.
1.1 Greenhouse Gases and Global Warming.

Since the beginning of industrialization, the concentration of carbon dioxide gas in the atmosphere has increased resulting in induced global warming (Ramanathan, 1988). Carbon dioxide release into the atmosphere from anthropogenic sources alone in 1997 was 7.4 billion tons and it is estimated that this would rise to 26 billion tons per year by the year 2100. Carbon dioxide (CO$_2$) contributes the highest proportion of the global greenhouse effect, due mainly to its higher concentration in the atmosphere (Global Warming, 2010). World temperatures could rise by 1.1 to 6.4 °C (2.0 to 11.5 °F) during the 21st century and sea levels would probably rise by 18 to 59 cm (IPCC, 2007). Consequences of global warming include droughts, flooding, expanding deserts, heat waves, ecosystem disruption, increasingly severe weather, and loss of agricultural productivity (Morrissey et al, 1997). Over the years many attempts have been made to reduce atmospheric carbon dioxide through geological, chemical and biological sequestration.

1.2 Geological Sequestration

In geological sequestration, gas phase CO$_2$ as well as supercritical liquid CO$_2$ can be stored in geological formations. Gas phase CO$_2$ has also been successfully used over the years for enhanced oil and gas recovery by injection into gas and oil reservoirs (DOE, 1999). The storage of CO$_2$ in the gas phase in geological formations would reduce storage capacities and limit fossil fuel use to only decades. With gas phase CO$_2$ sequestration, the gas could be released should there be an accidental penetration in the formation (Gunter W.D et. al 2004; Kaarstad O. 2002). Supercritical CO$_2$ at pressures exceeding 7.38 MPa, is highly favored over gas phase storages as
the holding capacity in geological formations is significantly increased. Supercritical CO₂ is also more reactive than in the gas phase and has the ability to combine chemically with metals to form solid carbonates. However these geochemical reactions that form carbonates would take centuries to millennia, and the possibility of leakage is very likely to occur as supercritical CO₂ attacks concrete which is a normally the material for capping wells (Duguid A, et al 2004; Perkins E, et al). Supercritical CO₂ is also mobile and could poison a potable aquifer should an underground fixture exist from the geological formation to the aquifer. Carbon capture and sequestration is currently expensive (IEA GHG, 2000). Deep ocean injection of CO₂ at depths of 100 meters, where CO₂ would dissolve has been proposed. Another option proposed is to create CO₂ underwater lakes by piping directly onto the sea floor CO₂ at depths greater than 3000 meters, where it would be denser than water. However ocean storage of CO₂ is likely to cause significant environmental problems as the CO₂ would combine with water to form carbonic acid, increasing the acidity of the water. As a result of this, shells of shellfish and corals will dissolve and reproduction of sea creatures would also be affected. Alternatives are being considered as potential problems and liabilities with geological sequestration are major.

![Carbon Capture and Storage Options](image_url)
1.3 Chemical CO₂ Capture

Before CO₂ is sequestered into geological or other storage sites, it must be purified or enriched beyond the 5-15% concentration typically found in the products of combustion (Kohl, A. O and Nielsen R, 1997). The two main methods used to purify CO₂ for sequestration are: 1) absorption – desorption separation and 2) oxygen based combustion. Monoethyamine (MEA or amine) is commonly used in the absorption – desorption method to absorb the CO₂ from the combustion gas. The CO₂ is then stripped (desorbed) in a separate heated chamber as a relatively pure gas. The oxygen–based combustion removes the nitrogen from the combustion air before combustion with the fossil fuels such as coal or natural gas. This results in combustion products of CO₂ and water which eliminates the task of having to remove nitrogen, as it is nonreactive and difficult to separate from CO₂ (Kohl, A. O and Nielsen R, 1997). To run an amine scrubbing system for CO₂ separation, it is estimated that about one-third of the energy output of a power plant would be required (Alstom Power Inc., 2001). This leads to significant cost of the energy produced.

Activated carbon powder impregnated with potassium carbonate has also been demonstrated to chemically adsorb CO₂ as high as 8 to 17% in the flue gas. The activated carbon is regenerated by stripping off the CO₂ gas at a higher temperature. When compared to other processes such as the conventional amine process, this approach is efficient, provides low utility cost and is energy-conservative (Ebune, 2008).

