

The Effectiveness of Hollow Fibre Membranes in Transferring Flue Gas into Microalgal Culture for Sequestration Purposes

by

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Submitted in partial fulfilment of the requirements  
for the degree of Master of Applied Science

at

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DALHOUSIE UNIVERSITY

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## ABSTRACT

Efficient gas transfer remains a technical limitation for microalgal sequestration of greenhouse gases. Hollow fibre membranes (HFM) have been shown by previous researchers to provide high mass transfer efficiency of CO<sub>2</sub> gas into solution. The effectiveness of these membranes in transferring CO<sub>2</sub> and NO<sub>x</sub> to microalgal cultures in terms of gas sequestration versus standard sparging has not been completely studied however which is the aim of this research.

Microalgal cultures were grown separately using a HFM and a standard bubble diffuser with both 100% CO<sub>2</sub> and 24% CO<sub>2</sub>/350 ppm NO<sub>x</sub> flue gas mixtures to test the effects that the gas transfer method might have on algal production and sequestration capabilities. Gas flow to the cultures was recorded and algal biomass was analyzed for carbon and nitrogen content to determine sequestration efficiency.

HFM cultures showed slightly improved CO<sub>2</sub> gas sequestration at the end of growth. Nitrogen fraction in algal biomass was nearly double in the HFM culture to the diffuser when cultivated with NO<sub>x</sub> gas meaning higher NO<sub>x</sub> sequestration.

## LIST OF ABBREVIATIONS AND SYMBOLS USED

HFM	Hollow Fibre Membrane
SGR	Specific Growth Rate
CO <sub>2</sub> e	Equivalent Carbon Dioxide
K	Mass Transfer Coefficient
K <sub>a</sub>	Volumetric Coefficient
$\Delta P$	Breakthrough Pressure
$\sigma$	Surface Tension of Wetting Fluid
$\theta$	Contact Angle of Wetting Fluid with Micro-pores
r	Average Radius of Micro-pore
C*	Saturation Concentration of Carbon Dioxide
C	Concentration of Carbon Dioxide at time (t)
A	Interfacial Surface Area for Mass Transfer
V	Volume of Tank for Mass Transfer

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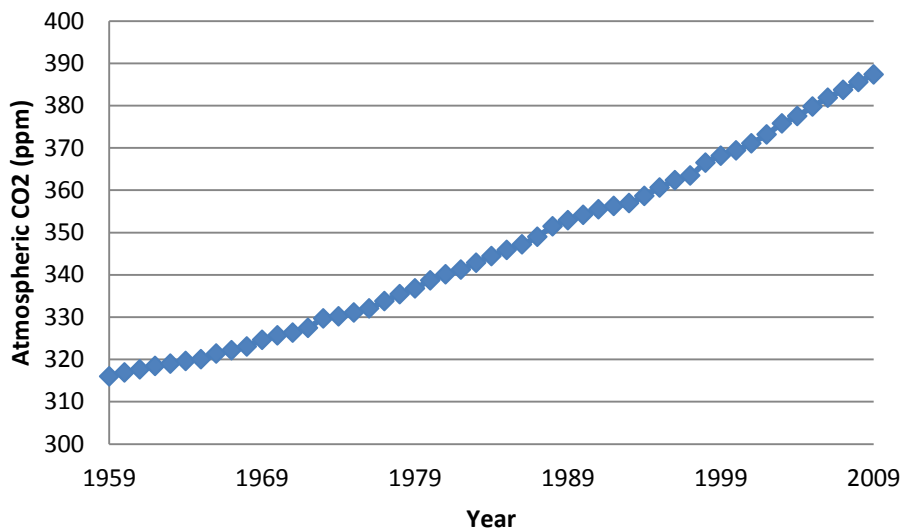
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## Chapter 1: Introduction

The combustion of millions of years of stored fossil energy over the past two centuries has resulted in the emission of billions of tonnes of carbon dioxide into the environment, and its ability to retain heat radiation in the atmosphere has been the single largest contributor to anthropogenic climate change (IPCC, 2007; U.S. Department of Energy, 2004). It is now no longer possible to ignore the effects of carbon dioxide emissions on the atmosphere as the increasing acidification of the ocean, accelerated melting of glaciers, snow and ice packs, and a rising global average sea level are becoming more pronounced (IPCC, 2007; World Meteorological Organization, 2011). Figure 1-1 shows the rising average annual atmospheric CO<sub>2</sub> levels observed at the Mauna Loa Observatory in Hawaii since 1959.



**Figure 1-1: Atmospheric CO<sub>2</sub> concentration (Tans, 2010)**

With international summits such as Kyoto (1997), Copenhagen (2009), and Cancun (2010) convened in the hopes of drafting carbon limitation policies for governments to uphold, it is clear that carbon pollution is a relevant and important environmental issue facing the world today. The IPCC Special Report on Emissions Scenarios projects that based on current climate change mitigation strategies, an increase in global greenhouse

gas emissions (CO<sub>2</sub>e) of up to 30% over year 2000 levels is projected by the year 2030 (IPCC, 2007).

Three options for limiting and reducing CO<sub>2</sub> concentrations in the atmosphere have been proposed: reducing demand for carbon intensive energy sources by increasing energy efficiency, replacing current fossil fuel sources with less carbon intensive ones, and restricting carbon emissions through sequestration (White, Strazisar, Granite, Hoffman, & Pennline, 2003; Hughes, 2009). The very effects of climate change could cause difficulty in implementing new energy production that is less carbon intensive such as hydroelectricity as the reduced ice packs from higher temperatures carried into the spring months may not provide as much power as originally planned (Hughes & Chaudhry, 2010). Similar with nuclear power, its use of rivers for cooling could be a detriment to its expansion in Canada as a less intensive carbon energy source (Hughes & Chaudhry, 2010).

These issues relate back to the overall problem of energy security facing the exponentially increasing population of the 21<sup>st</sup> century. Despite North America's immense energy wealth with domestic sources such as coal, hydro, oil, and nuclear power providing energy to its inhabitants, the dwindling supply of crude oil in the United States and its commitment to avoiding Middle Eastern supply in favour of the comparatively higher carbon costs of producing oil from Western Canadian tar sands (where 60% of production is exported to the U.S.A. through NAFTA agreements) could further escalate carbon pollution (Hughes, 2011). New energy security policy installed in the US to offset oil demand such as the Energy Independence and Security Act could also have unintended effects as it calls for increased production of electrically powered vehicles, amongst other stipulations. As approximately 50% of electricity in the United States is produced from domestic coal, a shift from an oil powered economy to an electric future could further increase carbon pollution and would necessitate a greater focus into mitigating this excess pollution before it results in more pronounced climate change (Hughes, 2011).

## 1.1 Carbon Sequestration

If emissions reduction is to be accomplished through sequestration, total carbon storage could reach more than 600 Gt during the 21<sup>st</sup> century, based on projected emissions (Lackner, 2003). Due to the large volume of carbon emissions projected for the 21<sup>st</sup> century, most natural forms of carbon sequestration are rendered irrelevant as they do not have the capacity and storage time to retain such high volumes of carbon; these include forests, peat bogs, and the ocean's capacity for absorbing carbonic acid (Lackner, 2003). In fact, average ocean surface pH has dropped 0.1 pH units from pre-industrial times and is expected to decrease a further 0.3-0.4 pH units before the end of this century (Fabry, Seibel, Feely, & Orr, 2008). This has implications for the marine biota as the excess CO<sub>2</sub> reduces the fraction of carbonate ions present in seawater which are required for some marine life in calcification including crustaceans, mollusks, and corals (Fabry, Seibel, Feely, & Orr, 2008).

Geological sequestration of carbon dioxide is accomplished by storing the gas inside geological cavities underground. While there are many forms of suitable geological formations for this application including basins, depleted oil fields, deep coal seams and saline aquifers, the uncertainty in storage lifetimes and security in terms of seismic instability within the sequestered area raise cause for concern (Solomon, 2007).

Adsorbent materials such as LiOH neutralize carbon into carbonates and bicarbonates and are a safe, long term storage option however the adsorbent materials used are expensive, generally non-renewable, and require significant space for storage (Kumar, et al., 2010). For these reasons, enhanced biological sequestration of CO<sub>2</sub> is one potentially feasible, long term solution to carbon sequestration currently being considered by some as an efficient means of mitigating carbon pollution (Kumar, et al., 2010; Huntley & Redalje, 2007).

Biological sequestration of CO<sub>2</sub> through photosynthetic organisms such as microalgae is one such option where the CO<sub>2</sub> emitted from flue gas stacks from stationary industrial

operations such as coal fired power plants and cement factories can be fixed by the autotrophic organisms. Here, inorganic carbon is converted into organic material using energy from light to drive the process. Due to algae being composed of approximately 45-50% carbon, this element is very important to maintain cell growth. Theoretically, 1.65g-1.83g of CO<sub>2</sub> is therefore required for every gram (dry weight) of algal biomass (Doucha, Straka, & Livansky, 2005). This form of sequestration is considered by some to be the most promising of all biological mitigation strategies (Huntley & Redalje, 2007).

For biological sequestration employing microalgae to become a feasible option, it will have to be economically viable. Microalgae have multiple end-use streams for the energy sector including straight combustion of the biomass (having roughly equal energy content to sub-bituminous coal (Pond Biofuels, 2010)) or as a feedstock for biodiesel fuel produced from its fatty acid content (Huntley & Redalje, 2007). Anaerobic digestion of the algae can produce methane gas (Vergara-Fernandez, Vargas, Alarcon, & Velasco, 2008) and fermentation can produce ethanol. Any of the above mentioned energy pathways will again emit carbon into the atmosphere once the energy source is combusted so they are technically better described as carbon recycling options over permanent sequestration. Microalgae also produce valuable commodities in the nutraceutical industry; for instance *Chlorella* is a high protein supplement (Becker, 1994) while strains of *Dunaliella* produce a  $\beta$ -carotene extract (Ben-Amotz & Avron, 1983). Further reduction to sequestration costs could be accomplished by coupling algae culturing with waste water treatment (Ono & Cuello, 2003). Algal culturing is an expensive process; however, with such valuable compounds produced from this biomass, the revenue from these high value products could pay for the cost of carbon sequestration (Olaizola, 2003; Ono & Cuello, 2003). With thousands of algae strains currently catalogued and studied, specific algal cultures can be grown with CO<sub>2</sub> for a target product based on their macronutrient content and biological properties. Of course, the process of carbon sequestration itself could be the most economic solution if carbon credit systems are to be installed across Canada such as that already in effect in the province of British Columbia.

One of the challenges associated with sequestration of CO<sub>2</sub> via microalgae in an industrial setting is finding an efficient method of transferring gas into algal solution (Kumar, et al., 2010). Traditionally, CO<sub>2</sub> enriched air has been bubbled into solution through a sparger (essentially spraying gas through an aperture into solution); however, this method results in poor overall gas transfer as well as low retention of gas in solution (Fan L. , Zhang, Zhang, & Chen, 2008). Hollow-fibre membranes are a relatively new method of introducing gas into solution that are being studied for their effectiveness in this type of application. With this technology, gas is passed through micro-porous hollow-fibres, where it diffuses into solution through the micro-pores assuming a concentration gradient exists at the gas-liquid interface. The improved gas transfer rate over sparging owes to a higher interfacial surface area for transfer to occur (Carvalho & Malcata, 2001). Moreover, hollow-fibre membranes do not impart any selectivity towards species being diffused across it (Gabelman & Hwang, 1999) which can allow dissolved oxygen build up inside culture (which can become photosynthetically inhibiting) to diffuse back across the membrane and bubble out to the surface (Kumar, et al., 2010).

## **1.2 Flue Gas Substrate Sequestration**

One of the advantages to biological sequestration of CO<sub>2</sub> via microalgae is the added benefit of retaining additional gases emitted with CO<sub>2</sub> from flue gas emitted from stationary operations such as coal-fired power plants, cement factories, and paper mills. These operations produce flue gases composed of H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>, SO<sub>2</sub>, NO, and NO<sub>2</sub>. As NO and NO<sub>2</sub> are almost always present with one another, they are collectively known as NO<sub>x</sub>. The exact composition of the flue gas depends on the material that is being combusted for the specific operation. Table 1-1 shows flue gas compositions for various operations in Canada.



**Table 1-1: Annual flue gas emissions by industry in Canada (kt) (Environment Canada, 2008)**

Industry	CO <sub>2</sub>	NO <sub>x</sub>	SO <sub>2</sub>
Electricity Generation	118,000	227	430
Petroleum Refining	65,300	472	372
Steel Refining	6,110	13	27
Pulp and Paper	4,280	34	41
Cement	4,270	38	31

NO<sub>x</sub> and SO<sub>2</sub> are primary components of acid rain and cause the primary nutritional elements for plant life (such as calcium, magnesium, and potassium) in soil to displace further underground due to the addition of hydrogen ions in a process called leaching (Ophardt, 2003). The displaced nutrients cause the surrounding plant life greater difficulty in continued health and growth. As an example, the province of Nova Scotia is particularly susceptible to acid deposition due to the low buffering capacity and neutralization ability of its land and water ecosystems (N.S. Dept. of the Environment, 2010).

Research by several authors show that microalgae have a tolerance for both NO<sub>x</sub> and SO<sub>x</sub> (Maeda, Owada, Kimura, Omata, & Karube, 1995; Yoshihara, Nagase, Eguchi, Hirata, & Miyamoto, 1996; Matsumoto, et al., 1995), and some species can even utilize the NO<sub>x</sub> emissions as a nitrogen source for protein synthesis (Nagase, et al., 2001). Microalgae could therefore be used for carbon dioxide and nitric oxides sequestration.

Using hollow-fibre membranes for acid gas capture is a promising alternative to conventional gas absorption systems currently employed to retain NO<sub>x</sub> and SO<sub>2</sub> (Mansourizadeh & Ismail, 2009), as research shows that membrane contactors are significantly more efficient than absorption towers for acid gas removal applications (Mavroudi, Kaldis, & Sakellaropolous, 2003). Conventional methods used in industry for acid gas capture include packed towers, spray towers, scrubbers and bubble columns which all disperse the gas phase in liquid to achieve large contact area between phases thereby increasing mass transfer ability. The drawbacks to these systems include great

difficulty in obtaining accurate mass transfer area and limitations in the gas and liquid flow rates due to operational problems brought on by dispersion of phases (Mansourizadeh & Ismail, 2009).

### **1.3 Objectives**

Previous research has focused on the capability of microalgae to retain flue gas substrate such as CO<sub>2</sub> and NO<sub>x</sub> when bubbled into culture inefficiently (Nagase, et al., 1997; Fan L. , Zhang, Cheng, Zhang, Tang, & Chen, 2007). However, there appears to be little work detailing how the efficiency in flue gas fixing by microalgae will be affected when gas is transferred into culture via hollow-fibre membranes, as there will be less gas lost to the atmosphere and the greater contact area between algae and dissolved gas could allow for greater fixing of the gases by the algae.

The objective of this thesis is to determine the effectiveness of a hollow-fibre membrane for the purpose of flue gas sequestration via microalgae. To meet this objective, the research will model the mass transfer behaviour of gas diffusion through the membrane device and compare the mass transfer coefficients for CO<sub>2</sub> being diffused through the membrane into water with that of industry standard sparging. The effects of using a hollow-fibre membrane on flue gas removal rate by algae and its effect on algae productivity will also be examined. The relevance of this research is directly related to the feasibility of using algae as a potential flue gas store as this method of sequestration should be able to accommodate large quantities of flue gas in an efficient manner (i.e., without gas lost to the atmosphere during transfer) in order to be an effective way of storing industrial effluent.

### **1.4 Organization**

This research thesis is organized as follows. Chapter 2 gives a detailed literature review of recent and related research done with hollow-fibre membranes and flue gas retention in algal culture. A description of the methods used to test these membranes for mass transfer efficiency as well as flue gas retention in algal culture is described in Chapter 3, while Chapter 4 analyzes the results and comes to conclusions about the

efficacy by which the membrane is capable of sequestering flue gas. Chapter 5 will conclude the thesis with a summary of results and potential future research in this area.

## Chapter 2: Literature Review

This chapter provides a detailed review of the research that has been conducted into the areas of mass transfer modeling of CO<sub>2</sub> diffused into solution through hollow-fibre membrane technology as well as the literature published that has studied the capability of microalgae in retaining flue gas substrate. Further emphasis in the literature review is placed on algal culturing technique and selection of microalgal cultures best suited towards flue gas sequestration.

### 2.1 Hollow-fibre Membranes

Efficient gas transfer is of critical importance to both maintaining healthy algal culture as well as ensuring maximum retention of transferred gas into solution for sequestration purposes (Kumar, et al., 2010). Presently, there are several ways of transferring gas into culture solution and they are listed in Table 2-1.

**Table 2-1:** Gas transfer methods for algae culturing (Kumar, et al., 2010)

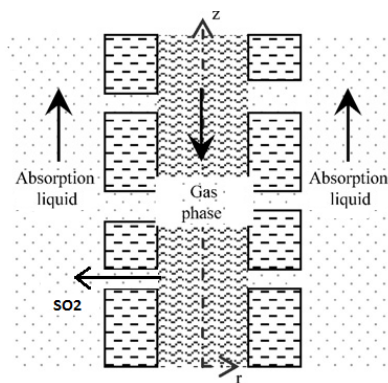
Process	Gas Transfer	Mixing	Scale-up
Hollow-fibre	Very good	Uniform	Medium
Bubble column	Fair to good	Uniform	Medium
Surface aeration	Poor	Poor	Difficult
Air lift	Fair to good	Uniform	Medium

This table gives the quality of gas transfer, mixing, and scale-up feasibility for multiple gas transfer techniques employed in algal culture. It shows that hollow-fibre membrane transfer exhibits the best gas transfer as well as uniform mixing of solution for algal cultures which is an important feature to ensure no gradient of nutrient and dissolved gas occurs within solution. Although gas injection (such as in bubble columns and air-lift reactors) is still the most common approach to gas transfer in algae culturing, hollow-fibre membranes are thought by several authors to be a promising development in CO<sub>2</sub> and flue gas sequestration by algae (Fan L. , Zhang, Zhang, & Chen, 2008; Carvalho & Malcata, 2001; Kumar, et al., 2010).

Scale-up with hollow-fibre membranes is more straightforward than with absorption towers as membranes normally scale linearly, so a predictable increase in desired capacity is achieved by simply adding an adequate amount of membrane modules to the operation (Gabelman & Hwang, 1999).

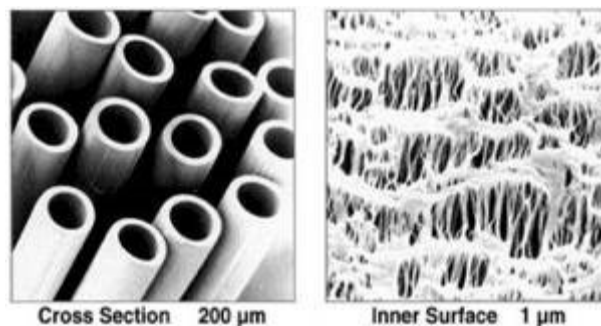
The principle behind hollow-fibre membranes for use in gas absorption involves a gas stream being directed through the fibres where it diffuses through micro-pores along the fibres into an absorbent. The two phases remain un-dispersed in one another assuming proper selection of membrane material coupled with polarity of solvent (i.e., hydrophobic or hydrophilic) has been performed (Feron & Jansen, 1995).

