Efficient CO₂ delivery from flue gas to microalgae ponds through a novel membrane system

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Abstract

Microalgae have great yet relatively untapped potential as a highly productive crop for production of animal and aquaculture feed, biofuels, and nutraceutical products. Compared to conventional terrestrial crops they have a very fast growth rate and can be produced on non-arable land. However, technological and scientific advances are required for the potential to be properly realised.

During microalgae cultivation, carbon dioxide (CO₂) is supplied as the carbon source for photosynthesising microalgae. The traditional strategy is to directly bubble CO₂ gas into photobioreactors or microalgae ponds. However, most CO₂ is lost into the atmosphere. Several technologies, such as microbubbles, porous membrane spargers or non-porous membrane contactors, have been applied to reduce the CO₂ losses. However, these CO₂ delivery technologies cannot eliminate the energy associated with the compression and transportation of CO₂.

In the present work, a novel system, consisting of chemical absorption, membrane separation and microalgae cultivation, was demonstrated to capture and transport CO₂ from flue gas to microalgae. Firstly, the chemical solvents captured CO₂ from flue gas. The CO₂ loaded solvents are then pumped through the tube side of hollow fibre polydimethylsiloxane (PDMS) membranes. CO₂ in the solvents diffuses through the membrane to the microalgae medium. The lean solvents are recycled back to capture further CO₂. With this system, CO₂ can be efficiently delivered to microalgae without any CO₂ loss. It can reduce energy requirements for the compression and transportation of CO₂, and avoid energy penalty for the regeneration of solvents as incurred in the conventional chemical absorption process.

Chemical solvents studied in the current work were potassium carbonate (K₂CO₃), monoethanolamine (MEA) and potassium glycinate (PG). They were studied in combination with a marine strain of *Chlorella* sp. and exhibited different performance. Potassium carbonate with CO₂ loadings (moles of CO₂ absorbed per mol solvent) of 0.2, 0.5 and 0.7 accelerated the growth of marine strain *Chlorella* sp. compared to the control (only atmospheric CO₂). MEA with a CO₂ loading of 0.5
improved the growth, however, with a loading of 0.2, growth was inhibited. PG with a CO₂ loading of 0.5 improved the growth of Chlorella sp., whereas with a loading of 0.2, growth was similar to that of the control.

No apparent solvent leakage was observed when K₂CO₃ was used in the combined system. However, MEA, especially with the loading of 0.2, was shown to pass through the PDMS membrane into the microalgae medium. The MEA permeation was shown to seriously impair the growth of the Chlorella sp. While a relatively minor permeation was also observed for PG, a toxicity test showed that the small PG leakage did not inhibit the growth of the microalgae, but instead could be utilized by the microalgae as a carbon and nitrogen source.

Different microalgae strains (freshwater Chlorella vulgaris, a marine strain of Chlorella sp. and marine Dunaliella tertiolecta) were also investigated in the novel system. All three strains presented enhanced growth with K₂CO₃, PG and MEA having CO₂ loadings of 0.5. Compared with a freshwater medium, a marine medium has higher CO₂ capacity due to the higher ionic strength. Additionally, the osmotic pressure difference resulted in less water loss for the marine medium than that for the freshwater medium.

The novel system has thus been verified to efficiently deliver CO₂ from flue gas to various microalgae strains through a PDMS dense membrane using different chemical solvents. It has established a novel method for CO₂ delivery to microalgae, reducing the energy for compression and transportation of CO₂. It represents important implications in CO₂ capture and utilization.
Declaration

This is to certify that:

1) this thesis comprises only my original work towards the PhD except where indicated in the Preface,

2) due acknowledgement has been made in the text to all other material used,

3) the thesis is less than 100,000 words in length, exclusive of tables, figures, bibliographies and appendices.