1.4 Biological Carbon Sequestration

Biological (or terrestrial) sequestration involves the net removal of CO₂ from the atmosphere by plants and micro-organisms and its storage in vegetative biomass and in soils. Advantages of biological sequestration include: 1) net sequestration of relatively large volumes of carbon at
comparatively low cost, 2) protection or improvement of soils, water resources, habitat, and biodiversity, and 3) promotion of more sustainable agriculture and forestry practices (Climate Change Connection, 2010).

### 1.4.1 Forest Carbon Sequestration

Forests as natural sinks sequester CO\(_2\) in cellulosic structure of trees and humus soil. With about 600 power plants in the United States; land, energy and the cost required to plant trees to sequester significant quantities of CO\(_2\) makes this option unattainable as each coal power plant on the average produces about 4 million tons of CO\(_2\) annually (Union of Concerned Scientist, 2010). Carbon stored in soils oxidizes quickly into the atmosphere or water. Forests also release the carbon stored in trees in at most decades as the forests burn or the trees are uprooted or damaged severely. An example is Hurricane Katrina destroying about 320 million large trees in the Gulf Coast forest (NASA, 2007).

### 1.4.2 Algae Carbon Capture

Algae represent about 0.5% of global biomass yet produces about 70% of the net oxygen on earth. In the process CO\(_2\) is sequestered by photosynthetic means in large quantities and algae biomass rich in lipids which can be used for biofuels is produced (Hall J, 2008). Algae thus offers an alternative and sustainable solution in two main ways; 1) value-added sequestration of CO\(_2\) through conversion to biomass and 2) biomass which can be use to produce renewable fuels (biofuels and/or biogas). There exist over 40,000 species of algae and cyanobacteria (photosynthetic prokaryotic organisms), in many forms and under different conditions that can
be optimized to sequester carbon dioxide through photosynthesis. These include microalgae species such as *Chlorella*, *Spirulina* and *Dunaliell*. 
Chapter 2 – Literature Review

2.1 Systems for Algae CO₂ Sequestration

Algae can be used in open systems (open ponds) as shown in Figure 2.1 and closed systems (closed photobioreactors) as show in Figures 2.2, 2.3 and 2.4 to sequester carbon. Open systems can be natural waters (lakes, lagoon, ponds) and artificial ponds or containers. Open ponds are easier to construct and operate than closed systems. Limitations to open ponds include poor light utilization by algae cells, evaporative losses of water, diffusion of CO₂ to the atmosphere, and requirement of large areas of land. Other problems include contamination by predatory microorganisms and other fast growing heterotrophs. Closed photobioreactors have attracted much interest because they especially allow better control for higher CO₂ capture and yield of biomass (Ugwu C. U et al, 2008).

Figure 2.1 Open ponds for Algae CO₂ Sequestration

2.2 Photobioreactors for Algae CO₂ Sequestration

A good number of photobioreactors have been proposed for CO2 mitigation using algae, and for that matter algae growth, however only a few of them can be practically used for mass
production of algae. One of the major factors that limit their practical application in algal mass cultures is less efficient mass transfer of CO₂ (Ugwu et al, 2008). Table 2.1 below presents the prospects and limitations of various photobioreactor systems for alga culture systems.

**Table 2.1 Prospects and limitations of various algae photobioreactor systems (Kaarstad O. 2002)**

<table>
<thead>
<tr>
<th>Photobioreactor System</th>
<th>Prospects</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertical - Column</td>
<td>Good mass transfer, good mixing with low shear stress, low energy consumption, high potentials for scalability, easy to sterilize, readily tempered, good for immobilization of algae, reduced photo inhibition and photo-oxidation.</td>
<td>Small illumination surface area, their construction require sophisticated materials, shear stress to algal cultures, decrease of illumination surface area upon scale-up</td>
</tr>
<tr>
<td>Flat-plate</td>
<td>Large illumination surface area, suitable for outdoor cultures, good for immobilization of algae, good light path, good biomass productivities, relatively cheap, easy to clean up, readily tempered, low oxygen buildup.</td>
<td>Scale-up requires many compartments and support materials, difficulty in controlling culture temperature, some degree of wall growth, possibility of hydrodynamic stress to some algal strains.</td>
</tr>
<tr>
<td>Tubular</td>
<td>Large illumination surface area, suitable for outdoor cultures, fairly good biomass productivities, relatively cheap.</td>
<td>Gradients of pH, dissolved oxygen and CO₂ along the tubes, fouling, some degree of wall growth, requires large land area.</td>
</tr>
</tbody>
</table>
Figure 2.2: Vertical Column Photobioreactor