Hollow-fibre membranes used in gas absorption applications can operate in two modes; wetted and dry mode. Wetted mode is in effect when the pores of the fibres are filled with liquid as in such applications where the liquid phase is aqueous and the membrane is hydrophilic. Dry mode is when the micro-pores are filled with gas and the solvent is immobilized outside the membrane pores (Gabelman & Hwang, 1999). Several authors have shown that dry mode operation offers an effective diffusivity of gas into solution several orders of magnitude higher than when operated in wet mode (Mavroudi, Kaldis, & Sakellaropolous, 2003; Yan, et al., 2007). Figure 2-1 shows basic operation principle behind hollow fibre membranes.



**Figure 2-1:** Hollow-fibre membrane diffusing SO<sub>2</sub> into absorption liquid (Luis, Garea, & Irbien, 2009)

Hollow-fibre micro-porous membranes deployed in algal culture benefit from being constructed of a hydrophobic material where the membrane will operate in dry mode, thereby ensuring that the solvent (i.e., water) will remain immobilized at the mouth of the micro-pores and will not become dispersed inside the fibres (Gabelman & Hwang, 1999). This allows the gas flowing through the hollow-fibres inside the gas transfer unit to operate at a lower pressure than the surrounding liquid phase, which results in a no bubble diffusion of gas into liquid (Fereira, Fernandes, Reis, & Mateus, 1998). With no bubble transfer, the retention of the gas in liquid will be greater than with more traditional sparging systems and there will be a decrease in gas lost to the atmosphere (Fereira, Fernandes, Reis, & Mateus, 1998). Figure 2-2 displays the magnified hollow-fibres bundled together at left and the micro-porous surface area of the hollow-fibres at right for the unit model that will be used in this research.



**Figure 2-2:** Hollow-fibres and microporous surface area of fibres (0.25 m<sup>2</sup> total surface area)  
(inVentures Technologies, 2007)

Gabelman et al (1999) reviewed the state of the art in hollow-fibre membrane technology and came to further conclusions of its advantages over traditional mass transfer contacting equipment such as a bubble column, including:

- Available surface area for contact between fluids remains undisturbed at both high and low flow rates as the fluid flows are independent. This is beneficial for applications where the solvent/feed ratio is required to be low or high (contacting towers have the propensity to flood at high flow ratios and unload at low ratios).

- Modular design allows hollow-fibre membrane devices to be employed in a wide range of capacities by using few or many modules.
- Substantially higher efficiency is achieved with membrane contactors over dispersive contactors (based on Height of Transfer Unit).

## 2.2 Mass Transfer

Previous research conducted into optimizing the operating conditions of gas transfer membranes conclude that a low gas flow coupled with high counter current liquid flow results in the best mass transfer based on mass transfer coefficients (Carvalho & Malcata, 2001; Fan L. , Zhang, Cheng, Zhang, Tang, & Chen, 2007). When the liquid flow is perpendicular to the micropores, both the overall mass transfer coefficient and the efficiency of gas transfer are increased (Fereira, Fernandes, Reis, & Mateus, 1998). Mass transfer coefficients that have been determined for CO<sub>2</sub> being diffused into liquid through membrane configurations of varying surface area and construction material are displayed in Table 2-2. It is important to note that Carvalho et al. and Fereira et al. used NaOH as a solvent to increase CO<sub>2</sub> mass transfer in their experiments while Kumar et al. (2010) used a wastewater solution for the purposes of their study.

**Table 2-2:** Optimized CO<sub>2</sub> mass transfer coefficients from different hollow-fibre membrane studies

Construction Material	Ka (s <sup>-1</sup> )	K (m/s)	A (m <sup>2</sup> )	Pore Diameter (μm)	Mode	Reference
Polypropylene	0.0148	1.45E-07	1.7	0.2	Dry	Carvalho et al. (2001)
Polysulfone	0.0133	1.59E-06	0.14	0.2	Wet	Carvalho et al. (2001)
Polypropylene	0.0075	2.64E-05	0.00238	0.2	Dry	Fereira et al. (1998)
Polyolefin, polyurethane	0.0682	5.60E-06	0.1	--	Dry	Kumar et al. (2010)

The overall mass transfer coefficient, 'K' (m/s), describes the diffusion rate as a function of the mass transfer rate, mass transfer area, and the concentration gradient driving force. With this it is assumed that the bulk solution is well mixed except at the gas-liquid interface, therefore it is sometimes referred to as a lumped parameter model (Cussler, 2009). It is used to quantify the mass transfer (i.e., diffusion) between phases and has

been used in previous hollow-fibre membrane studies as a benchmark for the particular membrane in its diffusion capability with CO<sub>2</sub>. 'Ka' (s<sup>-1</sup>) is the overall volumetric coefficient and takes into account the interfacial surface area to volume ratio of the diffuser. The total interfacial surface area available for transfer is denoted by 'A' (m<sup>2</sup>).

It would seem logical to assume that the interfacial area of the membrane is equal to the total surface area multiplied by the porosity, however due to the thin liquid boundary layer uniformly spread across the interface that exhibits the highest resistance to mass transfer, the used mass transfer area is actually equal to the entire surface area (Ferreira, Fernandes, Reis, & Mateus, 1998).

Similar findings were discussed in more detail in another study (Kreulen, Smolers, Versteeg, & van Swaaji, 1993). In this case, an experiment was performed where the mass transfer coefficients determined experimentally for a CO<sub>2</sub> absorption system for both polypropylene and polysulfone fibres agreed with the theoretical mass transfer coefficients predicted from their model when the total membrane surface area was used as the active transfer area.

Carvalho et al. (2001) determined that when the optimized mass transfer coefficients for two different hollow-fibre membranes were compared with that of a sparging unit with a total available interfacial surface area an order of magnitude less, the sparger showed higher diffusion efficiency in terms of mass transfer coefficients. It was concluded that the localized turbulent conditions occurring where the bubble formed diminished the laminar boundary layer of gas at the gas-liquid interface, which reduced the largest resistance of gas transfer to the bulk liquid resulting in an increased mass transfer coefficient.

The hollow-fibre membranes are generally designed so that a high mass transfer area to equipment volume ratio is achieved, which means fibres are small in diameter (Ferreira, Fernandes, Reis, & Mateus, 1998). With such restricted flow, the fibres must operate with a lower pressure inside so as not to exceed breakthrough pressure of the fibres. Therefore, the flux of gas through the fibres is much smaller than with sparging and a



thicker boundary layer will exist at the interface, causing a larger resistance to transfer compared with sparging. However, when comparing the volumetric mass transfer coefficients ( $K_a$ ) which take into account interfacial surface area, the hollow-fibre membranes expectedly surpassed the transfer efficiency of the sparger showing that the hollow-fibre membranes owe their higher transfer rates to their large interfacial surface areas.

Further consideration has to be given to breakthrough pressure of fibres when in operation. This is the minimum pressure required to force water through the largest opening of a hydrophobic membrane (Gabelman & Hwang, 1999; Gore Creative Technologies Worldwide, 2011). The breakthrough pressure is described by Equation (1).

$$\Delta P = (2 \sigma \cos\theta)/r \quad (1)$$

Where  $\Delta P$  is the pressure difference between gas and liquid (i.e. breakthrough pressure),  $\sigma$  is the surface tension of liquid contacting the membrane,  $\theta$  is the contact angle between liquid and membrane micro-pores, and  $r$  is the average radius of micro-pore. From Equation (1) it can be observed that decreasing surface tension of liquid immersed in membrane pores will decrease breakthrough pressure, which is an undesirable consequence. Therefore it is important to ensure the system is free of any surfactants that may decrease solvent surface tension in the immediate vicinity of the membrane micro-pores (Gabelman & Hwang, 1999).

### **2.3 Mass Transfer Modeling**

In mass transfer, Film Theory is a mechanism used to represent the behaviour and conditions occurring at the phase boundary between gas and liquid, suggesting that the resistance to transfer within each phase can be accounted for by a thin film close to the interface (Cussler, 2009). The total resistance to transfer or flow will be the sum of each individual resistance at all interfaces in the system.

Fan et al. (2008) show that the resistance to flow of  $\text{CO}_2$  from hollow-fibre membrane into algal culture can be summarized with eight individual resistances: in the gas film, at

the gas-liquid interface, in the liquid film surrounding the gas-liquid interface, in the liquid phase, in the liquid film surrounding the algal cell wall, at the liquid-solid interface, in the solid phase, and within the algal cell at the site of CO<sub>2</sub> uptake. However, assuming adequate mixing of solution is provided, the resistance to flow at the liquid boundary layer at the membrane surface has been shown to be orders of magnitude greater than the remaining resistances so much so that these resistances can be considered negligible to overall mass transfer resistance (Carvalho & Malcata, 2001; Ferreira, Fernandes, Reis, & Mateus, 1998). Therefore, the resistance to flow of CO<sub>2</sub> from membrane to culture can be accurately modeled by using just the resistance at the liquid phase boundary layer which can be estimated as the overall mass transfer coefficient K. Processes with larger K will have lower resistance to mass transfer (Fan L. , Zhang, Zhang, & Chen, 2008).

Karoor & Sirkar (1993) investigated the absorption of pure CO<sub>2</sub>, pure SO<sub>2</sub>, CO<sub>2</sub> from CO<sub>2</sub>/N<sub>2</sub> mixtures, and SO<sub>2</sub> from SO<sub>2</sub>/air mixtures into a water solvent. A parallel flow micro-porous hollow-fibre membrane constructed of polypropylene was used and tested with both wet and dry mode operation. They found that CO<sub>2</sub> absorption into water was limited by liquid phase resistance and best results were obtained when operated in the dry mode. Mass transfer coefficients for CO<sub>2</sub> were as much as five times greater than those typically obtained with packed towers and SO<sub>2</sub> absorption mass transfer coefficients were 10 times greater than those obtained with packed towers. Resistance to mass transfer of SO<sub>2</sub> into water was higher when the membrane was operated in the wetted mode compared with dry mode.

Jansen et al. (1993) used hydrophobic hollow-fibre membranes to absorb SO<sub>2</sub> from a SO<sub>2</sub>/N<sub>2</sub> synthetic gas mixture as well as a real flue gas mixture from a coal-fired boiler with a Na<sub>2</sub>SO<sub>3</sub> absorbing solvent. Over 99% recovery of the model gas was attained and similar results occurred for the flue gas over a 500 hour test period. From this study, a SO<sub>2</sub> absorption pilot plant was set up in Krim, Holland where a collaborative effort was undertaken between several research organizations that culminated in two six-month testing sessions. Recovery of SO<sub>2</sub> exceeded 95% in these tests and there were no

problems with membrane fouling (Jansen, Klaassen, Feron, Hannemaier, & ter Meulen, 1993).

## **2.4 Membrane Fouling**

Hollow-fibre membranes are subject to fouling although this tends to be a problem more with pressure driven applications (i.e., purification) than with concentration driven applications such as gas absorption (Gabelman & Hwang, 1999).

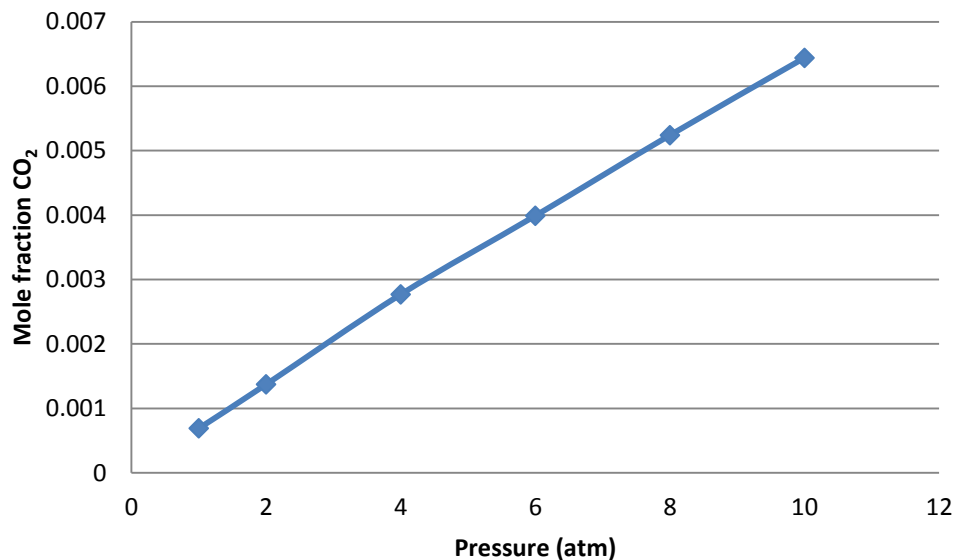
Membrane fouling from particulate present in gas phase or from absorbent has been studied to determine the severity in which this may hinder mass transfer efficiency. Pakala & Bhowan (1996) studied the effect of particulate matter in flue gas on the mass transfer capability of hollow-fibre membranes. They subjected a polypropylene hollow-fibre membrane to a SO<sub>2</sub>/N<sub>2</sub> mixture containing 0.2-0.3 µm diameter particulate matter (typical of ash and other particulates present in most flue gas exhaust) at a concentration of 30 mg/m<sup>3</sup> (approximately one order of magnitude higher than typical flue gas exhaust in order to reduce the time required to deposit a sufficient amount of particles in the membrane) and measured the mass transfer coefficient for SO<sub>2</sub> diffused into the surrounding water solvent intermittently. After 80 hours of run time, they found the final mass transfer coefficient decreased by 20% over initial results and a pressure drop of 100 inches of water. The authors conclude that this is not due to direct pore blockage from particulate but from a build-up of particulate matter on fibre walls as the porosity of the depositing layer partially inhibits the mass transfer coefficient. They found the pressure drop could be reversed when a back-pulse of air from a pressurized jet was passed through the fibres.

Organic fouling from microorganisms in a bioreactor could also be cause for concern with respect to fibre fouling. The effects of biological fouling on hollow-fibre membranes by testing groundwater treatment with fibres have been studied (Roggy, Novak, Hozalski, Clapp, & Semmens, 2002). A thick foulant layer (up to 100 micrometer) accumulated on the fibres and comprised of micro-organisms however gas delivery to the system did continue. Increasing flow rate of liquid across the fibres will decrease the

deposition of biomass on the fibres as well as increase mass transfer by reducing the laminar boundary layer adjacent to the membrane. However, algal cells have low tolerance for the shear stress induced from pumping so there are limits to how quickly the liquid can be circulated on the shell side (Fereira, Fernandes, Reis, & Mateus, 1998).

## 2.5 CO<sub>2</sub> Solubility

The solubility of carbon dioxide in water is an important concept to understand when modeling the mass transfer of CO<sub>2</sub> into solution. At a given temperature, CO<sub>2</sub> follows Henry's Law in that the ratio of partial pressure to concentration of gas in solution is constant. This is displayed in Figure 2-3 (Houghton, McLean, & Ritchie, 1957).



**Figure 2-3:** CO<sub>2</sub> solubility in water at 20°C for multiple pressure conditions, (data from Houghton, McLean, & Ritchie (1957))

Using this relationship, it is possible to calculate the theoretical saturation limit of a CO<sub>2</sub> water system for any gas composition being dissolved into solution. This is pertinent to determining the mass transfer coefficient for a CO<sub>2</sub> absorption system as the saturation level must be known.

## 2.6 Flue Gas Retention via Algae

Nitrous oxides (NO<sub>x</sub>) are formed during combustion processes where nitrogen in the fuel reacts with oxygen and forms NO. This NO is then further oxidized in the stack or

atmosphere to form  $\text{NO}_2$  (with  $\text{NO}$  and  $\text{NO}_2$  being collectively known as  $\text{NO}_x$ ). Previous research has looked at using microalgae as a store for  $\text{NO}_x$  as they can use these compounds for nitrogen sources in protein synthesis (Nagase, et al., 2001).

Yoshihara et al. (1996) investigated the simultaneous elimination of  $\text{CO}_2$  and  $\text{NO}$  in algal culture through a long tubular photo-bioreactor using a marine microalgae strain NOA-113. They used a 15%  $\text{CO}_2$ , 100-300 ppm  $\text{NO}$ , and  $\text{N}_2$  mixture (to simulate fuel oil-fired power plant exhaust) and varied flow rate into culture. They found that almost 50% of  $\text{NO}$  was retained by the algae culture at both 100 and 300 ppm concentrations. While the gas flow rate between 100 and 300 mL/min had no detrimental effect on  $\text{NO}$  retention, increasing flow rate above 300 mL/min caused froth floatation within the culture and resulted in unevenly distributed cells gradually concentrating at the top of the reactor. As a result, nitric oxide elimination by cells decreased. They exposed the culture to a continuous 12 hour light - dark cycle and found that while the health of algae and elimination of  $\text{NO}$  was good during the first light cycle, during the first dark cycle  $\text{NO}$  elimination had ceased. Nitric oxide elimination improved somewhat during the second light cycle but was still only approximately 25% of the elimination that occurred during the first light cycle. From this it was concluded that the dark cycle has a negative effect on algal  $\text{NO}$  retention due to the lack of photosynthetically generated oxygen available to the system during this period. This suggests that photosynthesis plus ample supply of oxygen is therefore required for  $\text{NO}$  retention in algae (Yoshihara, Nagase, Eguchi, Hirata, & Miyamoto, 1996).

Nagasse et al. (1997) found that the green algae *Dunaliella tertiolecta* can remove  $\text{NO}$  at wide ranges of concentrations and at varying gas flow rates. These experiments fed a bioreactor column with a synthetic flue gas of 15 vol%  $\text{CO}_2$ , 0-500 ppm  $\text{NO}$ , and 0-10 vol%  $\text{O}_2$  and investigated the effect of cell concentration, light and dark cycles, and column height on  $\text{NO}$  retention in algae. It was found that the cell concentration of the culture increased  $\text{NO}$  retention until a maximum 60%  $\text{NO}$  removal was achieved during light cycle at which point density of culture had no more effect on  $\text{NO}$  retention. When the algae culture was subjected to a dark cycle, similar results were observed.

The O<sub>2</sub> concentration of the feed gas greatly affected the NO retention ability of the algae. When the O<sub>2</sub> concentration was diminished, NO was not removed by algae during the dark cycle. It was postulated that this is due to the low solubility of NO in water; when there is sufficient O<sub>2</sub> in the system, NO will oxidize to form NO<sub>2</sub> which is much more water soluble. With NO<sub>2</sub> dissolved into water the contact time between algae and gas is much greater and more uptake of the nitrogen source will be accomplished. The oxidation of NO can occur in either the gas or liquid phase but as the rate constant for reaction is orders of magnitude higher in the liquid phase, it is probable that the majority of conversion occurs there. The dissolution of NO into solution was therefore found to be the rate limiting step for uptake of NO by algae and they recommended increasing the contact time between gas bubble and solution in order to improve this by decreasing bubble size (Nagase, et al., 1997).