Qi Zheng

May 2017
Preface

Sections of this thesis have been published as the following journal article:


Aspen simulations of CO₂ solubility in solvents, osmotic pressures in media and solvents were kindly completed by Mr (Frank) Yue Wu.
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<tbody>
<tr>
<td>AMP</td>
<td>2-amino-2-methyl-1-propanol</td>
</tr>
<tr>
<td>AOM</td>
<td>Algae Organic Matter</td>
</tr>
<tr>
<td>CA</td>
<td>Carbonic anhydrase</td>
</tr>
<tr>
<td>CCMs</td>
<td>CO(_2) concentrating mechanisms</td>
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<tr>
<td>CO(_2)</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>DEA</td>
<td>Diethanolamine</td>
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<tr>
<td>DIC</td>
<td>Dissolved inorganic carbon</td>
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<tr>
<td>DHA</td>
<td>Docosahexaenoic acid</td>
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<tr>
<td>EDTA</td>
<td>Ethylenediaminetetraacetic acid</td>
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<tr>
<td>EPS</td>
<td>Extracellular polymeric substances</td>
</tr>
<tr>
<td>EPA</td>
<td>Eicosapentaenoic acid</td>
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<tr>
<td>EOR</td>
<td>Enhanced Oil Recovery</td>
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<tr>
<td>GHG</td>
<td>Greenhouse Gas</td>
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<tr>
<td>IPCC</td>
<td>Intergovernmental Panel on Climate Change</td>
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<tr>
<td>IOM</td>
<td>Intracellular Organic Matter</td>
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<tr>
<td>K(_2)CO(_3)</td>
<td>Potassium carbonate</td>
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<tr>
<td>MDEA</td>
<td>Methyldiethanolamine</td>
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<tr>
<td>MEA</td>
<td>Monoethanolamine</td>
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<tr>
<td>MF</td>
<td>Modified F medium</td>
</tr>
<tr>
<td>MOFs</td>
<td>Metal organic frameworks</td>
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<tr>
<td>PG</td>
<td>Potassium glycinate</td>
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<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
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<td>PSf</td>
<td>Polysulfone</td>
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<td>Abbreviation</td>
<td>Full Form</td>
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<tr>
<td>PUFA</td>
<td>Polyunsaturated Fatty Acids</td>
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<tr>
<td>PZ</td>
<td>Piperazine</td>
</tr>
<tr>
<td>RuBisCO</td>
<td>Ribulose bisphosphate carboxylase oxygenase</td>
</tr>
<tr>
<td>TC</td>
<td>Total carbon</td>
</tr>
<tr>
<td>TN</td>
<td>Total nitrogen</td>
</tr>
<tr>
<td>UNIDO</td>
<td>United Nations Industrial Development Organization</td>
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Chapter 1 Introduction

In 2015, fossil fuel consumption, including oil (33%), natural gas (24%) and coal (29%), accounted for 86% of primary energy consumption in the world, which is the largest contributor to greenhouse gas emissions [1]. As these non-renewable fossil fuels are limited resources and that impose a large carbon footprint, the world is looking to alternative, renewable sources of energy. While much progress has been made establishing technologies for renewable generation of stationary energy, for example wind and solar PV, replacement of fossil-based liquid transportation fuels is so far very limited. In 2015, biofuel consumption, including ethanol and biodiesel, only accounted for 0.6% of primary energy consumption in the world [1]. There is an enormous need and potential market for biofuel production.

Every year around $10^{11}$ ton of atmospheric carbon is biologically converted to biomass by photosynthetic organisms [2, 3]. Biofuels derived from this biomass are renewable and near-carbon neutral. They can compensate for the depleting non-renewable fossil fuel resources and reduce global carbon emissions. So-called ‘first generation’ biofuels are produced from established food crops, such as ethanol from sugarcane or corn, or biodiesel from oil crops [4-6]. However producing fuel from these crops creates competition for arable land, fertilizer and water that would otherwise be used for food production [6]. So-called ‘second generation’ biofuels are derived from either crop wastes or dedicated energy crops that can be grown on marginal land [5]. These are typically lignocellulose-based biomass from agricultural and forest harvesting residues, or high-yielding grasses [7]. However, these lignocellulosic feedstocks cannot meet the large demand for biofuel production and are still costly to convert to fuel [8]. Microalgae is regarded as the ‘third generation’ biofuel due to its ability to be grown at very high productivity on completely non-arable land [8, 9]. While this means that microalgae has promise as a feedstock for biofuel production, the costs are currently prohibitively high [10]. Technologies to reduce the cost of both producing and processing microalgal biomass are required.
Microalgae contain several nutrients, including proteins, amino acids, polyunsaturated fatty acids (PUFA), vitamins, antioxidants and pigments [11, 12]. Beside biofuel production, it has various applications [13, 14]. *Chlorella* and *Dunaliella* have been applied to produce health food in the form of tablets and capsules [14, 15]. They have also been regarded as important potential food supplements in the event of widespread food shortages [16]. In addition to human consumption, around 30% of global microalgae production is currently supplied for animal feed [12]. *Chlorella* has been applied as a dietary supplement (blended at approximately 5-10%) for chickens, with the rich protein, PUFA, antioxidants and pigments in the microalgal biomass shown to have beneficial effects on meat and egg quality [17]. Another important application is in aquaculture. The addition of microalgal products to fish feeds can improve the PUFA content of fish [13, 18]. The production of microalgae for the growing aquaculture industry has the potential to reduce the pressure on supplies of fish meal and fish oil that are straining the ocean environment. Some high value compounds can also be extracted from microalgae. For instance, microalgae can produce PUFA which higher plants and animals are lack the enzyme to create. The PUFA extracted from microalgae, such as DHA and EPA, can be added to infant formula and nutrient supplement [13, 14, 19]. Microalgae are rich in pigments. Natural β-carotene produced by *Dunaliella saline* is regarded as provitamin A [19], and astaxanthin extracted from *Haematococcus* is a necessary pigment for salmon and trout production [20].