Figure 2.3: Horizontal Column Photobioreactor

Figure 2.4: Plate Photobioreactor
2.3 Concepts in Mass Transfer

Gas absorption involves the mass transfer from the gas phase to the liquid phase where the gas molecules diffuse from the main body of the gas phase to the gas-liquid interface, then cross this interface into the liquid side, and finally diffuse from the interface into the main body of the liquid. The interface can represent any location in the gas absorption equipment where the gas contacts the liquid. A typical gas-liquid interface is show in Figure 2.5 below.

Figure 2.5: Typical Gas-Liquid interface
Three gas flow regimes can be visualized, as listed below:

- Fully developed turbulent region where most of the mass transfer takes place by eddy diffusion
- A transition zone with some turbulence
- A laminar film with molecular diffusion

Normally for analysis as well as development of various correlations of mass transfer phenomena, the Two-Film Theory of mass transfer is used. Figure 2.6 shows the two gas film interface that can be represented at any point in the gas absorption equipment where the gas contacts the liquid (Separation Processes, 2010).

Figure 2.6: Counter-current gas-liquid interface
2.4 Resistance to Mass Transfer in Bioreactors

Resistance to mass transfer in bioreactor equipment can be encountered in eight (8) different ways;

1) In the gas film
2) At the liquid-gas interface
3) In the liquid film surrounding the gas interface
4) In the liquid phase
5) In the liquid film surrounding the solid (microorganism)
6) At the liquid-solid (microorganism) interface
7) In the solid phase
8) At the site of reaction (within the microorganism)

These resistances occur in series and the largest would be the rate controlling step. The entire mass transfer is normally modeled using a single mass transfer correlation (Harvey W. Blanch, Douglas S. Clark. 1997).

The resistance of the gas film within the bubble (1) can be neglected relative to the liquid film surrounding the bubble (4) as gas-phase diffusivities are typically much higher than liquid-phase diffusivities. Interfacial resistance to transport [for (2) and (6)] is small and can also be neglected. Transport through the liquid is rapid when the liquid is adequately mixed; hence (4) may also be neglected with adequate mixing (Harvey W. Blanch, Douglas S. Clark. 1997). In the case of microbial particle of single cell of size 1 to 2 micron, their small size (could have large surface interfacial area) relative to that of a gas bubble and result in the liquid film
surrounding the gas bubble, and thus becoming the rate determining step. The rheology of the liquid also has a strong influence on the rate of mass transfer (Harvey W. Blanch, Douglas S. Clark. 1997).

2.5 Requirements for Algal Photobioreactor

Availability and intensity of light are the major factors controlling the productivity of photosynthetic cultures. Light intensity requirement of microalgae are relatively low compared to higher plants (Eiichi Ono et al, 2010). In microalgae, the biomass productivity is a function of the cell concentration in the culture at steady state and the growth rate is governed by the amount of light (average irradiance) which is the rate controlling factor. The growth rate increases with increasing irradiance to a maximum irradiance limit beyond which the growth is inhibited – a phenomenon known as photo inhibition (Lee, Y.K, 1999). Photo inhibition is often suspected as the major cause of reducing algal productivity (Eiichi Ono et al, 2010). Like any other living organism, algae require nutrients to sustain, grow and thrive. These nutrients are similar to what plants requires and consist mainly of nitrogen, phosphorus, potassium and trace amounts of iron and other metals. Growth media for algae are prepared by using mixtures of these nutrients suitable for the maintenance of the algal culture.