Nagase further studied NO retention as a function of bubble size and was able to diminish bubble size of NO transferred into solution through the use of an elongated bubble column to increase gas-liquid contact time. Their results are displayed in Table 2-3 and show the NO removal rate by algae increases as the mean bubble diameter of NO is reduced due to the increase in gas-liquid contact area (Nagase, Eguchi, Yoshihara, Hirata, & Miyamoto, 1998). This bodes well for NO<sub>x</sub> retention in hollow-fibre diffused culture as the NO can be dissolved directly into solution without bubbles.

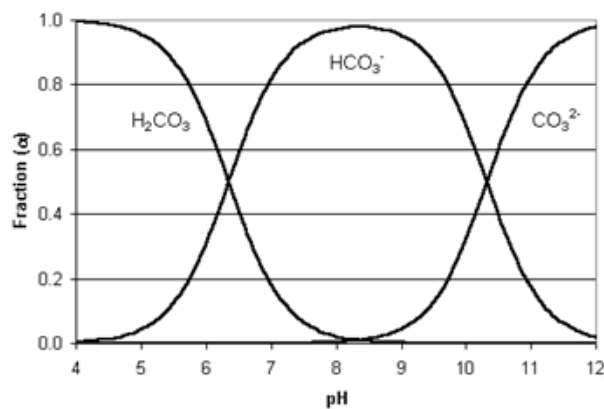
**Table 2-3: Bubble size effect on NO retention by algae (Nagase, Eguchi, Yoshihara, Hirata, & Miyamoto, 1998)**

Mean Bubble Diameter (mm)	NO Removal (%)	Ka (s <sup>-1</sup> )
4.5	20	0.0027
2	26	0.0041
1.6	35	0.0055
0.46	65	0.012
0.26	n/a	n/a

Further research into the uptake pathway of NO<sub>x</sub> into algae was undertaken in another effort with the green algae *Dunaliella tertiolecta* (Nagase, et al., 2001). The authors

theorize that once  $\text{NO}_x$  in the gaseous phase is dissolved in solution, direct diffusion of  $\text{NO}_x$  through the algal cell wall occurs. Like  $\text{O}_2$ ,  $\text{NO}_x$  is a non-polar molecule and can be diffused through the non-polar membrane of the algal cell wall and ultimately fixed as a nitrogen source. In their research, they found that the algal cells actually prefer uptake of  $\text{NO}$  as nitrogen source over nitrates, which are the standard nitrogen sources contained in algal culturing media.

Carbon dioxide can take the form of  $\text{CO}_2$  (aq) (or carbonic acid), bicarbonate, and carbonate ions in water and the likelihood of which form of carbon in water is dominant depends strongly on the alkalinity and pH of solution (Goldman, Dennett, & Riley, 1981). This is important when considering carbon dioxide as a nutrient source from flue gas for biological sequestration as the microalgae are predisposed to more efficiently uptake carbon when in  $\text{CO}_2$  (aq) form. This is due to the non-polarity of the algal cell membrane more easily allowing diffusion of similar hydrophobic compounds (i.e.,  $\text{CO}_2$ ) that are small and uncharged across the membrane (Simmons, 2007). This is known as passive transport across the cell membrane as no energy from the cell is required to diffuse the compound across its membrane. Active transport across the cell wall is required for polar compounds and charged compounds such as carbonate and bicarbonate ions which require the cell to expend energy (normally in the form of ATP) in order to facilitate transport (Simmons, 2007). Figure 2-4 shows the fraction of carbon form available at various pH.



**Figure 2-4:** Fraction of carbon available as carbonic acid, bicarbonate, and carbonate ions depending on pH of seawater (Bialkowski, 2006)

The CO<sub>2</sub> absorption rate by algal culture was studied by (Lee & Pirt, 1984) where a *Chlorella sp.* culture was subjected to a CO<sub>2</sub>-air mixture injection. The pH of the culture environment was varied by NaOH and HCl buffers to test for maximum growth rate based on pH. The results show that maximum growth occurred when the culture was kept between pH of 6.5 and 7.5, where the fraction of inorganic carbon available to culture was predominantly in the CO<sub>2</sub>(aq) form. Another study grew algae at pH ranging from 6.5 to 8.5 and found for certain strains productivity diminished with increased alkalinity of solution (Olaizola, 2003). Further research into this area tested *Scenedesmus obliquus* and *Chlorella vulgaris* at pH of 7.5 and 9.5 by injection of high and low concentrations of CO<sub>2</sub> into culture, respectively (Azov, 1982). It was found that cell density for the low pH *Scenedesmus* was 65% higher than its more alkaline counterpart while the low pH *Chlorella* sample showed a 95% increase in cell density over the high pH culture.

Various researchers have had success in culturing algae from flue gas CO<sub>2</sub> sources; for example, Negoro et al. compared the fixation rate of bombed CO<sub>2</sub> with that from actual flue gas (de-sulphurized) discharged from a boiler for strains of *Nannochloopsis salina* and *Phaeodactylum tricornutum* and found negligible difference in growth rates (Negoro, Hamasaki, Ikuta, Makati, Hirayama, & Suzuki, 1993). In another study, flue gas containing 6-8% (v/v) CO<sub>2</sub> generated from a natural gas boiler was used for outdoor cultivation of *Chlorella sp.* in a bioreactor (Doucha, Straka, & Livansky, 2005). The decarbonisation of flue gas via microalgae ranged from 10-50% of gas fed into the system and decreased with increasing injection rate into culture as the culture became saturated.

Sulphur dioxide is a compound that is formed from combustion of sulphur within fuel. It is highly soluble in water and forms sulphuric acid (H<sub>2</sub>SO<sub>3</sub>) when in aqueous solution. Although some research has shown that certain algal species have a tolerance for SO<sub>2</sub> and can grow in its presence (Maeda, Owada, Kimura, Omata, & Karube, 1995; Negoro, Hamasaki, Ikuta, Makati, Hirayama, & Suzuki, 1993), there does not appear to be any



research conducted to suggest that this compound can be fixed by algae similar to CO<sub>2</sub> and NO<sub>x</sub>.

## **2.7 Hollow-fibre Membranes in Flue Gas Biological Sequestration Applications**

As far is known, research published into hollow-fibre membrane effectiveness in removing CO<sub>2</sub> and other gases via algal culture as absorbent has been sparse. Fan et al. (2008) report that CO<sub>2</sub> retention in a *Chlorella* culture increased over 30% when compared with a sparging unit. The feed gas was composed of 0.093% (v/v) CO<sub>2</sub> laden air and was passed at a rate of 3.60 L/min through a hollow-fibre membrane constructed of polyvinylidene fluoride installed in a helical tubular photo-bioreactor. There has not been any literature found that has detailed the effects of using hollow-fibre membrane technology in biologically sequestering flue gas such as NO<sub>x</sub> via microalgae as absorbent.

More interest has been placed on hollow-fibre membranes for use in flue gas sequestration via alternative biological absorbents to microalgae. Research conducted by Min et al. (2002) evaluated the effectiveness of using a hollow-fibre membrane in removing NO from combustion gases at varying temperatures into a nitrifying bio-film. In this experiment, a synthetic combustion gas similar in composition to coal fired flue gas containing 100 ppm NO was diffused through membrane micro-pores (at a pressure lower than surrounding solution to ensure limiting of bubble formation) and was partitioned into a nitrifying bio-film where it was oxidized to NO<sub>3</sub><sup>-</sup> and other products by bacteria. They reached a maximum NO removal efficiency of 73% when a flow rate of 1.5 cm/s of solution was passed across the membrane fibres at room temperature (20°C). As the temperature of the bioreactor was increased to 55°C, no change in the removal efficiency of NO by the nitrifying bacteria occurred. They noted that an increase in solution flow rate above 1.5 cm/s across the fibres had no further effect on increasing mass transfer efficiency from fibre to solution. Kumar et al. (2009) conducted research similar to Min et al. (2002) and experimented with hollow-fibre membranes for NO removal from combustion gas into a nitrifying bio film. They found the ammonia-

oxidizing microbial organisms *Nitrobacter* were able to retain between 68-73% of the 100ppm NO feed gas diffused into the system.

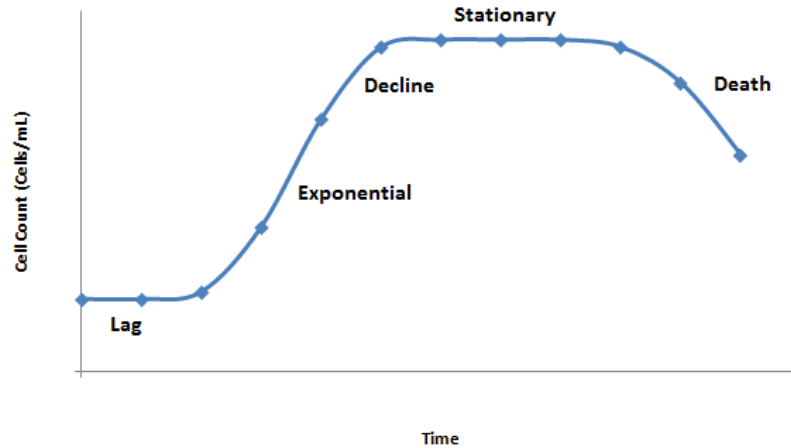
## **2.8 Algae Culturing**

A thorough understanding of algal culturing is required for successful testing of hollow-fibre membrane with suitable strains of microalgae for the purpose of flue gas sequestration. Algal cultures are prone to contamination by other microbial entities including bacteria. Therefore, it is important when selecting algae strains for experimentation that they be robust and capable of fending off bacterial or other microbial contamination. This is especially true when looking at sequestering flue gas via microalgae at an industrial scale as sterilization methods can become less effective with such large capacities.

To date, three taxa of algae have been successfully cultivated at industrial scale which include *Chlorella vulgaris*, *Spirulina platensis*, and *Dunaliella salina* (Huntley & Redalje, 2007). In each case this was due to the extreme conditions in which the algae taxa is capable of surviving, relative to other algal species. *Spirulina platensis* is a cyanobacterium (also known as a blue-green algae) that grows best in highly alkaline (with pH up to 10) media (Jimenez, Cossio, & Niell, 2003). *Dunaliella salina* is the most salt tolerant algal species known to exist and produces a valuable B-carotene product at salinities up to ten fold higher than seawater (Huntley & Redalje, 2007). Due to these extreme environments, these taxa are capable of continued growth without contamination from bacteria as such organisms cannot survive under the adverse conditions.

Two distinct ways of culturing microalgae include open pond systems and bioreactors and the best selection of algae strain for flue gas sequestration would depend on which system the microbes will be grown in (Ono & Cuello, 2003). There is ongoing debate for which system would better suit a sequestration application as the open pond systems have low operating costs while the bioreactor has better productivity potential due to the controlled environmental conditions within (Ono & Cuello, 2003). When inoculating

a bioreactor or open pond with algae, it is important to understand how the initial cell concentration can affect future growth. The growth dynamics of algae in batch culture include five reasonably well established stages, shown in Figure 2-5.



**Figure 2-5: Typical algal growth rate in batch culture, with data from Australian National Algae Culture Collection, 2010**

The specific growth rate can be calculated from Equation (2):

$$SGR = \ln \frac{\left(\frac{N2}{N1}\right)}{(t2 - t1)} \quad (2)$$

Where  $N2$  and  $N1$  are the cell concentrations at the extremes of the linear slope of the exponential phase and  $t2$  and  $t1$  are the corresponding time values. After the exponential phase the culture will level off due to some limiting growth condition (for example, self-shading or nutrient deprivation) at which point the biomass must be harvested. The lag phase of growth can be shortened by inoculating a larger quantity of algae into place.

Microalgae require nutrients for sustained health and growth which consists of various trace metals, vitamins, carbon, nitrogen, and phosphorous. The Redfield Ratio is the stoichiometric ratio between carbon, nitrogen, and phosphorous in phytoplankton and is defined as C:N:P = 106:16:1 (Redfield, 1958). This ratio is the basis for most algal nutrient media.

## 2.9 Algae Selection Criteria for Flue Gas Sequestration

The tolerance of algal species to flue gas emissions (CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub>) is also an important factor to consider when selecting strains for sequestration purposes. Much research has been devoted to studying the effects of potentially toxic compounds present in most industrial effluent that could hinder the growth of algal culture that is subjected to the gas for sequestration purposes. Table 2-4 shows the tolerance levels for CO<sub>2</sub>, SO<sub>2</sub> and NO<sub>x</sub> being transferred into different species of algae. In each of these experiments, it was determined that the specific algal strain cultured with the corresponding gas mixture could maintain healthy culture growth. Yoshihara et al (1996) found that a tolerance for low pH was a prerequisite for tolerance to CO<sub>2</sub> and NO.

**Table 2-4:** NO<sub>x</sub>, SO<sub>2</sub>, and CO<sub>2</sub> tolerance for different algal species

Species	Flue Gas	CO <sub>2</sub> (vol%)	NO <sub>x</sub> (ppm)	SO <sub>2</sub> (ppm)	Reference
<i>Nanochloropsis sp.</i>	Synthetic	15	100	n/a	(Yoshihara, et al., 1996)
<i>Tetraselmis sp.</i>	Actual	14.1	125	185	(Matsumoto, et al., 1995)
<i>Dunaliella tertiolecta</i>	Synthetic	15	1000	n/a	(Nagase, et al., 1998)
<i>Chlorella sp.</i>	Actual	100	20	60	(Maeda, et al., 1995)

Carbon dioxide assimilation ability is unique for each type of microalgae. Ribulose-1,5-bisphosphate carboxylase oxygenase (also known as rubisco) is the primary enzyme that is responsible for catalyzing the reaction of CO<sub>2</sub> into organic material through photosynthesis within most autotrophic organisms (Creighton, 1999). The efficiency of this enzyme varies with microalgal strains and therefore in their efficiency in inorganic carbon uptake. For instance, cyanobacteria (i.e., blue-green algae), evolved billions of years ago when the earth's atmosphere was mostly carbon dioxide and therefore CO<sub>2</sub> uptake was easily accomplished even without an efficient rubisco. As the planet evolved and the concentration of CO<sub>2</sub> in the atmosphere declined, this group of algae has had to develop carbon concentrating mechanisms (CCM) to saturate their cells with CO<sub>2</sub> to make up for their inefficient rubisco (Moroney & Somanchi, 1999). Green algae are a separate lineage of photosynthetic organisms which evolved after cyanobacteria during

a period of relative CO<sub>2</sub> decline. Therefore, there was more selective pressure on this group to evolve rubiscos more efficient at fixing CO<sub>2</sub> and less pressure to develop very active CCMs.

The use of thermophilic, or heat loving, algal species has been considered for use in flue gas sequestration as the gas emitted from thermal power stations can reach approximately 120°C (Bayless, et al., 2001). Thermophilic algae can grow in conditions ranging from 42-100°C, which can be advantageous with flue gas sequestration due to reduced cooling costs of gas (Feron & Jansen). A disadvantage to this option would be the increased loss of water due to evaporation.

Marine microalgae are being considered for flue gas sequestration so that culturing systems can take advantage of using saline water unsuitable for consumption or agricultural purposes. Microalgae specific to each coastal region could be utilized to reduce introduction of foreign algal species to the area. Many heavy polluting sources are located on coastal areas as well including power plants and refineries which could be targets for marine microalgae sequestration (Feron & Jansen).

No overwhelmingly suitable set of algal species has been identified for flue gas sequestration purposes (Ono & Cuello, 2003). Certain species have been shown to be suitable for various selection criteria mentioned in this section but no species has been studied that satisfies all constraints.

## **2.10 Summary**

This chapter provided a detailed background of research accomplished already into CO<sub>2</sub> mass transfer into water through hollow fibre membranes and microalgal retention of flue gas substrate including CO<sub>2</sub> and NO<sub>x</sub>. This information will be used in the following chapter to describe the best methods for maximizing CO<sub>2</sub> dissolved into solution through membrane technology as well as increasing flue gas substrate sequestration efficiency via microalgae.

## Chapter 3: Method and Implementation

This chapter describes the method devised for operating hollow fibre membranes and biologically sequestering flue gases and how this was implemented into this research to study the efficacy of hollow fibre membranes in transferring flue gas into microalgal culture for uptake by the photosynthetic organisms.

### 3.1 Method

Micro-porous hollow-fibre membrane mass transfer systems operate best in terms of mass transfer coefficients when operated in dry mode (i.e. constructed of hydrophobic material for algae culturing purposes), while a high liquid flow coupled with a low gas flow through the hollow-fibres will optimize the operation of this technology (as this will diminish the laminar boundary layer of gas on the fibres). High liquid flow across fibers is also necessary for reducing biological fouling of the unit.

For calculation of CO<sub>2</sub> mass transfer coefficients into water for both the membrane and diffuser, Equation (3) should be used.

$$V \frac{dC}{dt} = KA(C^* - C) \quad (3)$$

Where V= volume of tank (m<sup>3</sup>)

K= mass transfer coefficient (m/s)

A= membrane surface area (m<sup>2</sup>)

C\*= saturation concentration of CO<sub>2</sub> (mol/L)

C = concentration of CO<sub>2</sub> in solution (mol/L)

Separate equal sized tanks, one for membrane gas transfer and one for diffuser gas transfer and containing equal quantities of water, should be set-up where easy access to the solution can be made to take dissolved CO<sub>2</sub> samples to be used in Equation (3). Equal amounts of CO<sub>2</sub> should be directed through both the membrane and diffuser gas transfer systems and elapsed time at each sampling of dissolved CO<sub>2</sub> should be

recorded. The temperature of each water tank needs to be kept constant and identical to each other as varying temperatures could affect total CO<sub>2</sub> in solution. Dissolved CO<sub>2</sub> samples will need to be analyzed using a mass spectrometer to determine total CO<sub>2</sub> in solution. From this data, mass transfer coefficients for both gas transfer methods can be calculated. Algae should not be included in tanks as they contribute negligible resistance to CO<sub>2</sub> mass transfer.

Microalgal strains best suited towards acid gas sequestration should be freshwater species as they are more capable of handling lower pH levels with continued health. To achieve superior gas sequestration efficiency, decreasing the gas bubble size into solution will increase retention (or fixing) of flue gas substrate by algae. Therefore a higher degree of gas sequestration may be achieved with the use of a hollow fibre membrane, as this provides near bubble-less transfer of gas.

To test efficiency of CO<sub>2</sub> and NO<sub>x</sub> sequestration via microalgae based on gas transfer method, the tank set-up described above should be followed again. Gas flow to each culture will need to be controlled. The best way to do this would be to match total biological carbon demand in each tank with corresponding CO<sub>2</sub> gas flow by measuring biomass in each tank (and knowing that algae is ~50% carbon based) and using this measured demand to alter total gas flow to each tank. The total quantity of gas delivered to each tank will also need to be recorded to calculate the capture efficiency of the algae.