Efficient large-scale microalgae production requires the addition of a carbon source to enhance microalgae growth. Current CO₂ sources are atmospheric air, commercial purified CO₂ or raw flue gas. Among these sources, 10540 Mt of CO₂ was emitted from large point sources, such as power plants, cement processing, the steel industry and gas production [21]. This means effective utilization of large points CO₂ emissions is an opportunity to reduce global greenhouse gas emissions.

In mass microalgae cultivation, simply relying on diffusion of CO₂ from the atmosphere will mean the culture are limited by carbon, rather than light availability, reducing productivity, and essentially wasting the solar energy resource (the available light falling on that area of land). To date the most common
strategy has been to bubble gases into the microalgae cultures [22]. However, in the process, approximately 50% to 90% of the CO₂ delivered to microalgae pond exits to the atmosphere [23], and around 80 to 530 MJ t⁻¹ CO₂ of energy is required for gas compression and transportation to open ponds [24-26]. As CO₂ has been estimated to account for over 50% of the raw material cost in microalgal cultivation [27], effective delivery of CO₂ to microalgae is vital for both efficient microalgae production and reduction of CO₂ emissions.

Instead of directly bubbling carbon dioxide gas, this thesis will investigate a novel technology that uses CO₂ loaded chemical solvents as the carbon source and a dense PDMS membrane to deliver CO₂ into microalgae ponds. The CO₂ loaded solvents are obtained from chemical absorption technology, which is one common strategy in the post-combustion capture process. The usage of CO₂ loaded solvents can also reduce the energy associated gas compression and transportation, and on the other hand, to avoid the energy penalty for solvent regeneration in the chemical absorption process.


Chapter 2 Literature review

The novel technology to be investigated in this thesis requires understanding of a number of different technical areas including carbon dioxide capture technology, chemical absorption, membrane separation, microalgae cultivation, CO₂ effects on microalgae growth and current CO₂ delivery technology. This chapter will review the relevant literature to establish the necessary contextual background for the thesis.

2.1 Carbon dioxide capture technology

Several strategies have been demonstrated for carbon dioxide capture processes, such as pre-combustion capture, oxy-fuel combustion capture and post-combustion capture [1]. Pre-combustion capture removes CO₂ before combustion and is usually used in an Integrated Gasification Combined Cycle (IGCC) power plant by modifying the water gas shift unit to incorporate a CO₂ separation component [2, 3] (Figure 2.1). In the pre-combustion capture process, the fossil fuel is firstly reformed with oxygen or water to form H₂ and CO syngas. Then the CO is shifted by steam to produce a mixture of CO₂ and H₂. The high CO₂ concentration and high feed pressure facilitates efficient separation of CO₂ from H₂. Commercial physical absorbents which do not rely on chemical reaction with CO₂, such as Selexol and Rectisol, have been applied to capture CO₂ in pre-combustion capture processes [4]. Potassium carbonate is also often used as a chemical solvent, in the well-known Benfield process [5].