2.6 Chlorella vulgaris for CO₂ Sequestration in a Photobioreactor

Several species of microalgae have been tested to grow in CO₂ concentration over 15% v/v (Eiichi Ono et al, 2010). Chlorella sp. is one of the most studied and researched algae for use in CO₂ sequestration. *Chlorella vulgaris* algae are unicellular from 5 to 10 micron in size (*Chlorella vulgaris*, 2010).
2.7 Purpose of this Research

In response to increasing pressure to reduce carbon emissions, fossil-fired utilities are pursuing deep geological sequestration as one of the options for handling the enormous quantities of CO$_2$ being introduced to the atmosphere. However for environmentally-sustainable mitigation strategies for carbon capture, the use of algae has become central as it also offers a potential for producing renewable transportation fuels like biodiesel. Although a good number of photobioreactors have been proposed, only a few of them can be practically used for large scale algal CO$_2$ sequestration and for that matter mass production of algae. One of the major factors that limit their practical application in algal mass cultures is mass transfer.

The purpose of this research was to test a scalable bench scale photobioreactor with a capacity to enhance the mass transfer of CO$_2$ (gas) into a *Chlorella vulgaris* algal culture (liquid) phase. To achieve this, a packed vertical column being referred to as a Packed Bubble Column Photobioreactor (PBCP) was used. It was proposed that as the liquid (algal culture) trickles downwards through the pores of the packing counter-currently to the gas (CO$_2$) flow, gas-liquid mixing and for that matter contacting surface area would be increased and this would enhance the mass transfer of the gas into the liquid phase.
Chapter 3 - Methods, Procedures and Materials

3.1 Experimental Setup and Approach

A schematic of the packed bubble column is shown in Figures 3.1 and 3.2. The bench-scaled experimental setup of the packed bubble column photobioreactor as shown in Figure 3.3 consists of a transparent polycarbonate absorption column packed with glass beads. Gas in the range of 4 – 10% CO$_2$ was obtained by mixing air (supplied from a Welch compressor and vacuum pump) with CO$_2$ from a tank (PAXAIR) in a mixing chamber (17 cm internal diameter by 10 cm height) and through rotameters to control the flow. The gas was fed at the bottom of the photobioreactor through a gas sparger which was 2 cm below the bottom of the packing. The algal culture was sprayed at 200 mL/min at the top of the column 4 cm above the tip of the packing. The culture (liquid) trickled downwards through the packing in counter-currently to the gas flowing upwards. The algal culture collects into a holding flask from which it is semi-continuously re-circulated using a mechanically actuated diaphragm (MAD) pump (Liquid Mectronics Inc. MAD Pump with a suction lift) at a flow rate of 200 mL/min. The diaphragm pump was used to minimize any stress to the algae cells. Light energy for the photosynthetic fixation of CO$_2$ by the algae was provided by a cool fluorescence light source. For the effect of gas velocity on mass transfer of CO$_2$ to the liquid phase the gas volumetric flow rate was increased from 25 to 112 mL/min at constant concentration of CO$_2$. For the effect of algal culture on CO$_2$ transfer into the algal culture, the experiment was carried out at different concentrations of algae culture (0.21 to 0.70 g/L). The inlet and outlet gas concentrations to the column were monitored using CO$_2$ Venier Gas sensors to determine steady state composition and analyzed using a Gas Chromatograph (Varian CP – 3800 Gas Chromatograph).
The algal mass concentration of the culture was determined by filtering 10 mL samples of the culture and determining the dry weight. All experiments were with 350 mL of culture at a recirculation rate of 200 mL/min. Gas samples were analyzed for CO$_2$ concentration after 45 minutes of steady state CO$_2$ concentrations. The pH was continuously monitored during the experiments using a Vernier pH sensor and it ranged from 6.8 to 7.9

<table>
<thead>
<tr>
<th>Equipment Properties.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Column Height</td>
</tr>
<tr>
<td>Packing Height</td>
</tr>
<tr>
<td>Column Diameter</td>
</tr>
<tr>
<td>Glass Bead Diameter</td>
</tr>
</tbody>
</table>

Figure 3.1: Schematic of Packed Bubble Column
Figure 3.2: Packed Bubble Column Equipment for Experiment
Figure 3.3: Packed Bubble Column Photo bioreactor for Experiment

3.2 Medium and Chemicals

The microalgae *Chlorella vulgaris* on proteose agar medium in a 25 ml screwed-cap tube was obtained from UTEX in University of Texas at Austin. This was cultured for 3 days in 10 mL of Bold 3N Medium; an artificial fresh water medium for axenic cultures in a test tube. This was transferred into a 250-mL flask and the medium made up to 50 mL and cultured for 5 days. This was further cultured in a 1-L flask with 400 mL of the medium. Table 3.1 outlines the chemical (nutrient) components in Bold 3N medium.