Ash free dry weight (AFDW) samples of algae will need to be taken regularly to track biomass productivity in each tank as well as for later elemental analysis to measure total carbon and nitrogen stored in each algal culture. As the purpose of this research is to study both carbon and nitrogen capture efficiency in the algae, nitrate assays will have to be done regularly from each tank to understand the nitrogen fixation rate based on gas transfer method. Total nitrogen and phosphorus nutrients prepared for each test will need to be recorded. The total gas capture efficiency for each microalgal culture can be calculated using Equation (4).

$$S = \frac{B \times f}{T \times g \times \frac{Mmf}{Mm}} \times 100 \quad (4)$$

Where S= sequestration efficiency (%)

B= total algal biomass in each tank (g)

f= fraction of elemental compound in algal biomass measured (i.e. carbon or nitrogen)

T= total gas delivered to culture (g)

g= fraction of fixable gas species in total gas stream (i.e. CO<sub>2</sub> or NO<sub>x</sub>)

Mmf= molar mass of elemental carbon or nitrogen (g/mol)

Mm= molar mass of gas (g/mol) (i.e. CO<sub>2</sub> or NO<sub>x</sub>)

### 3.2 Implementation of CO<sub>2</sub> Mass Transfer Measurements

The first objective of this thesis was to determine the mass transfer efficiency of a hollow-fibre membrane with carbon dioxide. The membrane (Solutions4CO<sub>2</sub> Algaemax Mini membrane) used in this thesis is constructed of a polyethylene material with a total available interfacial surface area of 0.25 m<sup>2</sup> and average porosity diameter of 0.1 μm. Polyethylene is a hydrophobic material therefore the unit will operate in dry mode when suspended in water. The diffuser (Sweetwater Generation II diffuser) that the membrane was tested against has a total interfacial surface area calculated at 0.004 m<sup>2</sup> (refer to Carvalho & Malcata) for mass transfer area calculations).

Similar to what has been done in previous research efforts (Ferreira, Fernandes, Reis, & Mateus, 1998; Carvalho & Malcata, 2001), this membrane was tested for its efficacy in diffusing CO<sub>2</sub> into water at various gas compositions and compared with an industry standard sparger. The membrane and sparger were suspended in separate 36 L tanks (Bellco Jar) with continuous flow of CO<sub>2</sub> gas directed through each mass transfer system at 0.06 L/min for 2 hour spans. The freshwater was 0.35 μm filtered and maintained at 20°C during testing by keeping the reactors inside an environmentally controlled area (Conviron® ATC26). To ensure no gradient of dissolved gas in solution and to diminish



the laminar boundary layer formed on the periphery of the fibres the tanks were continually stirred at identical rates of 75 RPM with paddle-wheel impellers.

Samples of water were drawn every 20 minutes from each tank with a gas tight syringe (60 mL). These samples were quickly measured using a membrane inlet mass spectrometer (model no. HPR40 Hiden Analytical) and the dissolved CO<sub>2</sub> content in each sample was recorded. Saturation tests with each gas composition were also carried out for mass transfer calculations.

### **3.3 Implementation of Microalgal Sequestration Efficiency of Flue Gas**

The second objective of this thesis was to determine the efficiency of hollow-fibre membranes in retaining flue gas emissions via microalgae compared with standard sparging. Freshwater species *Scenedesumus obliquus* was tested with the hollow-fibre membrane and sparging systems for flue gas retention capabilities. The *Scenedesumus* genus was chosen for testing as it is a robust alga that grows well (with maximum growth rate of 1.2 doublings per day) and can withstand comparatively low levels of pH compared to marine species, therefore suited for acid gas sequestration.

The first experiments carried out with algae used a 100% CO<sub>2</sub> gas source as this is a standard for algal culturing at the National Research Council of Canada's Institute for Marine Biosciences. These tests were done to establish a reference in terms of algal growth and CO<sub>2</sub> sequestration without potentially toxic compounds such as NO<sub>x</sub> and SO<sub>2</sub> dissolved into solution, as well as to provide an additional operating environment to demonstrate any uptake efficiency of CO<sub>2</sub> with the HFM system over the diffuser.

For these tests, nutrient media was prepared containing nitrates. The total starting concentration of nitrates in the nutrient media was 650 µmol/L. Phosphorous concentration in the media was increased to a 10:1 N:P ratio to ensure phosphorous was not a limiting factor in the growth of algae and that solely nitrogen and light penetration were.

For flue gas testing with algae, nitrates in the nutrient media were eliminated to understand how the algae cultures could potentially fix  $\text{NO}_x$  from the flue gas without any other sources of nitrogen available to it.

The synthetic flue gas composition that was used for the algal retention tests is modeled after a sub-bituminous coal-fired power plant. Table 3-1 displays its composition. The gases were prepared by Air Liquide and were supplied in three separate tanks to minimize conversion of gases before reaching the bioreactor. Water was not included in this mixture as it would hinder mass transfer behavior in the hollow fibres by wetting the inside of the micro-pores. Each gas cylinder contained three times the desired concentration so that when blended together at the same pressure, the mixture will be exactly as it is in Table 3-1.

**Table 3-1:** Flue gas composition for algae sequestration tests

Gas	Fraction	Unit
$\text{N}_2$	68.9	vol%
$\text{O}_2$	7	vol%
$\text{CO}_2$	24.1	vol%
$\text{SO}_2$	0.1	vol%
NO	250	ppm
$\text{NO}_2$	100	ppm

A pH-stat control system was installed into the membrane bioreactor that served as a rudimentary control of the level of dissolved  $\text{CO}_2$  in each tank. The control set point was kept at pH of 6.0 so that minimal bicarbonate formed in the water and the majority of carbon in the system (i.e. ~70 vol%) remained as dissolved  $\text{CO}_2$ . The lower pH set point was also used to ensure gas flow to the cultures did turn on for the flue gas tests. Normally, the filter sterilized fresh water used for these algae culturing experiments was approximately at pH 5.8 at inoculation. If the pH set point was higher than 6, the cultures would have great difficulty raising the pH of the water (i.e. by growing and removing dissolved  $\text{CO}_2$ ) sufficiently to turn on gas flow as their only source of nitrogen (required for growth) is from the  $\text{NO}_x$  gas that is provided on demand. Therefore, by

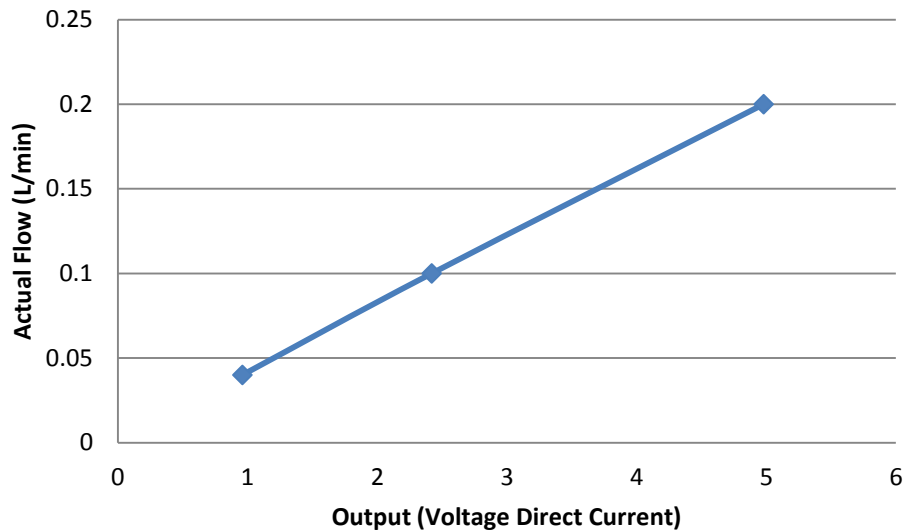
setting pH control at 6.0, gas flow did turn on to the cultures and sequestration could be accomplished.



**Figure 3-1:** Bellco jars set-up with HFM (L) and diffuser (R). Flowmeters and gas flow sensor in background.

A gas flow meter (Dwyer) interfaced with data acquisition software (Vernier LoggerPro) was installed in line to the HFM bioreactor to record total gas delivered to this tank. As each tank had a rotameter installed in line set at approximately 0.06 L/min (total gas flow), both tanks received identical quantities of gas for each on demand delivery (i.e. once pH of 6 was surpassed in the membrane tank). The gas flow meter produced a voltage to the acquisition system proportional to the rate of gas flow across the sensor. Figure 3-2 shows the calibration for the sensor (for air).

The vessels had their headspaces vented to a manifold in the test area which sent the headspace gas outside, so as to avoid pressure build up inside the tanks and to prevent any potentially dangerous gases from escaping.



**Figure 3-2:** Calibration curve for flow gas sensor

Samples from each bioreactor were taken daily and enumerated with a particle counter (Beckman Coulter). *Scenedesmus* has a propensity to clump at higher densities which makes accurate cell counts difficult to achieve. Therefore, the bio-volume option of the cell counter was used where the total volume of cells counted was returned and was divided by the average cell area for *Scenedesmus* of approximately  $59 \mu\text{m}^2$  to give a more accurate cell count. During each test, water samples were taken daily for nitrate analysis to determine total nitrate uptake rate with both gas delivery methods in the 100%  $\text{CO}_2$  tests and to ensure negligible nitrate levels were available to the algae for the flue gas tests. For nitrate analysis, a nitrate kit (Nitrate Elimination Company) was used. After 4 days of growth, 20 mL biomass samples were taken daily and filtered on to 25  $\mu\text{m}$  filter paper both to track biomass density and for later elemental analysis of biomass. The filtered biomass was stored in an oven overnight at approximately  $40^\circ\text{C}$  to dry any residual moisture off the filter. The filter was then measured to obtain biomass concentration (g/L).

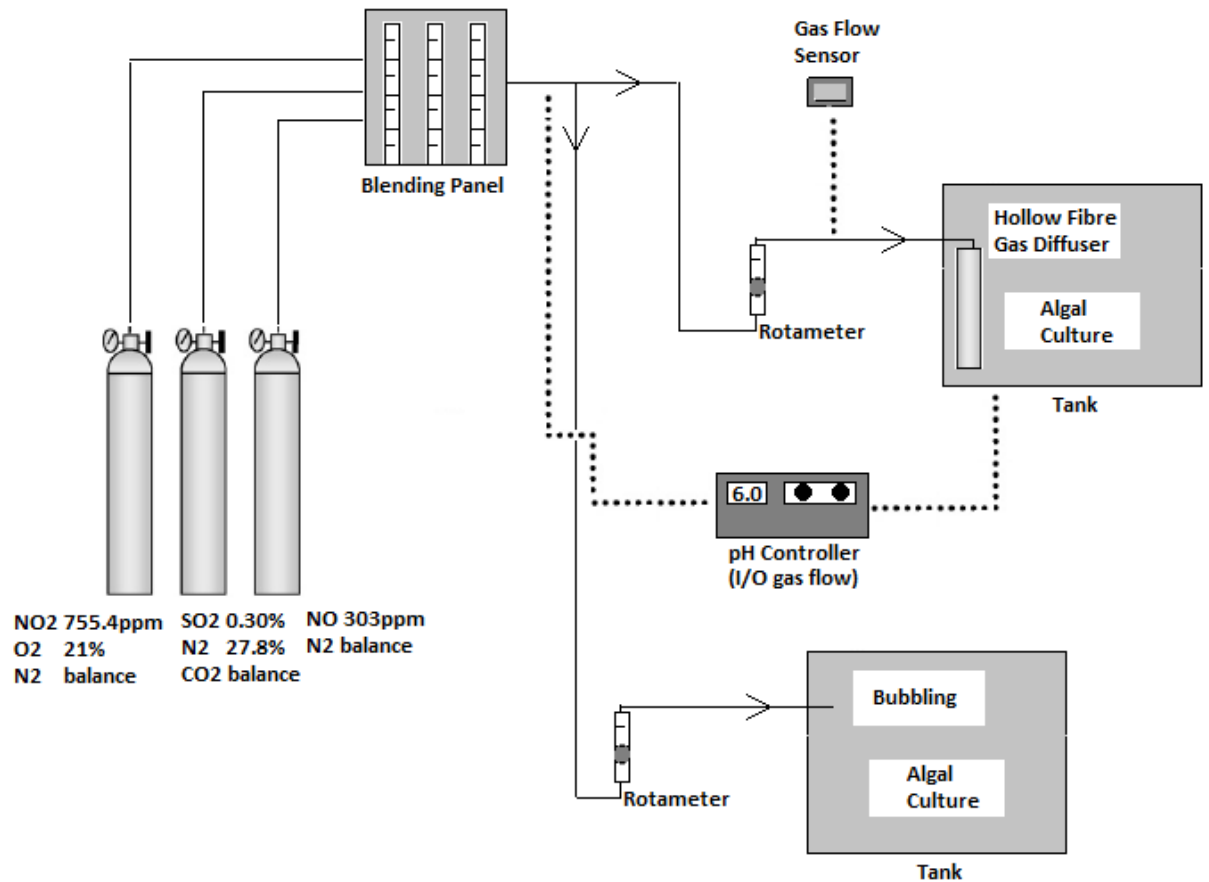
For initial testing, filters were pre-combusted in a muffle furnace at approximately  $230^\circ\text{C}$ , weighed, and then used for biomass filtering. After filtering, the filters were placed in the oven at  $40^\circ\text{C}$  overnight. These filters were then placed in the muffle furnace at

280°C to remove all biomass and ash. The difference in filter weights from pre-combustion to that after was negligible (meaning ash in the samples was negligible) therefore it was concluded that the dried biomass samples for the remainder of testing would be Ash Free Dry Weights (AFDW).

The dried biomass filters were analyzed for carbon and nitrogen using an elemental analyzer (Elementar Vario Microcube) which returned carbon, nitrogen, oxygen, and sulphur composition in the algae samples. Knowing total gas delivered to each system and gas retained by microalgae in both cultures allowed for a total mass balance to be performed. From this mass balance, the efficiency by which the hollow fibre membrane is capable of making available CO<sub>2</sub> and NO<sub>x</sub> to microalgae for sequestration compared with sparging was made.

The gas flow sensors were not accurate enough to provide total NO<sub>x</sub> gas delivered to the cultures given the small ppm quantities of NO<sub>x</sub> in the gas source therefore a total sequestration efficiency could not be calculated for this compound. However, elemental analysis of the biomass was precise enough to determine any variations in nitrogen fixation between gas transfer methods so that a relative change in sequestration efficiency between the membrane and diffuser could be made.

Figure 3-3 shows the experimental set-up for the algae growing tests with flue gas.



**Figure 3-3:** Experiment set-up for algal flue gas retention tests

### 3.4 Summary

In this chapter the experimental method followed for determining CO<sub>2</sub> mass transfer efficiency into water based on gas transfer method (i.e. membrane or sparger) was conceptualized for both a 5% CO<sub>2</sub> enriched air mixture as well as a 24% CO<sub>2</sub> flue gas modeled after a sub-bituminous coal fired power plant exhaust. The dissolved CO<sub>2</sub> in water over time for each gas transfer method was measured using a mass spectrometer as well as the saturation limits for each gas mixture were determined to calculate the mass transfer coefficient, 'K', and the volumetric coefficient, 'Ka' for each transfer method and compared. A freshwater *Scenedesmus obliquus* species was used for testing the effects of gas transfer method on microalgal productivity and sequestration

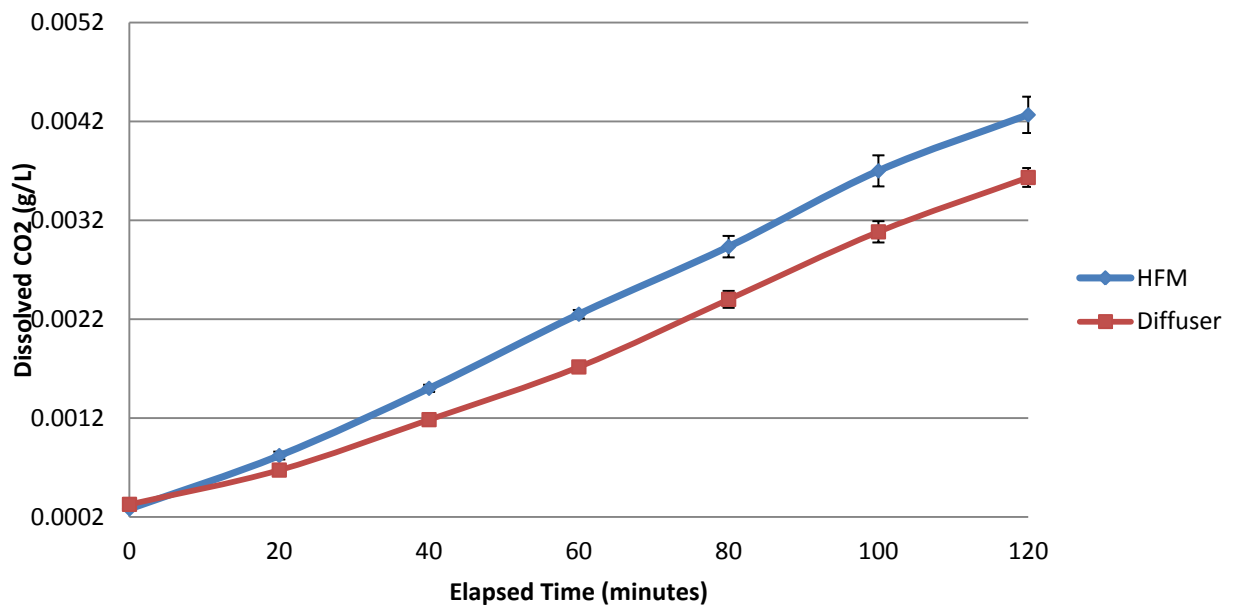
capability of CO<sub>2</sub> and NO<sub>x</sub> directed into each growth system. Gas flow sensors recorded total gas delivery to each growth system and elemental analysis of the dried algal biomass provided information on total carbon and nitrogen uptake by algae for each gas transfer method.

## Chapter 4: Results and Discussion

This chapter presents the experimental results pertaining to the mass transfer modeling of CO<sub>2</sub> through the hollow fibre unit compared with that of conventional gas transfer technology used in microalgal cultivation industry. The efficacy by which flue gas substrates and CO<sub>2</sub> enriched air can be sequestered via microalgae based on the method of transferring gas into solution (either by membrane or standard sparger) is also studied and summarized in this chapter.

### 4.1 Mass Transfer

The results for the dissolved-CO<sub>2</sub>-over-time tests for flue gas described in Chapter 3 are displayed in Figure 4-1. From this data, the mass transfer coefficients for each test were calculated to quantify which system was capable of providing superior gas absorption.