![Figure 2.1 Pre-combustion capture process](image)

In oxy-fuel combustion, the strategy is to combust fossil fuel with pure O₂ (Figure 2.2) [6]. A gas separation unit at the front of the process removes N₂ from air to
obtain pure O$_2$. Then the fossil fuel combusts with a mixture of pure O$_2$ and recycled flue gas in the furnace. The exhausted flue gas has up to 90% CO$_2$ and low NO$_x$ concentration. This approach has been commercially utilized in Enhanced Oil Recovery (EOR) since 1982 [7]. The oxy-fuel combustion system includes an air separation unit, an oxy-fuel furnace, a flue gas recycle unit and a carbon dioxide capture unit. However, to retrofit the power plant, higher capital expenses are required [8].

Figure 2.2 Oxy-fuel combustion capture process

Instead of retrofitting the existing power plant, post-combustion capture is a common strategy used to capture CO$_2$ from a conventional pulverized coal power plant (Figure 2.3) [9]. In this case, the carbon dioxide capture unit is simply added downstream of the combustion furnace. Several technologies have been applied in post-combustion capture, such as chemical absorption, physical adsorption, membrane separation and cryogenic technology [10-17].

Figure 2.3 Post-combustion capture process

Physical adsorption processes can be classified as either temperature swing adsorption (TSA) or pressure swing adsorption (PSA), dependent upon the regeneration method used [18]. In TSA, the adsorbents capture CO$_2$ at low temperature and release it at high temperature. The high energy consumption for
cooling and heating gases and the long cycling times (hours or several minutes) limit TSA application at large scale \cite{19}. In PSA systems, absorbents adsorb CO$_2$ at high pressure and release it under low pressure or vacuum conditions. Compared with TSA, PSA has cycling times of minutes or seconds, making it more suitable for large scale implementation \cite{20}. Adsorbents, such as zeolites \cite{21,22}, carbon molecular sieves \cite{23} and metal organic frameworks (MOFs) \cite{14,24,25}, have been investigated for these physical adsorption process.

In cryogenic distillation, the gas components are cooled down and sequentially liquefied based on their boiling points \cite{26}. To avoid hydrate formation in the column, a dehydration unit is necessary prior to cryogenic distillation \cite{27}. As the CO$_2$ concentration of flue gas in post combustion capture process is only around 15% or less, the high energy consumption for compression and cooling of gases make it impractical for the post combustion capture process \cite{28}.

**2.2 Chemical absorption**

Chemical absorption has already been utilized in industry to capture CO$_2$ from natural gas for many years. The two main parts of a chemical absorption process are the absorber and desorber (Figure 2.4) \cite{29}. Flue gas emitted from the power plant is firstly pumped into the absorber, where a chemical (such as potassium carbonate or monoethanolamine) reacts with the CO$_2$ and forms a CO$_2$ rich solvent. This CO$_2$ rich solvent is regenerated in the desorber by increasing the temperature, and the CO$_2$ lean solvent is cycled back to the absorber. Purified CO$_2$ exiting from the desorber is finally compressed and transported for storage.
Chemical absorption is the closest to industrial implementation for post combustion carbon capture [4]. A variety of solvents have been proposed as candidates for this process. In solvent selection, several criteria have to be considered [30]. Solvents should have high absorption capacity and fast reaction kinetics with CO$_2$, which can reduce the absorbent volume and absorber size and thus minimize the capital costs of the carbon capture system [29-31]. In chemical absorption processes, the heat supplied to the desorber is the greatest contributor to the operating costs, due to its high energy demand [30]. For instance, the energy penalty for regenerating 30 wt% MEA is approximately 4.2 GJ t$^{-1}$ CO$_2$ [4], which may account for 10% to 40% of the energy output of the power plant [32]. So solvents requiring less regeneration energy are preferred in these applications. Some issues, such as thermal and chemical stability and solvent volatility, also need to be addressed [30]. Solvents, which are resistant to impurities in the flue gas, can tolerate high temperature and with low vapour pressure, can reduce the solvent makeup required and this also helps to reduce operation cost [33]. Other environmental and health issues, such as solvent toxicity and the by-products produced in regeneration are important aspects in solvent selection [34]. Based on
the above criteria, different solvents have been proposed and investigated in recent decades.