Preparation of 1 Liter Bold 3N Medium (UTEX):

1. To approximately 850 mL of deionized H₂O, add each of the components in the order specified (except vitamins) while stirring continuously.

2. Bring the total volume to 1 L with deionized H₂O.
3. Cover and autoclave medium (at 240°F).

4. When cooled add Vitamin B₁₂ and store at refrigerated temperature.

**Table 3.1: Chemical Components of Bold 3N Medium**

<table>
<thead>
<tr>
<th>#</th>
<th>Component</th>
<th>Amount</th>
<th>Stock Solution Concentration</th>
<th>Final Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaNO₃ (Fisher BP360-500)</td>
<td>30 mL/L</td>
<td>10 g/400 mL H₂O</td>
<td>8.82 mM</td>
</tr>
<tr>
<td>2</td>
<td>CaCl₂·2H₂O (Sigma C-3881)</td>
<td>10 mL/L</td>
<td>1 g/400 mL H₂O</td>
<td>0.17 mM</td>
</tr>
<tr>
<td>3</td>
<td>MgSO₄·7H₂O (Sigma 230391)</td>
<td>10 mL/L</td>
<td>3 g/400 mL H₂O</td>
<td>0.3 mM</td>
</tr>
<tr>
<td>4</td>
<td>K₂HPO₄ (Sigma P 3786)</td>
<td>10 mL/L</td>
<td>3 g/400 mL H₂O</td>
<td>0.43 mM</td>
</tr>
<tr>
<td>5</td>
<td>KH₂PO₄ (Sigma P 0662)</td>
<td>10 mL/L</td>
<td>7 g/400 mL H₂O</td>
<td>1.29 mM</td>
</tr>
<tr>
<td>6</td>
<td>NaCl (Fisher S271-500)</td>
<td>10 mL/L</td>
<td>1 g/400 mL H₂O</td>
<td>0.43 mM</td>
</tr>
<tr>
<td>7</td>
<td>P-IV Metal Solution</td>
<td>6 mL/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Soilwater: GR+ Medium</td>
<td>40 mL/L</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Vitamin B₁₂</td>
<td>1 mL/L</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Details of chemical composition of P-IV Metal Solution, Soilwater and Vitamin B₁₂ are presented in Tables 3.2, 3.3 and 3.4 respectively.
Preparation of 1 Liter P-IV Metal Solution:

1. To approximately 950 mL of deionized H₂O, add the nutrients in the order listed while stirring continuously. Note: The Na₂EDTA should be fully dissolved before adding other components.

2. Bring total volume to 1 L with deionized H₂O.

3. Store at refrigerator temperature.

**Table 3.2: Chemical Components of P-IV Metal Solution**

<table>
<thead>
<tr>
<th>Component</th>
<th>Amount</th>
<th>Final Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Na₂EDTA·2H₂O (Sigma ED255)</td>
<td>0.75 g/L</td>
<td>2 mM</td>
</tr>
<tr>
<td>2 FeCl₃·6H₂O (Sigma 1513)</td>
<td>0.097 g/L</td>
<td>0.36 mM</td>
</tr>
<tr>
<td>3 MnCl₂·4H₂O (Baker 2540)</td>
<td>0.041 g/L</td>
<td>0.21 mM</td>
</tr>
<tr>
<td>4 ZnCl₂ (Sigma Z-0152)</td>
<td>0.005 g/L</td>
<td>0.037 mM</td>
</tr>
<tr>
<td>5 CoCl₂·6H₂O (Sigma C-3169)</td>
<td>0.002 g/L</td>
<td>0.0084 mM</td>
</tr>
<tr>
<td>6 Na₂MoO₄·2H₂O (J.T. Baker 3764)</td>
<td>0.004 g/L</td>
<td>0.017 mM</td>
</tr>
</tbody>
</table>

Preparation of 200 mL Soilwater: GR + Medium:

1. Combine all components listed.

2. Cover the medium container and steam for 2 consecutive days, 3 hours on each day.

   Pasteurization is a gradual rising of temperature to approximately 95°C in 15 minutes.
Then increase the temperature to just over 98°C for the 3 hour duration. Cooling occurs gradually at room temperature.