**Figure 4-1:** Dissolved CO<sub>2</sub> over time for hollow fibre membrane and diffuser with flue gas at 20°C (n=6, +/- standard error)

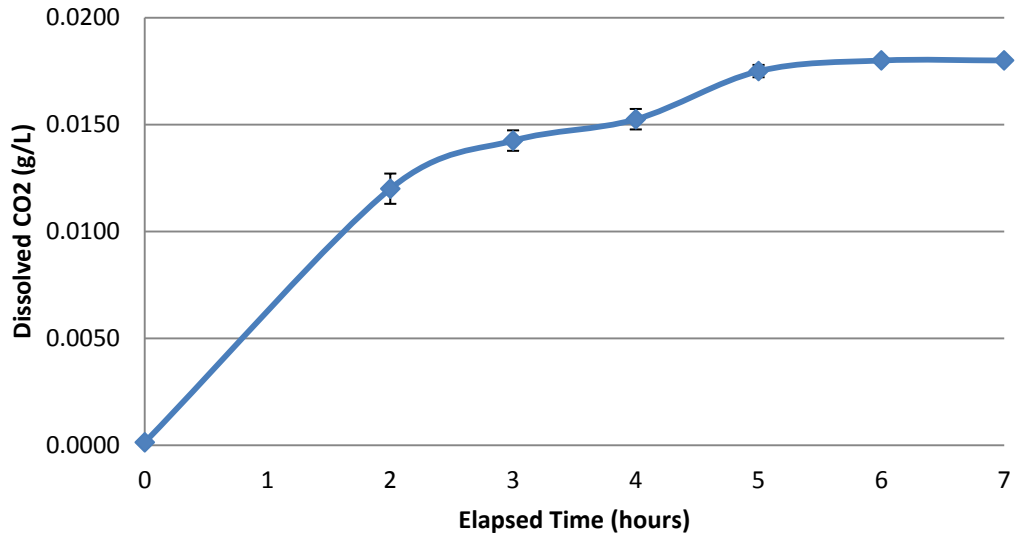
A paired t-Test was performed using the final dissolved gas concentrations from each data set and shows that the hollow fibre membrane is capable of increasing dissolved CO<sub>2</sub> absorbed into solution by a small but statistically significant quantity with an over 99% confidence in the findings (i.e. P < 0.01). This test is summarized in Table 4-1.



**Table 4-1:** Paired, two sample t-Test for means comparing final dissolved CO<sub>2</sub> concentrations for flue gas testing in each gas transfer system

	<i>Membrane</i>	<i>Diffuser</i>
Mean	0.0043	0.0036
Variance	2.01E-07	5.47E-08
Observations	6	6
Pearson Correlation	0.96	
Hypothesized Mean Difference	0	
df	5	
t Stat	6.64	
P(T<=t) one-tail	0.00059	
t Critical one-tail	2.02	
P(T<=t) two-tail	0.0012	
t Critical two-tail	2.57	

To calculate the mass transfer coefficient for these tests, the saturation limit for this particular gas composition in water at the set environmental conditions must be known. Therefore, a further series of tests were carried out to saturate the same quantity of fresh water with the flue gas until no change in dissolved CO<sub>2</sub> was measured with the mass spectrometer and the vessel was saturated with the gas. The tests were carried out with a sparger so that a high flow of flue gas into solution could be achieved (which would cause a gas burst pressure to exceed the hydrostatic head pressure had the membrane been used) to quickly saturate the solution. Figure 4-2 shows the saturation tests carried out for flue gas.



**Figure 4-2:** Saturation tests for flue gas at 20°C levelled at 0.018 g/L using a sparger (n=4, +/- standard error)

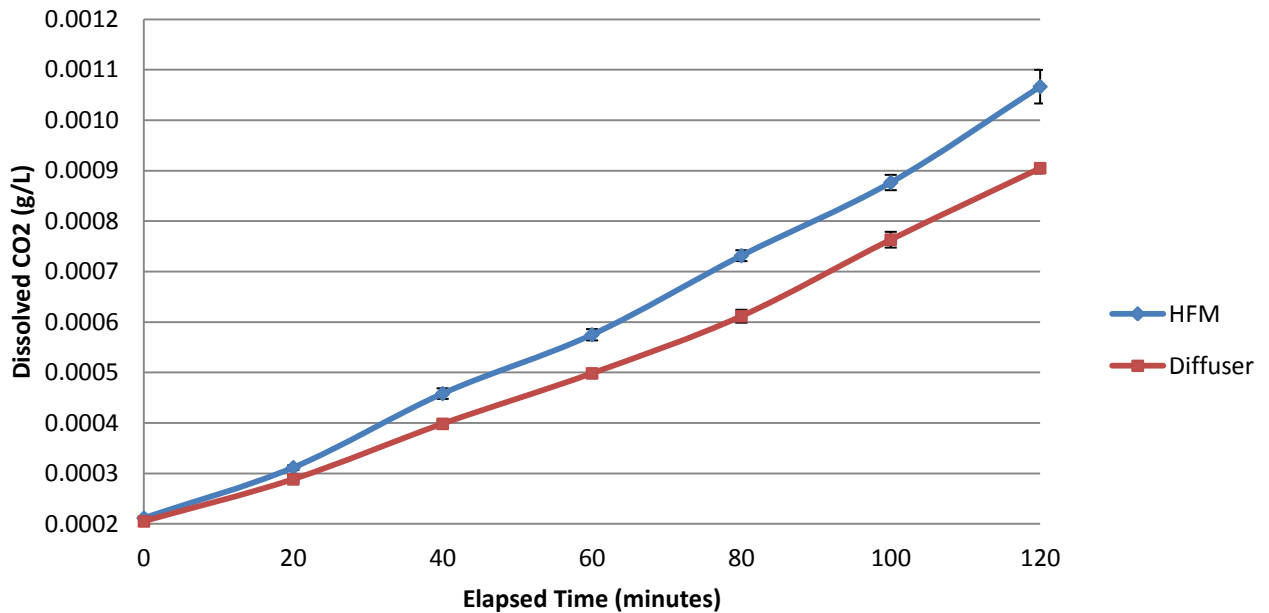
Using the saturation level from Figure 4-2, the mass transfer coefficients and volumetric coefficients (using the specific mass transfer area values for each gas transfer system described in Chapter 3) for each test were calculated and are displayed in Table 4-2.

**Table 4-2:** Mass transfer coefficients and volumetric coefficients for both gas transfer systems using flue gas

Gas Transfer Method	K (m/s)	Ka (s <sup>-1</sup> )	Standard Error
Membrane	5.40E-06	3.76E-05	2.59E-07
Diffuser	2.62E-04	3.13E-05	7.26E-06

The results from the mass transfer tests are in good agreement with the literature in that sparging gas into solution offers an effectively higher mass transfer coefficient, 'K'; however, total gas dissolved into solution will be higher with the hollow fibre membrane due to the substantially higher area for mass transfer to take place which is accounted for with the volumetric mass transfer coefficient, 'Ka'.

The previous tests were repeated using a 5% CO<sub>2</sub> enriched air gas composition and the results follow the flue gas tests closely. Figure 4-3 shows the dissolved gas concentration results for these tests.



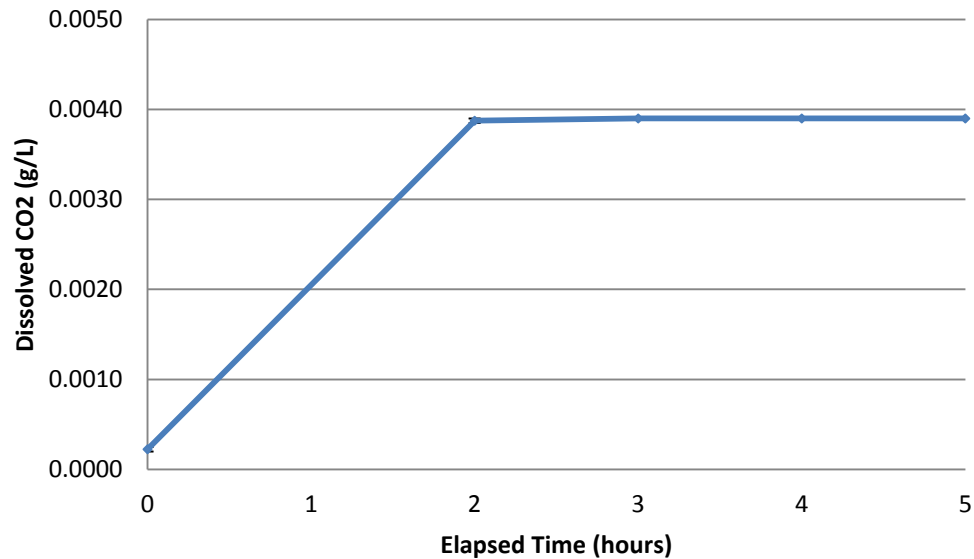
**Figure 4-3:** Dissolved CO<sub>2</sub> over time for hollow fibre membrane and diffuser with 5% CO<sub>2</sub> enriched air at 20°C (n=6, +/- standard error)

A t-Test on the final dissolved CO<sub>2</sub> measurements for each run was performed which showed a greater than 99% confidence level that the hollow fibre membrane was capable of transferring more CO<sub>2</sub> into solution than the diffuser in the same period of time. Table 4-3 gives the results of the t-Test.

**Table 4-3:** Paired, two sample t-Test for means comparing final dissolved CO<sub>2</sub> concentrations for CO<sub>2</sub> enriched air testing in each gas transfer system

	<i>Membrane</i>	<i>Diffuser</i>
Mean	0.0011	0.00091
Variance	6.67E-09	6.30E-10
Observations	6	6
Pearson Correlation	0.88	
Hypothesized Mean Difference	0	
df	5	
t Stat	6.51	
P(T<=t) one-tail	0.00064	
t Critical one-tail	2.02	
P(T<=t) two-tail	0.0013	
t Critical two-tail	2.57	

Similar to the flue gas tests, a saturation test was carried out to determine the maximum level of CO<sub>2</sub> capable of being dissolved into solution at the specific environmental conditions and gas composition. Figure 4-4 shows the saturation test results for the 5% CO<sub>2</sub> enriched air mixture.



**Figure 4-4:** Saturation tests for 5% CO<sub>2</sub> enriched air at 20°C levelled at 0.0040 g/L using a sparger (n=4, +/- standard error)

Using this saturation level, the mass transfer coefficients and volumetric coefficients for both gas transfer systems with CO<sub>2</sub> enriched air was calculated. The results for these calculations are displayed in Table 4-4. For these results, the coefficients remain in the same order of magnitude as the 24% CO<sub>2</sub> tests for each transfer method.

**Table 4-4:** Mass transfer coefficients and volumetric coefficients for both gas transfer systems using 5% CO<sub>2</sub> enriched air

Gas Transfer Method	K (m/s)	Ka (s <sup>-1</sup> )	Standard Error
Membrane	6.38E-06	4.44E-05	1.35E-07
Diffuser	3.07E-04	3.66E-05	3.66E-06

Again, the results for the CO<sub>2</sub> enriched air tests agree with the literature in that the mass transfer coefficient, 'K', for diffusers (i.e. bubbling) will be greater than that for hollow fibre membranes when transferring CO<sub>2</sub> into solution. This is due to the turbulent conditions that are developed when the bubbles are formed with the diffuser allow for the laminar boundary layer at the gas-liquid interface to thin, thereby reducing the greatest resistance to mass transfer in the system (Carvalho & Malcata, 2001). As the principle behind the operation of the membrane system is that there is a lower gas phase pressure inside the fibres compared with the outside pressure of surrounding water, there are no bubbles formed so the laminar boundary that forms on the fibre wall remains intact, thereby increasing resistance to mass transfer. The amount of dissolved CO<sub>2</sub> measured over time in each system is greater however with the membrane system as the substantially higher area for interfacial mass transfer allows more gas to diffuse into solution compared with diffusers.

The results from this section of the thesis show that hollow fibre membranes can dissolve slightly greater amounts of CO<sub>2</sub> into solution (i.e. less gas is lost to the atmosphere during transfer) compared with diffusers. Therefore, when each transfer system is deployed in algal culture there may be more efficient gas sequestration with the membrane culture.

## 4.2 Validity of Measurements

To ascertain whether the results summarized in the previous section are accurate in terms of theoretical basis, the ratio of partial pressure to concentration of dissolved CO<sub>2</sub> in water at equilibrium should remain constant as the CO<sub>2</sub> water system follows Henry's Law. Theoretical saturation limits for each gas mixture was calculated using this relationship and are compared with the experimental results for the 5% and 24% CO<sub>2</sub> tests.

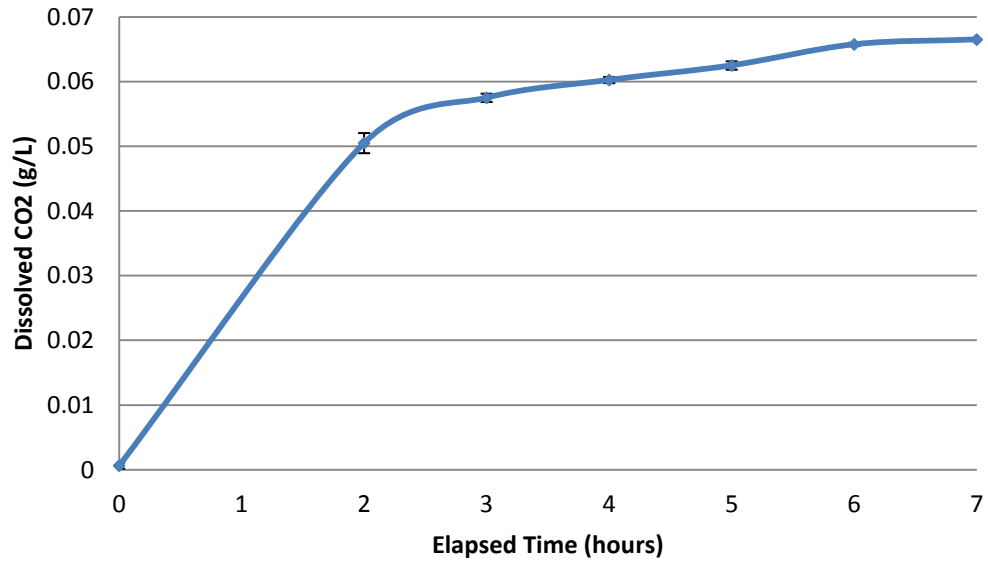
Table 4-5 shows that there appears to be a consistent error between theoretical and measured saturation limits, there may be some error associated with the set-up or execution of this experiment.

**Table 4-5:** Error associated with each saturation test based on Henry Law Coefficient (Perry & Green, 2007)

CO <sub>2</sub> %	Saturation (g/L)		Error (%)
	Experimental	Theoretical	
5	0.004	0.08	95
24	0.018	0.36	95
100	0.067	1.50	96

As a result, a further series of saturation tests were carried out with 100% CO<sub>2</sub> to provide additional experimental data; these are displayed in Figure 4-5. Given the three tests show comparable error, it is concluded for the mass transfer section of this research that there is a consistent error in either set-up or execution of these experiments. This likely emanates from the calibration of the mass spectrometer as a controlled buffer of calcium carbonate in HEPES solution (buffer solution) was not used (as is standard procedure at the NRC-IMB for this piece of equipment) for a known quantity of dissolved CO<sub>2</sub> in initial calibration. Distilled water left to equilibrate with surrounding ambient air was used instead for an approximate dissolved CO<sub>2</sub> concentration (calculated via Henry's Law) as this particular method allowed the prepared dissolved CO<sub>2</sub> measurement program provided by the manufacturer of the mass spectrometer to be used.

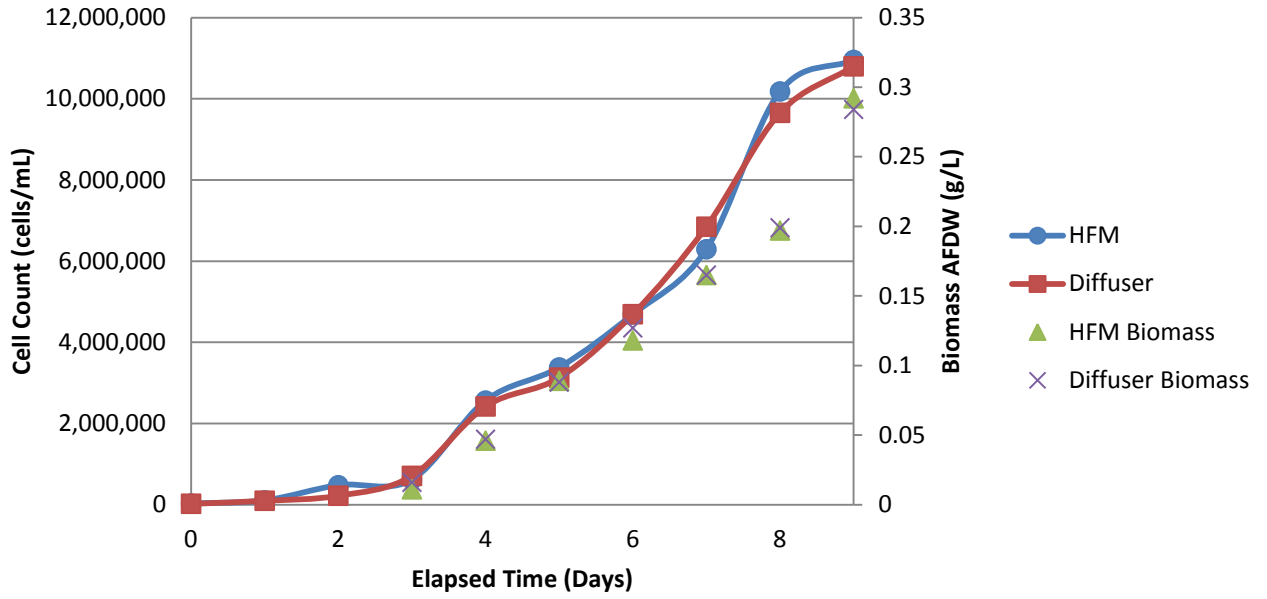
Despite this error, the relative difference between the mass transfer coefficients based on gas transfer method will not change so it is concluded that the volumetric coefficient for the membrane tests was higher than that of the diffuser tests, which agrees well with the literature.



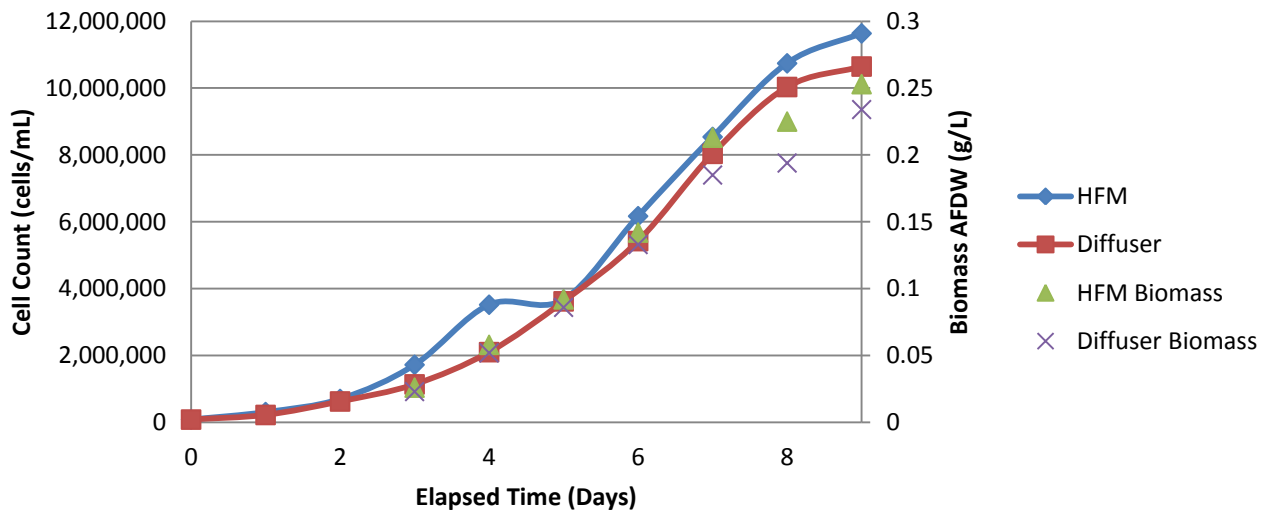
**Figure 4-5:** Saturation tests for 100% CO<sub>2</sub> at 20°C, sparger (n=4, +/- standard error)

### 4.3 Microalgal Production, 100% CO<sub>2</sub>

The results of algae growth tests based on gas transfer using 100% CO<sub>2</sub> are displayed in Figures 4-6 through 4-8.

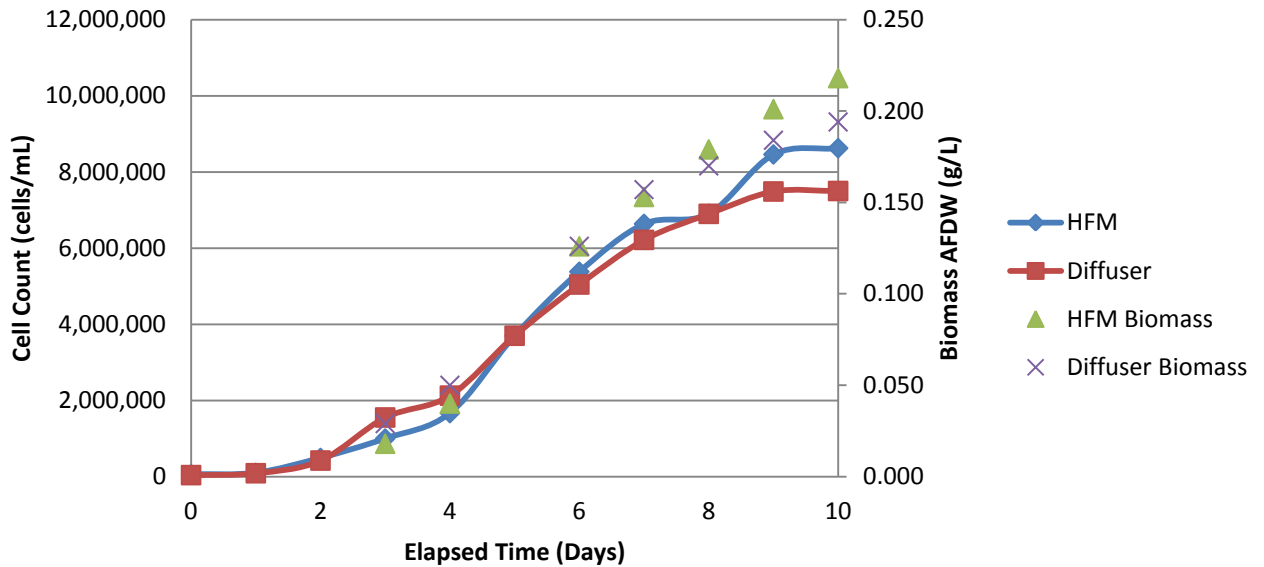


**Figure 4-6:** Algal cell count and biomass production for HFM and diffuser reactors (100% CO<sub>2</sub>), Test 1



**Figure 4-7:** Algal cell count and biomass production for HFM and diffuser reactors (100% CO<sub>2</sub>), Test 2



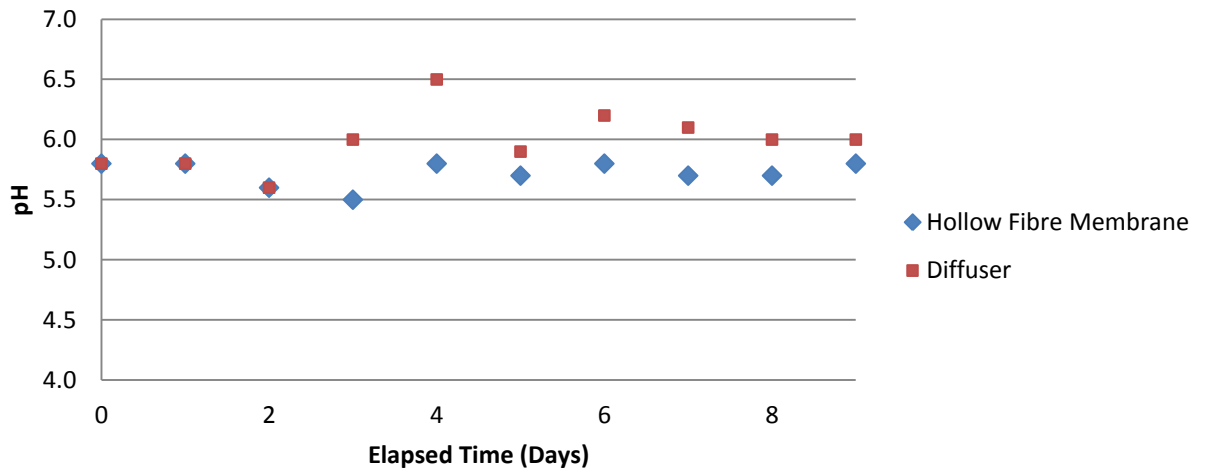


**Figure 4-8:** Algal cell count and biomass production for HFM and diffuser reactors (100% CO<sub>2</sub>), Test 3

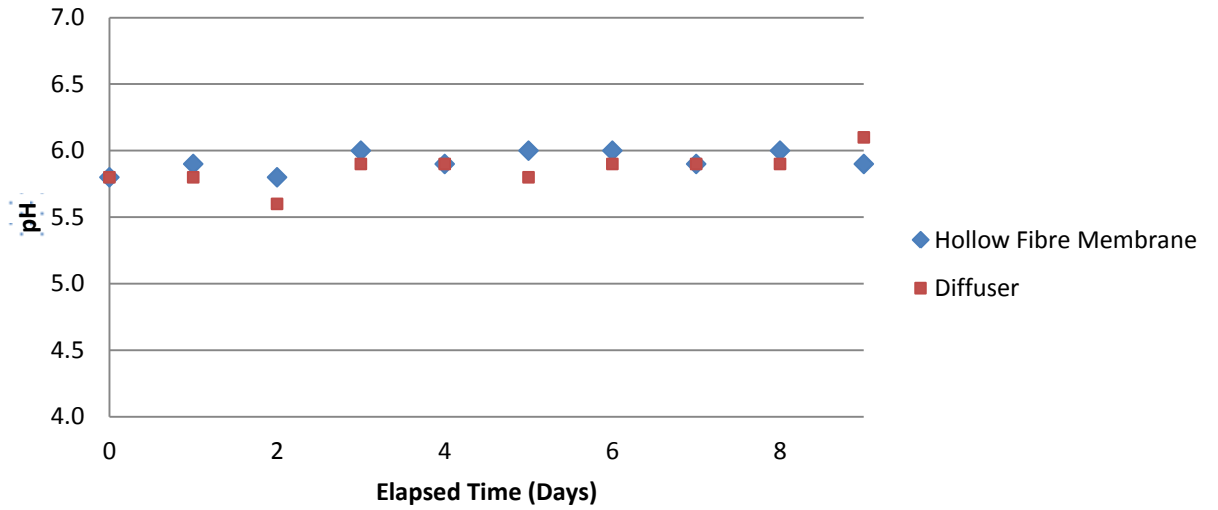
The results suggest a negligible change in algae production based on gas transfer method for the duration of growth until cultures are close to reaching density. This implies that the gas transfer method (i.e. hollow fibre membrane or diffuser) does not impact growth in the beginning stages. This makes sense intuitively as at the time of inoculation and the following days afterwards, very little biomass (less than 0.025 g/L AFDW) is present in solution which means low biological demand for CO<sub>2</sub>. Each time CO<sub>2</sub> delivery is turned on to the cultures the algae receive ample supply regardless of efficiency in gas transfer as so little CO<sub>2</sub> is required to remain in solution to sustain growth. However, at the end of the growth period the cultures are very dense (two orders of magnitude higher compared with inoculation) so gas transfer efficiency may be important at this stage as carbon is in high demand. The membrane is capable of transferring gas into solution with limited bubble formation whereas the diffuser bubbles all the gas into solution where a large portion likely does not have sufficient gas-liquid contact time to dissolve before rising to the surface and into the headspace. Given that the set-up for gas delivery is controlled by the needs of the membrane tank, the diffuser culture may begin to be carbon limited at the end of growth period as the

volume of CO<sub>2</sub> capable of satisfying the biological carbon demand delivered by the HFM is not sufficient when delivered by the diffuser (due to lower retention in solution). This could explain the increase in biomass for the membrane system compared with the diffuser tank at the end of growth period.

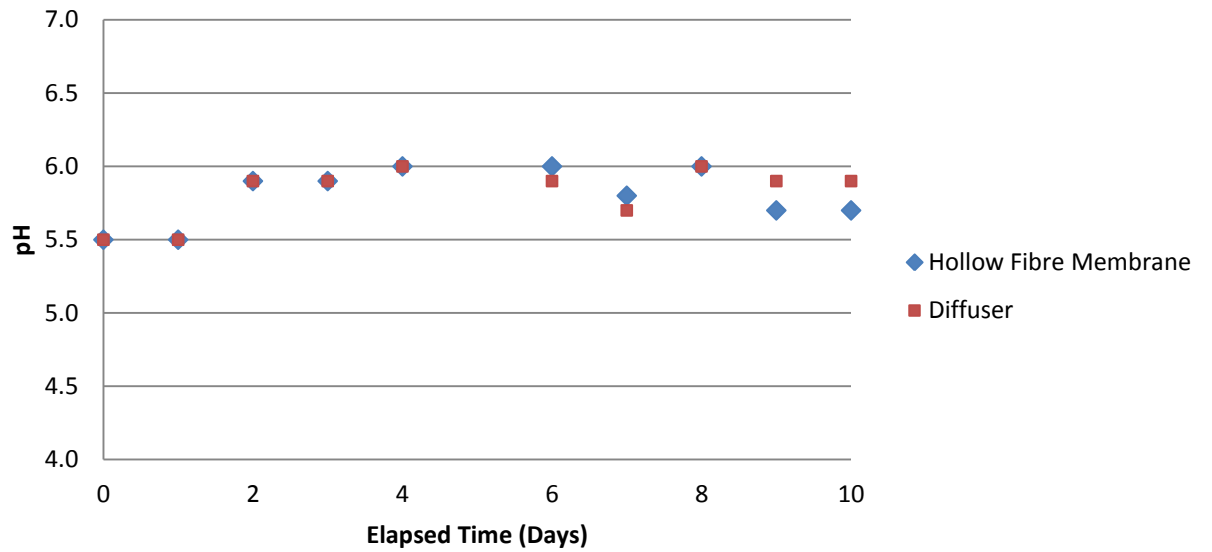
Figures 4-9 through 4-11 summarize pH levels in each bioreactor throughout the growth period. For Test 3, pH in both tanks was lower to begin with than in previous tests for unknown reasons. This caused a prolonged lag period in both tanks for this growth campaign. pH levels remained similar for each tank throughout the experiments which shows the pH on/off control installed in just the membrane tank was adequate in controlling dissolved CO<sub>2</sub> levels for both tanks equally. Note the increased pH at the end of each run for the diffuser tank versus the membrane tank. This lends credence to the conclusion that the diffuser cultures may be carbon limited at the end of the growth period as less carbonic acid is in the system.



**Figure 4-9:** pH of solution throughout algal growth (100% CO<sub>2</sub>), Test 1

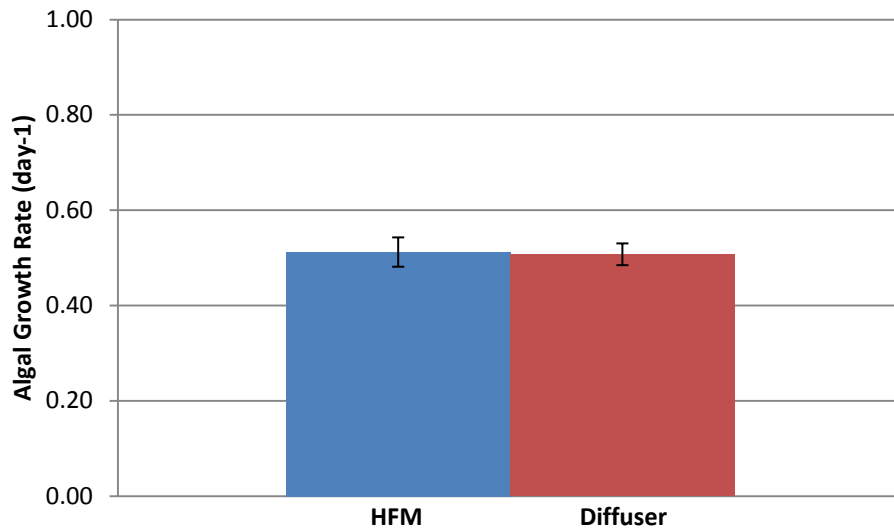


**Figure 4-10:** pH of solution throughout algal growth (100% CO<sub>2</sub>), Test 2



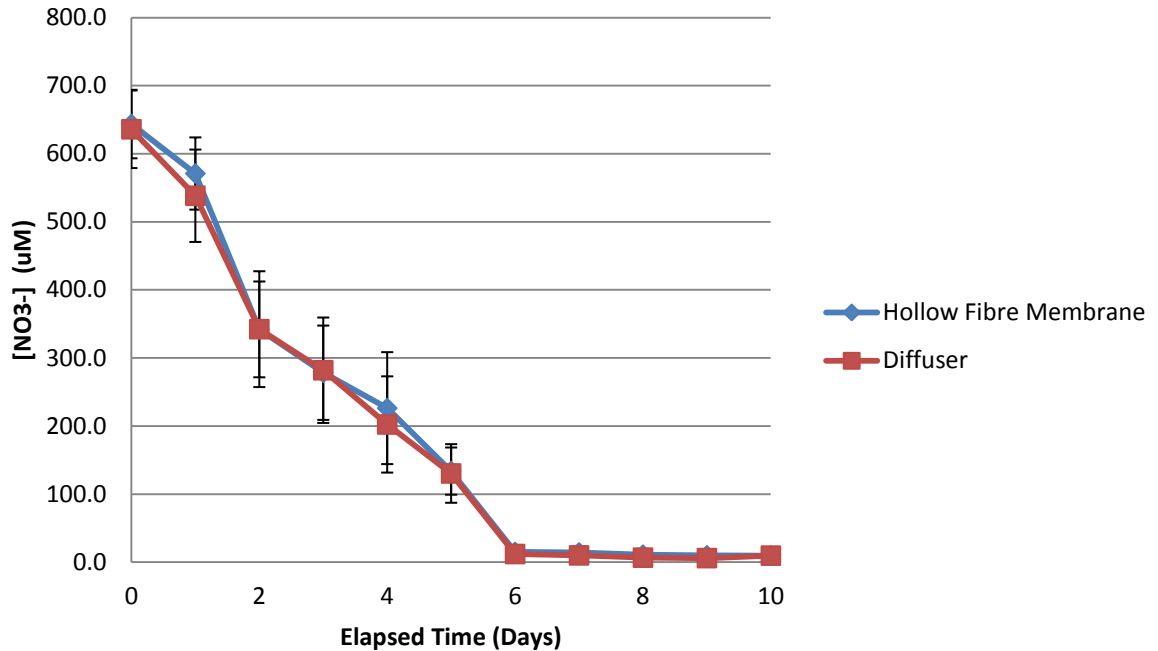
**Figure 4-11:** pH of solution throughout algal growth (100% CO<sub>2</sub>), Test 3

Figure 4-12 demonstrates the negligible impact the gas transfer method has on maximum algal growth rate.



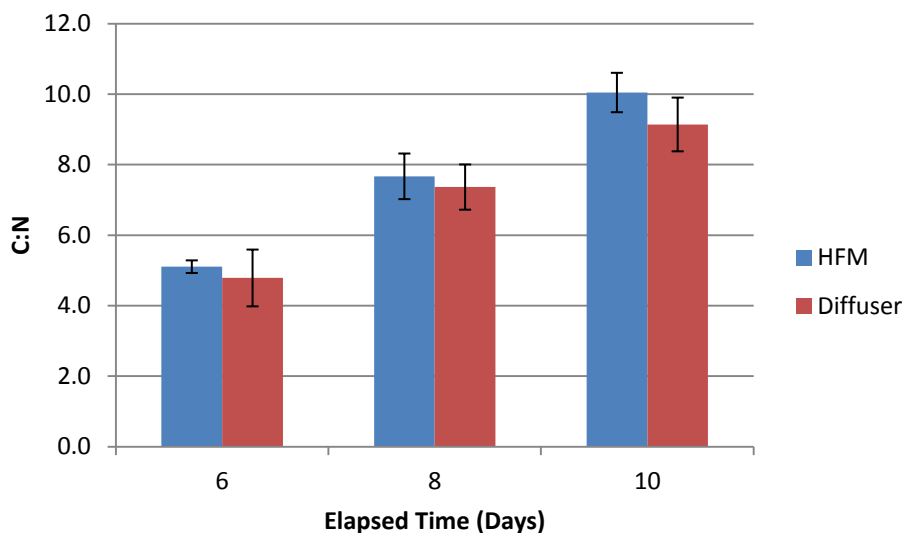
**Figure 4-12:** Maximum algal growth rate for both gas transfer systems (100% CO<sub>2</sub>, Day 3 to 8) (n=3, +/- standard error)

Nitrates were added to the cultures at inoculation for nitrogen fixation and samples were drawn each day. Figure 4-13 shows the nitrate uptake for both gas transfer systems. It can be seen that for each growth test, nitrate ions were depleted by the sixth day of growth for both gas transfer systems. This is expected as Figure 4-12 shows nearly identical algae production between systems (and therefore similar nitrate uptake) and generally algae will accumulate and store nitrate and can continue to grow after depletion, as both cultures continued growth for 3 or 4 days afterwards. This means that cultures likely reached density due to nitrate starvation and perhaps light limitation.