**Table 3.3: Chemical Components Soilwater**

<table>
<thead>
<tr>
<th>#</th>
<th>Component</th>
<th>Amount</th>
<th>Final Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Green House Soil</td>
<td>1 tsp/200 mL H₂O</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>CaCO₃ (optional) (Fisher C 64)</td>
<td>1 mg/200 mL H₂O</td>
<td>0.05 mM</td>
</tr>
</tbody>
</table>

**Preparation of 200mL Vitamin B₁₂**

1. Prepare 200 mL of HEPES buffer (50 mM)

2. Adjust the pH to 7.8

3. Add Vitamin B₁₂ (0.1 mM) wait until fully dissolved

4. Sterilize using a 0.45 µm Millipore filter. Store in dark at freezer temperature.

**Table 3.4: Chemical Components of Vitamin B₁₂**

<table>
<thead>
<tr>
<th>#</th>
<th>Component</th>
<th>Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HEPES buffer pH 7.8 (Sigma H-3375)</td>
<td>2.4 g/200 mL dH₂O</td>
</tr>
<tr>
<td>2</td>
<td>Vitamin B₁₂ (cyanocobalamin, Sigma V-6629)</td>
<td>0.027 g/200 mL dH₂O</td>
</tr>
</tbody>
</table>
Chapter 4 - Results and Discussion

4.1 Material Balance on CO₂

Based on the assumption that the molecules of a gas experience no intermolecular forces and that
the molecules occupy no volume, the ideal gas law (PV = nRT) gives an accurate description of
the behavior of real gases at low pressure and temperatures. At room conditions of 25°C (298K)
and atmospheric pressure of 1 atmosphere at which the experiment was carried out, the molar
volume, \( V_m \) is given by Equation (1) below, where \( R \) is the ideal gas constant.
\( R = 0.08206 \text{ L.atm. K}^{-1} \text{ mol}^{-1} \).

\[
V_m = \frac{RT}{P} = 24.465 \text{ L/mole} 
\]

(Eqn. 1)

The moles of CO₂ transferred, \( N \) (mol/min) is given by:

\[
N = G_1 y_{CO_2,1} - G_2 y_{CO_2,2} 
\]

(Eqn. 2)

Where:

\( G_1 y_{CO_2,1} \) = Moles of CO₂ in the inlet gas stream, (mol/min)

\( G_2 y_{CO_2,2} \) = Moles of CO₂ in outlet gas stream, (mol/min)

\( y_{CO_2,1} \) = Mole fraction of CO₂ in the inlet gas stream

\( y_{CO_2,2} \) = Mole fraction of CO₂ in the outlet gas stream

\( G_1 \) = Molar flow rate of inlet gas, (mol/min) given by:

\[
G_1 = \frac{F_1}{V_m} 
\]

(Eqn. 3)

Where:

\( F_1 \) = Flow rate of inlet gas, (mL/min)

\( G_2 \) = Molar flow rate of outlet gas, (mol/min) given by:
\[ G_2 = \frac{G_1(1 - y_{CO_2,1})}{1 - y_{CO_2,2}} \]  
(Eqn. 4)

4.2 Experimental Results

4.2.1 Gas flow rate versus outlet CO\(_2\) concentration

Tables 4.1 and 4.2 list the data collected for experiments where the total inlet gas flow, the inlet carbon dioxide composition and the algal concentration were varied.

Table 4.1: Results of varying inlet CO\(_2\) gas flow rate and corresponding outlet CO\(_2\) gas concentration at algal concentration of 0.21 g/l and flow rate of 200 mL/min.

<table>
<thead>
<tr>
<th>Inlet Gas Stream</th>
<th>Concentration of CO(_2) (Mol %)</th>
<th>CO(_2) Molar Flow rate (\times 10^{-3}) (mol/min)</th>
<th>Outlet Gas Stream</th>
<th>Concentration of CO(_2) (mol %)</th>
<th>CO(_2) Transferred %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Rate (mL/min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>5.31</td>
<td>0.05</td>
<td></td>
<td>3.62</td>
<td>33.03</td>
</tr>
<tr>
<td>50</td>
<td>5.16</td>
<td>0.11</td>
<td></td>
<td>4.13</td>
<td>20.90</td>
</tr>
<tr>
<td>50</td>
<td>4.58</td>
<td>0.09</td>
<td></td>
<td>3.98</td>
<td>13.63</td>
</tr>
<tr>
<td>67</td>
<td>4.56</td>
<td>0.12</td>
<td></td>
<td>3.87</td>
<td>15.64</td>
</tr>
<tr>
<td>112</td>
<td>11.98</td>
<td>0.55</td>
<td></td>
<td>12.10</td>
<td>-</td>
</tr>
<tr>
<td>25</td>
<td>14.03</td>
<td>0.15</td>
<td></td>
<td>11.22</td>
<td>22.53</td>
</tr>
<tr>
<td>37</td>
<td>16.98</td>
<td>0.26</td>
<td></td>
<td>13.10</td>
<td>26.32</td>
</tr>
<tr>
<td>50</td>
<td>15.81</td>
<td>0.32</td>
<td></td>
<td>13.32</td>
<td>18.15</td>
</tr>
<tr>
<td>67</td>
<td>12.63</td>
<td>0.35</td>
<td></td>
<td>13.11</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.2: Results of varying inlet CO\(_2\) gas flow rate and corresponding outlet CO\(_2\) gas concentration at algal concentration of 0.35 g/L and flow rate of 200 mL/min.

<table>
<thead>
<tr>
<th>Inlet Gas Stream</th>
<th>Concentration of CO(_2) (Mol %)</th>
<th>CO(_2) Molar Flow rate (\times 10^{-3}) (mol/min)</th>
<th>Outlet Gas Stream</th>
<th>Concentration of CO(_2) (mol %)</th>
<th>CO(_2) Transferred %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Rate (mL/min)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>9.45</td>
<td>0.10</td>
<td></td>
<td>4.15</td>
<td>58.53</td>
</tr>
<tr>
<td>37</td>
<td>8.08</td>
<td>0.12</td>
<td></td>
<td>5.87</td>
<td>29.08</td>
</tr>
<tr>
<td>50</td>
<td>10.11</td>
<td>0.21</td>
<td></td>
<td>7.68</td>
<td>26.07</td>
</tr>
<tr>
<td>67</td>
<td>10.53</td>
<td>0.29</td>
<td></td>
<td>10.04</td>
<td>5.18</td>
</tr>
<tr>
<td>37</td>
<td>7.6</td>
<td>0.11</td>
<td></td>
<td>6.72</td>
<td>12.38</td>
</tr>
<tr>
<td>50</td>
<td>9.62</td>
<td>0.20</td>
<td></td>
<td>7.30</td>
<td>25.98</td>
</tr>
<tr>
<td>67</td>
<td>9.66</td>
<td>0.26</td>
<td></td>
<td>8.41</td>
<td>14.10</td>
</tr>
<tr>
<td>89</td>
<td>9.02</td>
<td>0.33</td>
<td></td>
<td>8.75</td>
<td>3.27</td>
</tr>
<tr>
<td>112</td>
<td>9.46</td>
<td>0.43</td>
<td></td>
<td>8.97</td>
<td>5.75</td>
</tr>
</tbody>
</table>
Molar Inlet CO\textsubscript{2} flow rate vs. outlet CO\textsubscript{2} Concentration

![Graph showing the relationship between molar inlet CO\textsubscript{2} flow rate and outlet CO\textsubscript{2} concentration for different algal culture concentrations.]

Figure 4.1: Molar CO\textsubscript{2} flow rate effect on outlet CO\textsubscript{2} concentration at different algal culture concentrations and CO\textsubscript{2} inlet compositions.

4.2.2 Gas flow rate versus Moles of CO\textsubscript{2} Transferred

Experimental data on effect of moles of CO\textsubscript{2} fed to the reactor on the moles of CO\textsubscript{2} transferred into culture was investigated at constant inlet CO\textsubscript{2} concentration and algal culture concentrations are presented in Table 4.3 and Table 4.4 and relations in Figures 4.2 and 4.3.