**Figure 4-13:** Nitrate uptake during algae growth for both gas transfer systems (100% CO<sub>2</sub>) (n=3, +/- standard error)

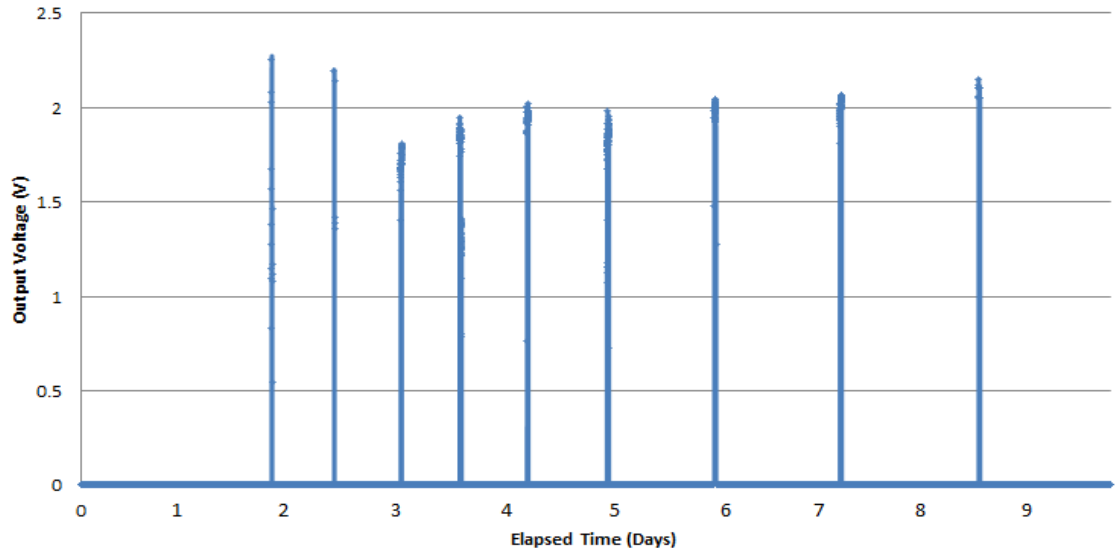
Figure 4-14 demonstrates how the carbon to nitrogen ratio in the algal biomass increases over time for both cultures. This again indicates that the algae were likely nitrogen starved at the end of growth meaning a ceiling in biomass was reached (i.e. the maximum cell density afforded by the growth environment). Also, note the consistently higher C:N for the HFM culture compared with the diffuser, especially at the end of the growth period. If the nitrogen stores were depleted for both cultures by the last day of growth as observed in Figure 4-13, then a higher C:N in the HFM culture could only be obtained with an increase in carbon to the culture compared with the diffuser culture.



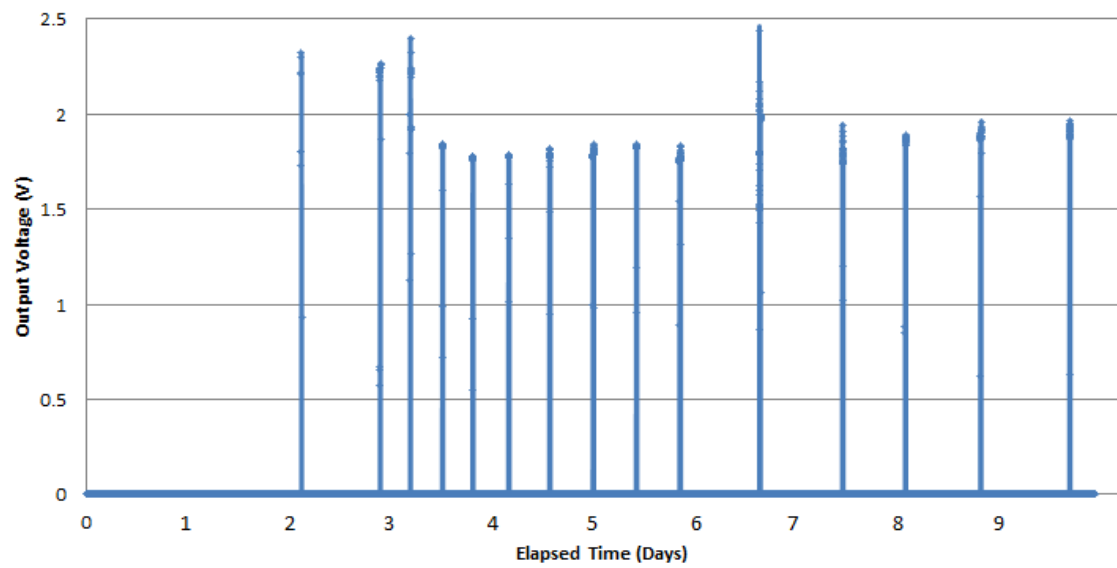
**Figure 4-14:** Carbon to nitrogen ratio in algal biomass for both gas transfer methods over time (100% CO<sub>2</sub>) (n=3, +/- standard error)

#### 4.4 Microalgal Gas Sequestration, 100% CO<sub>2</sub>

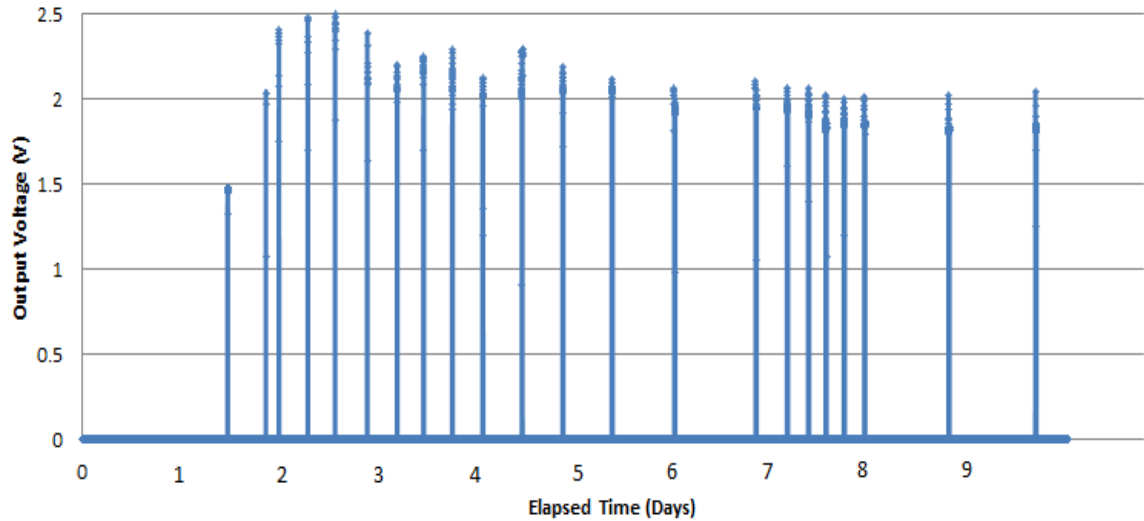
Figures 4-15 through 4-17 show the total CO<sub>2</sub> delivery to the cultures. Note the prolonged period of inactivity in gas delivery at the beginning of each test which matches the lag period in algal growth in Figures 4-6 to 4-8. Once algae production entered the exponential phase, gas delivery began to increase in frequency to match the biological carbon demand. As the cultures began to reach maximum density, demand for CO<sub>2</sub> decreased so gas delivery became more infrequent. Using the calibration curve in Figure 3-2, total CO<sub>2</sub> delivery can be determined by integrating the trends in Figures 4-15 through 4-17 and correcting for density factor.



**Figure 4-15:** On-demand CO<sub>2</sub> delivery to cultures (100% CO<sub>2</sub>), Test 1

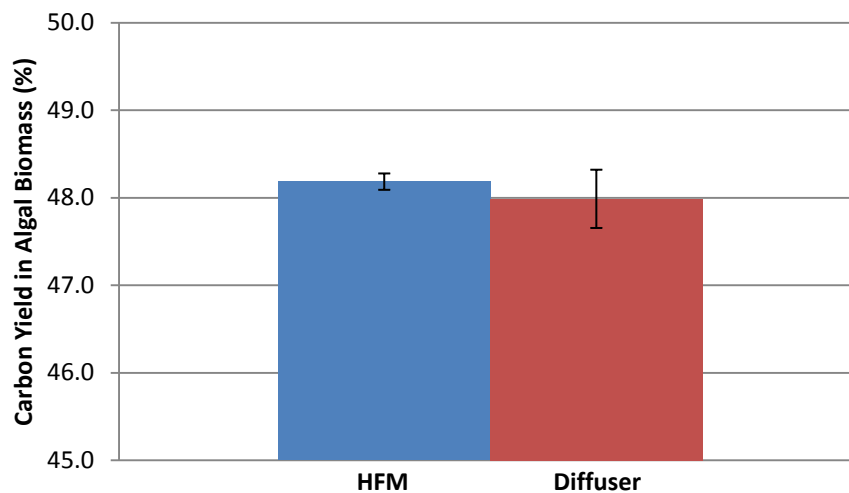


**Figure 4-16:** On-demand CO<sub>2</sub> delivery to cultures (100% CO<sub>2</sub>), Test 2



**Figure 4-17:** On-demand CO<sub>2</sub> delivery to cultures (100% CO<sub>2</sub>), Test 3

Figure 4-18 gives the results of biomass carbon analysis in the final day of growth for each test. Carbon yield is nearly identical for both gas transfer systems. Knowing total carbon sequestered by the algae, a mass balance can be performed to determine sequestration efficiency by both gas transfer methods. Table 4-6 gives the results for sequestration efficiency by gas transfer method for each test.



**Figure 4-18:** Carbon yield in algal cultures for both gas transfer systems (100% CO<sub>2</sub>) (n=3, +/- standard error)

From Table 4-6 a trend can be observed that carbon sequestration is consistently more efficient with the hollow fibre membrane gas transfer system over the diffuser system.



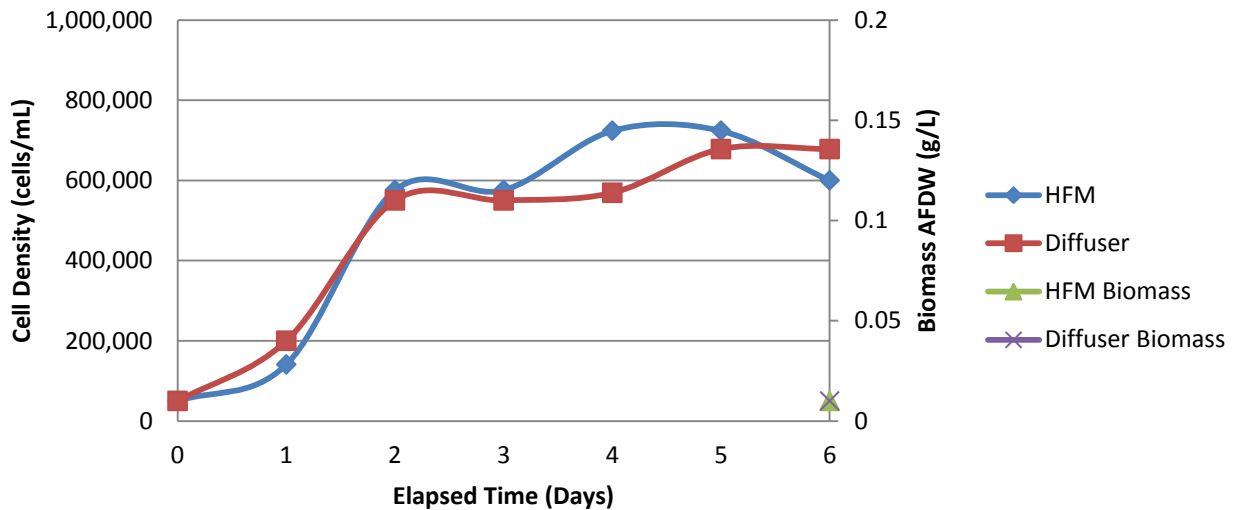
This is in good agreement with the literature reviewed in Chapter 2. With increased delivery of CO<sub>2</sub> gas, sequestration efficiency goes down likely due to the fact that the pH gas control did not match algae growth as well and the extra deliveries of gas were not as necessary for algae growth.

**Table 4-6:** Microalgal sequestration of carbon based on gas transfer method (pure CO<sub>2</sub>)

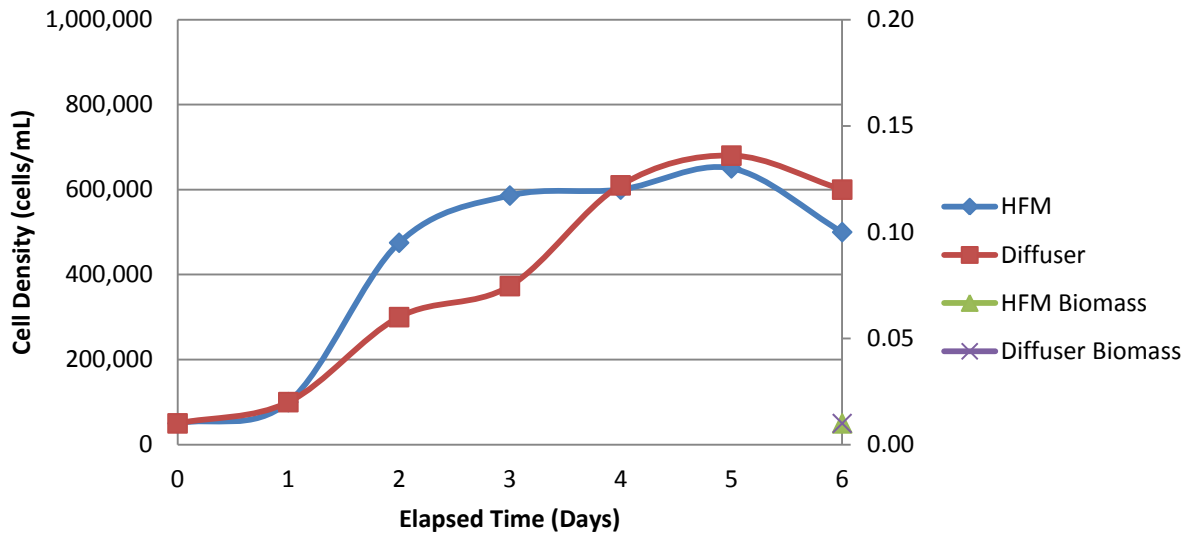
Test	Gas Transfer Method	Total Carbon		Sequestration Efficiency (%)
		Delivered to Cultures (g)	in Biomass (g)	
1	HFM	6.6	5.0	76
	Diffuser	6.6	4.9	74
2	HFM	6.5	4.3	66
	Diffuser	6.5	4.0	62
3	HFM	7.4	3.8	51
	Diffuser	7.4	3.4	46

#### 4.5 Microalgal Production, Flue gas

The results for algae production based on gas transfer method using the flue gas mixture summarized in Table 3-1 are displayed in Figure 4-19 and Figure 4-20. AFDW biomass samples were only taken at the end of each test as large samples were required to acquire enough biomass for analysis due to the lack of algae growth in these tests.



**Figure 4-19:** Algal cell count and biomass production for HFM and diffuser reactors (flue gas), Test 1

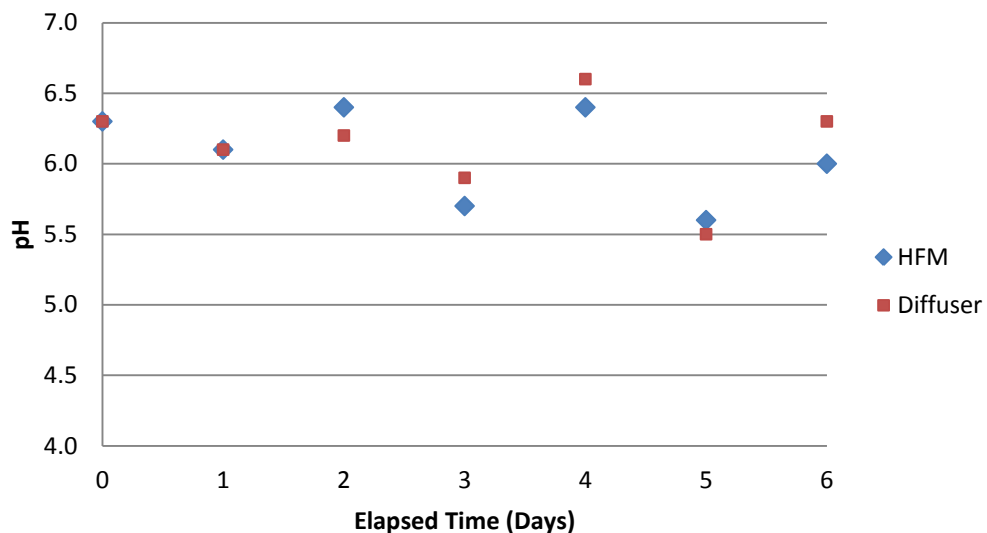


**Figure 4-20:** Algal cell count and biomass production for HFM and diffuser reactors (flue gas), Test 2

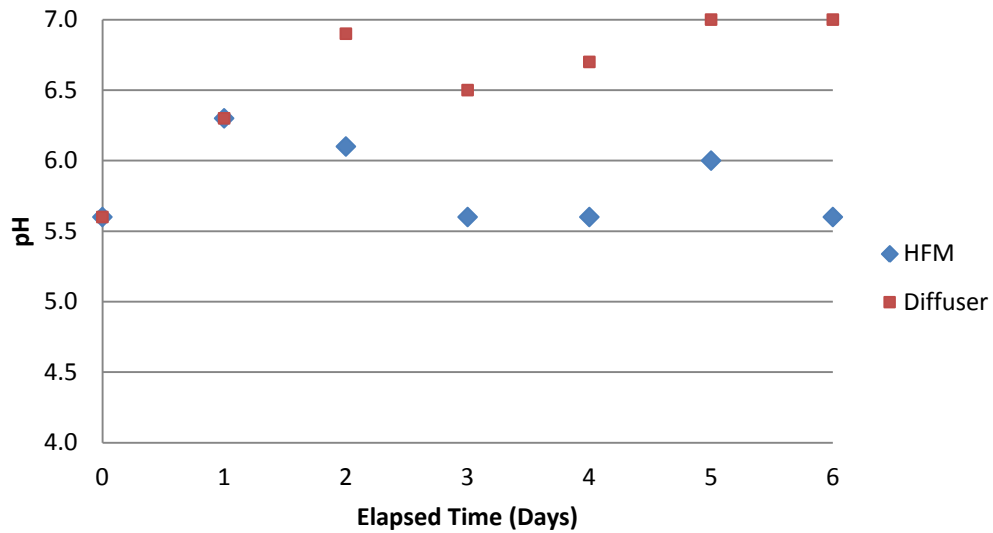
The results show a trend of higher growth productivity based on gas transfer method in favour of the membrane culture. This is more evident in test 2 where a 1.6 doublings per day to 1 for the membrane over the diffuser culture was achieved in the first 2 days of growth. The ceiling in algal cell density for the flue gas tests compared with 100% CO<sub>2</sub> show a greater than one order of magnitude difference in productivity in favour of the 100% CO<sub>2</sub> tests which means the NO<sub>x</sub> gas present in the flue gas mixture was likely not capable of sustaining algal growth as well as the nitrates present in the nutrient media for the 100% CO<sub>2</sub> tests. There is evidence that some algal growth occurred during the flue gas tests assuming the nitrogen stores in the inoculum was negligible and did not contribute as much towards growth. The algal inoculum source used for these tests had reached density and therefore should not have had significant nitrogen stored in its cells, meaning the fraction of nitrogen stored at the end of these tests would have been fixed from the NO<sub>x</sub> gas.

During these tests, the colour of each culture was a pale green/yellow as opposed to the dark green observed during the pure CO<sub>2</sub> tests with nitrate added. This is likely evidence of chlorosis occurring within the cultures meaning nitrogen was limited to the algae and the cells were not able to synthesize enough chlorophyll.

Due to the lower cell density in the flue gas tests compared to the pure CO<sub>2</sub> tests, the gas transfer method would not have any significant impact on algal productivity, as already concluded in section 4.3. The pH of solution for each gas transfer method during both flue gas tests are displayed in Figure 4-21 and Figure 4-22. The figures show a more obvious difference in pH between gas transfer methods throughout the growth tests, compared with the pure CO<sub>2</sub> tests. The pH of the hollow fibre membrane tank is consistently lower throughout most of the algae growth for both tests, especially in Test 2. This could be the efficiency of gas transfer coming into play as the diffuser would be entraining more CO<sub>2</sub>, NO<sub>x</sub>, and SO<sub>2</sub> out of solution due to the large fraction of nitrogen (which is highly insoluble in water) present in the gas mixture. The large nitrogen bubbles could be essentially absorbing the more soluble gases and carrying them out to the surface. The membrane would be capable of diffusing the more soluble gas species across the membrane into solution while leaving the less soluble gases such as nitrogen to bubble off to the surface, effectively separating the nitrogen from the rest of the gas mixture so that it does not entrain the acid gases out of solution as easily as with the diffuser. Regardless of gas transfer efficiency however, it did not affect algae growth as the biological demand for the gases was limited.



**Figure 4-21:** pH of solution throughout algal growth (flue gas), Test 1



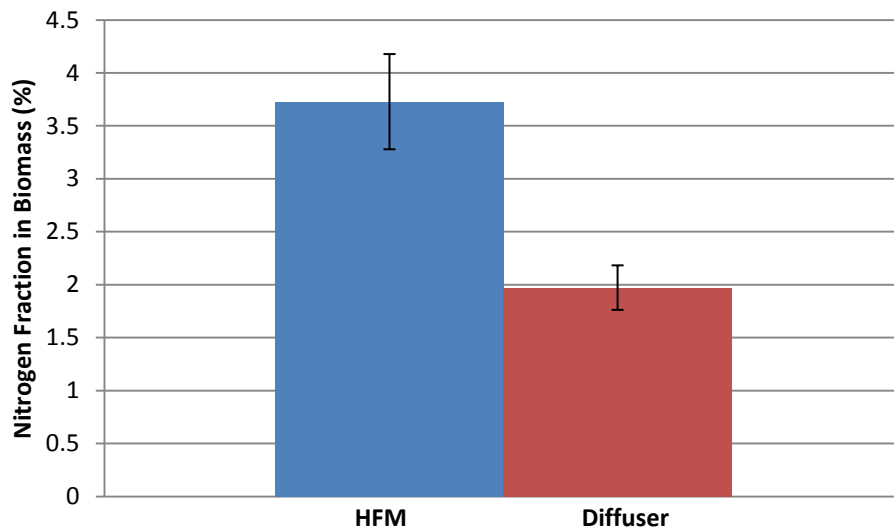
**Figure 4-22:** pH of solution throughout algal growth (flue gas), Test 2

Expectedly, the nitrate levels were negligible as no nitrates were added to either gas transfer bioreactor to study if  $\text{NO}_x$  gas would be capable of sustaining algal growth without nitrates present.

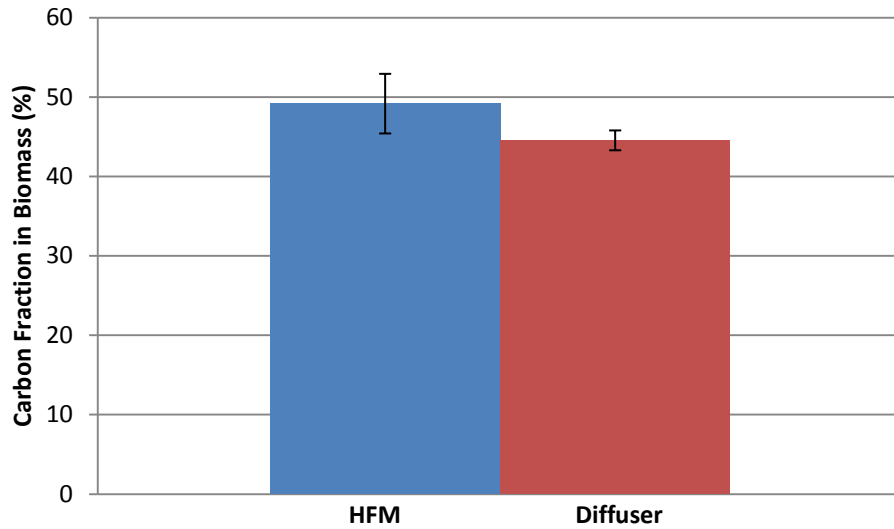
Figure 4-23 and Figure 4-24 give the nitrogen and carbon fractions in the algal biomass samples taken on the last day of growth for both flue gas tests. They show a near doubling in nitrogen in the membrane sample compared to the diffuser sample for both tests with biological carbon content in each test remaining relatively constant. This means that the hollow fibre membrane was capable of providing more  $\text{NO}_x$  gas to its culture compared with the diffuser, which agrees well with the literature. This is likely due to the lack of bubbles formed during gas transfer of  $\text{NO}_x$  into the system with the HFM allowing more of the gas to remain in solution longer than its diffuser counterpart, which allows the algae more time to fix the gas. Also, note the much higher overall C:N with both gas transfer systems compared with the pure  $\text{CO}_2$  tests in section 4.3. This is an expected outcome given the lack of algae production for both tanks as nitrogen was likely a limiting nutrient to the algae.

A higher C:N ratio could mean greater stores of lipids or carbohydrates in the algal cells which translates to potentially higher bio-diesel yields per cell. Therefore, using flue gas

without nitrates present in the media to stress the algae and sequester some of the effluent while simultaneously altering the macronutrient content of the algae to a higher lipid yield could be an attractive process to the bio-energy industry. Of course, overall oil yield would be less if grown this way as the algae is less productive with only  $\text{NO}_x$  to provide a nitrogen source for growth but if a two phase growing system is installed, like that proposed by (Huntley & Redalje, 2007), primary growth could take place in a nitrate rich environment and then when the cells begin to reach density, can be transferred to the flue gas environment where the lack of nitrogen to the cells increases their lipid yield, while also sequestering the  $\text{NO}_x$  pollution.



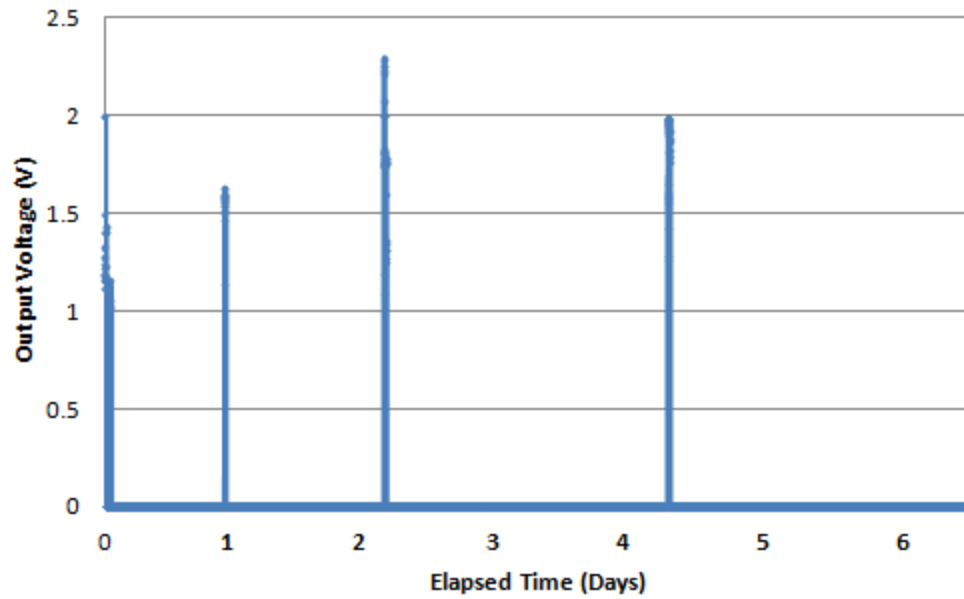
**Figure 4-23:** Nitrogen analysis for both gas transfer methods on the last day of growth using flue gas (n=2, +/- standard error)



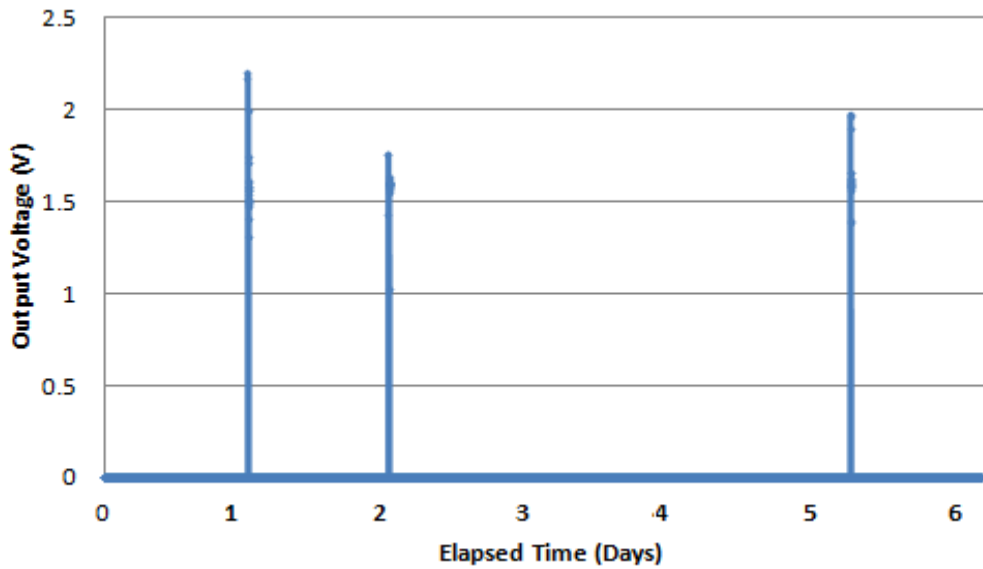
**Figure 4-24:** Carbon analysis for both gas transfer methods on the last day of growth using flue gas (n=2, +/- standard error)

#### 4.6 Microalgal Gas Sequestration, Flue gas

Figure 4-25 and Figure 4-26 show flue gas delivery to the cultures for both tests. Gas delivery frequency was much lower with the flue gas tests than for the pure CO<sub>2</sub> tests as the cultures did not grow as well without the nitrates available to them. However, the fact that there was gas delivery to each bioreactor and some growth did occur (Figure 4-19 and Figure 4-20) means that some sequestration of CO<sub>2</sub> and NO<sub>x</sub> was possible. Also, note the more frequent call for gas delivery (i.e. the first 3 deliveries) in Figure 4-25 corresponds with the most pronounced growth in algal culture from Figure 4-19, meaning the NO<sub>x</sub> (and CO<sub>2</sub>) appears to be supporting limited growth of the cultures.



**Figure 4-25:** On-demand gas delivery to cultures (flue gas), test 1



**Figure 4-26:** On-demand gas delivery to cultures (flue gas), test 2

Given the total CO<sub>2</sub> delivered to each system and the fraction of carbon in the algal cells, the sequestration efficiency of both gas transfer methods for the flue gas was calculated and tabulated in Table 4-7. Overall carbon sequestration was not as impressive for the

HFM compared with the diffuser as observed in the pure CO<sub>2</sub> tests. However, given the comparatively low algal cell density the cultures would probably have not needed as efficient gas transfer as the biological demand for carbon was much lower for these tests as compared to when the cells reached density in the pure CO<sub>2</sub> tests.

**Table 4-7:** Microalgal sequestration of carbon based on gas transfer method (flue gas)

Test	Gas Transfer Method	Total Carbon		Sequestration Efficiency (%)
		Delivered to Cultures (g)	Total Carbon in Biomass (g)	
1	HFM	0.57	0.19	33
	Diffuser	0.57	0.16	28
2	HFM	0.23	0.16	70
	Diffuser	0.23	0.16	70

#### 4.7 Summary

The hollow fibre membrane used in this research was able to consistently provide greater absorption of CO<sub>2</sub> into water compared with a bubble diffuser for both the 5% CO<sub>2</sub> enriched air and 24% CO<sub>2</sub> flue gas mixtures. Although the mass transfer coefficient was greater for the bubble diffuser, the volumetric coefficient was greater in the case of the membrane. This agrees with previously established literature (Carvalho & Malcata, 2001) that due to the effectively higher mass transfer area the membrane provides over the diffuser, it is capable of transferring more CO<sub>2</sub> into solution as less gas is lost to the atmosphere due to the absence of bubbles formed during transfer.

Microalgal production was not affected by gas transfer method except at the end of growth where CO<sub>2</sub> demand was greatest. For each test with the 100% CO<sub>2</sub> mixture and nitrates added in solution, dense cultures of greater than 0.2 g dried algal biomass/L water were achieved with increasing C:N ratios in the biomass for both gas transfer methods; an expected outcome given the depletion of nitrates (the sole source of nitrogen to the cultures for these tests) as the cultures progressed in density. Carbon sequestration was consistently higher for the membrane cultures given the slight increase in biomass production at the end of each run.



For the flue gas tests with no nitrates added, algal growth was limited for both gas transfer methods to approximately 0.01 g/L dried biomass and chlorosis appeared in both cultures due to a nitrogen deficiency. However, the C:N ratio for biomass from each gas transfer method showed a near doubling in C:N for the diffuser culture versus the membrane culture for both tests carried out. This likely means that the NO<sub>x</sub> gas in the mixture (i.e. the only source of nitrogen to the biomass), although not capable of supporting as dense growth as nitrates in the previous tests, was more efficiently sequestered by the membrane transfer system. This was likely due to the increased retention time in solution for the NO to oxidize to NO<sub>2</sub>, a more soluble gas, and be fixed by the algae (Nagase, et al., 1997).

## Chapter 5: Conclusions

Increasing CO<sub>2</sub> pollution will have to be mitigated to avoid further damage to the planet's ecosystems. Biological mitigation through microalgae is a promising option but that which still has limitations. Microalgal production on a large scale offers multiple technical challenges that must be overcome including limited area for production, access to properly sterilized water, and the costs associated with parasitic power used for processing (i.e. dewatering, lighting etc).

Efficient gas transfer in microalgal production remains a problem in terms of a carbon pollution mitigation strategy. Currently, CO<sub>2</sub> is bubbled into solution in most algal production systems which offers low retention of carbon in solution where most of it will be off-gassed into the atmosphere before it has the chance to be fixed by the autotrophic organisms. Several researchers have shown that hollow fibre membranes can offer an effectively higher mass transfer efficiency of gas into solution compared with sparging. This is due to the larger mass transfer area over spargers allowing a greater quantity of gas to be dissolved into solution with limited bubbling and less gas lost to the atmosphere. This has implications for using microalgae as a biological mitigation strategy for carbon pollution as the CO<sub>2</sub> emitted by stationary operations needs to be retained in solution long enough for fixing by the algae and not lost to the atmosphere, as is the case with spargers.

There is evidence that microalgae can also sequester other polluting gases such as NO<sub>x</sub> which makes it an attractive pollution mitigation strategy. Previous research has shown that decreasing the bubble size of NO<sub>x</sub> transferred into algal solution increases its sequestration efficiency.

The research goals of this thesis built upon this literature in that there appears to have been limited effort to study the effect of using hollow fibre membranes in sequestering NO<sub>x</sub> and CO<sub>2</sub> via microalgae compared with a standard bubble diffuser, these being the objectives of this thesis.

## **5.1 Objectives Achieved**

The overall objective of this thesis was to determine if a hollow fibre membrane deployed in microalgal culture could provide greater sequestration efficiency of flue gas (i.e. CO<sub>2</sub> and NO<sub>x</sub>) compared with a sparging device (a diffuser). This objective was achieved as the results show that NO<sub>x</sub> gas when used as the sole nitrogen source to a microalgal culture will be more efficiently fixed by the algae if transferred into solution via HFM (this being determined by nitrogen fraction in biomass). This is likely due to the greater retention time in solution the NO<sub>x</sub> gas is afforded by the membrane compared with the diffuser allowing more time for fixing by the algae. In the pure CO<sub>2</sub> tests where nitrates were the primary source of nitrogen to the algae, there was also a consistent trend showing that carbon sequestration efficiency was higher for the HFM tank over the diffuser. This seemed to occur at the point where the algal cell density was greatest, which makes sense as the biological demand for carbon would then be maximized and the efficiency of gas transfer into solution would be more pertinent to maintaining growth.

## **5.2 Limitations of Research**

The flue gas used in the NO<sub>x</sub> sequestration tests was lab grade and not reflective of the typical flue gases encountered in practice that would include water vapour and ash particulate. Both these additions would surely hinder mass transfer in the membrane by fouling the micro-pores so they were not included in the gas mixture. In practice, an upstream unit operation would have to be installed to dry and filter the flue gas to remove these items before they reach the membrane.

Although the algae tests show trends that the membrane is capable of superior gas sequestration for both CO<sub>2</sub> and NO<sub>x</sub> compared with the bubbling diffuser, a larger sample size will be required to establish any statistical significance in these findings. The calculation of the total NO<sub>x</sub> sequestration efficiency by the algae cultures was not capable with the concentrations of gas and quality of gas flow sensor used in this

experiment however the relative change in nitrogen stores by the algae based on gas transfer method allowed for a comparative efficiency between transfer methods.

### **5.3 Future Work**

Given the slight increase in efficiency in carbon sequestration by the hollow fibre membrane tank once the algal culture reached its highest density and biological carbon demand was maximized, repeating these experiments in a continuous, stable culture where a dense biomass concentration could be maintained (as opposed to the batch culture method used in this thesis) might improve sequestration efficiency even more. With a consistent biomass concentration, the approximate carbon and nitrogen requirement for the culture could be calculated and delivery of gas to the culture could be better controlled to maximize microalgal sequestration ability. Further investigation into the effects of stressing the algal cells with flue gas and the effects it may have on the bio-oil yield of the cells should also be done. The bio-oil yield per cell may increase substantially and if combined with a two phase growth system, overall bio-oil production could be increased.

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