Table 4.3: Result of varying inlet gas flow rate at algal Concentration of 0.21 g/L and inlet CO\textsubscript{2} concentration of 5.0 mol%  

<table>
<thead>
<tr>
<th>Inlet Gas Stream</th>
<th>Outlet Gas Stream</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Flow Rate (mL/min)</td>
</tr>
<tr>
<td></td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>67</td>
</tr>
</tbody>
</table>
Table 4.4: Result of varying inlet gas flow rate at algal Concentration of 0.21 g/L and inlet CO₂ concentration of 9.5 mol%  

<table>
<thead>
<tr>
<th>Inlet Gas Stream</th>
<th>Outlet Gas Stream</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Rate (mL/min)</td>
<td>Concentration of CO₂ (Mol %)</td>
</tr>
<tr>
<td>50</td>
<td>9.62</td>
</tr>
<tr>
<td>67</td>
<td>9.66</td>
</tr>
<tr>
<td>112</td>
<td>9.46</td>
</tr>
</tbody>
</table>

Inlet Gas flow rate vs. Moles of CO₂ Transferred at  
Different CO₂ mol% Concentrations

Figure 4.2: Gas flow rate effect on moles of CO₂ transferred at different inlet CO₂ concentrations
Inlet Gas flow rate vs. Moles of CO$_2$ Transferred at Different Culture Concentrations

![Graph showing the relationship between inlet gas flow rate and moles of CO$_2$ transferred at different culture concentrations.]

**Figure 4.3:** Gas flow rate effect on outlet CO$_2$ concentration at different alga culture concentrations at 5% CO$_2$ inlet composition.

### 4.2.3 Gas flow rate versus Moles of CO$_2$ Transferred

Figure 4.4 (obtained from data on Table 4.1 and 4.2) presents the relation between molar flow rate of CO$_2$ into the reactor and the CO$_2$ transferred at 0.21 and 0.35g/L of culture.
4.3 Discussion of Results

Figure 4.1 indicated a general trend of increase in CO₂ composition in the outlet gas from the reactor when increasing the molar rate of CO₂ into the reactor. Algal concentration at 0.35 g/L showed lower concentration of CO₂ in outlet gas than at 0.21 g/L. This was confirmed in Figure 4.3 where at the same inlet concentration of 5% CO₂ more moles of CO₂ were transferred at higher concentration (0.35 g/L) of culture. Figure 4.2 shows that at same culture concentration, more moles of CO₂ were transferred at higher composition (9.5%) of inlet CO₂ compared to
5.0%. The moles of CO$_2$ transferred with culture at 0.21 g/L and 5% inlet CO$_2$ composition in Figures 4.2 and 4.3 show an increasing trend of CO$_2$ transferred at lower feed rates, after which further increase in inlet gas flow rate results in decreasing the moles of CO$_2$ transferred. This trend is replicated in Figure 4.1 for cultures at 0.21 and 0.35 g/L.

Figure 4.4 shows a general trend that higher percentages of carbon dioxide are absorbed at lower inlet molar flow rates of carbon dioxide. Reductions of carbon dioxide greater than 30% are achievable, which warrants further study for this style of reactor.
Chapter 5 – Conclusion and Recommendation

Overall, this is an initial attempt in testing the dynamics of the mass transfer of CO₂ with this Packed Bubble Column Photobioreactor using *Chlorella vulgaris* microalgae. The results have shown that the PBCP is able to substantially enhance the transfer of CO₂, typically in a range of 10 to 30% into *Chlorella vulgaris* culture at 0.21 and 0.35 g/L. Further study should entail the following:

1. Increasing the reactor length and diameter to determine the influence of holdup time and gas velocity on the mass transfer of carbon dioxide.

2. Control of light source to understand the photo-inhibition effect on carbon dioxide uptake.

3. Increasing the algal concentration further for enhance mass transfer and to determine whether the system is controlled by carbon dioxide metabolism or mass transfer resistance.

4. Long term study on algal viability and nutrient requirements.

5. Analysis of the algae composition to determine if biofuel precursors are formed.

6. Application of appropriate models to determine scale-up requirements.
References


Kaarstad O., 2002. Geological storage including costs and risks, in saline aquifers, Proceedings of workshop on Carbon Dioxide Capture and Storage. Regina, Canada


UTEX, The Culture Collection of Algae at the University of Texas at Autin