2.2.1 Alkanolamines

The most widely used class of solvents is the alkanolamines. According to the number of hydrogens bonded to the nitrogen, alkanolamines can be classified as primary, secondary and tertiary amines\[16\]. Primary and secondary alkanolamines react with CO\(_2\) to form carbamates via a zwitterion mechanism \[35\]. CO\(_2\) firstly reacts with the alkanolamine (AmH) to form a zwitterion (Reaction 2.1), which is then deprotoned by a base (which can be another alkanolamine molecule or water, Reaction 2.2, 2.3). The overall reaction is shown as Reaction 2.4.

\[
\begin{align*}
\text{CO}_2 + \text{AmH} & \leftrightarrow \text{AmH}^+\text{COO}^- \\
\text{AmH}^+\text{COO}^- + \text{AmH} & \leftrightarrow \text{AmCOO}^- + \text{AmH}_2^+ \\
\text{AmH}^+\text{COO}^- + \text{H}_2\text{O} & \leftrightarrow \text{AmCOO}^- + \text{H}_3^+\text{O} \\
\text{CO}_2 + 2\text{AmH} & \leftrightarrow \text{AmCOO}^- + \text{AmH}_2^+ 
\end{align*}
\]

Tertiary alkanolamines do not directly react with CO\(_2\). Rather, these just work as a base catalyst to promote CO\(_2\) hydration to produce bicarbonate \[35\].

\[
\text{CO}_2 + R_3\text{N} + \text{H}_2\text{O} \leftrightarrow R_3\text{N}^+\text{H} + \text{HCO}_3^- \tag{2.5}
\]

Monoethanolamine (MEA) is the most commonly used carbon dioxide capture alkanolamine \[31, 36\], due to its fast reaction rate with CO\(_2\). SaskPower has operated the Boundary Dam project in Canada since October 2014 where one million tons of CO\(_2\) is captured using MEA \[4, 36, 37\]. However, applying MEA to CO\(_2\) capture has some disadvantages. As a primary alkanolamine, 2 moles of MEA are required by 1 mole CO\(_2\), which results in a lower absorption capacity. MEA is volatile and easily degraded by oxygen and impurities (NO\(_x\) and SO\(_x\)) in the flue gas, or with high temperatures in the desorber \[15\]. As solvent loss occurs via evaporation and these degradation reactions, 1.4-1.6 kg MEA t\(^{-1}\) CO\(_2\) captured is needed as make-up in the system \[38, 39\]. Some carcinogenic bi-products (such as nitrosoamines) may be released in the degradation process \[40-42\]. Inhibitors such as ethylenediaminetetraacetic acid (EDTA) and N,N-bis(2-hydroxyethyl)glycine have
been proved to be efficient to reduce MEA degradation\(^{[43]}\). Other additives such as carboxylic acid can be used to reduce the corrosive nature of MEA\(^{[44]}\).

Other alkanolamines such as Diethanolamine (DEA), 2-amino-2-methyl-1-propanol (AMP) and methyldiethanolamine (MDEA), piperazine (PZ) have also been demonstrated as effective CO\(_2\) capture solvents \(^{[45-49]}\). Mixed amine-based solvents have also been studied, for instance, a mixture of MEA/MDEA can reduce the regeneration energy and maintain chemical stability \(^{[36]}\).

### 2.2.2 Potassium carbonate

Hot potassium carbonate was firstly demonstrated as the Benfield process \(^{[50]}\) in 1954 for gas purification, and recently has been developed for carbon dioxide capture from the flue gases of power plants such as in the UNO MK3 process in Australia \(^{[51]}\). The overall reaction is described as follow,

\[
\text{CO}_2 + \text{K}_2\text{CO}_3 + \text{H}_2\text{O} \leftrightarrow 2\text{KHC}_3\text{O}_3
\]  

(2.6)

Potassium carbonate needs less energy to be regenerated than the alkanolamines. A study by Anderson et al. \(^{[52]}\) suggested an energy penalty of 2-2.5 GJ t\(^{-1}\) CO\(_2\) for K\(_2\)CO\(_3\) regeneration, which is approximately half that required for MEA (4.2 GJ t\(^{-1}\) CO\(_2\)). K\(_2\)CO\(_3\) is a cheap inorganic solvent that is able to be used at high temperature without degradation \(^{[53]}\). It is less volatile than MEA and is environmentally benign. However, K\(_2\)CO\(_3\) has relatively slow reaction kinetics compared with other solvents. In order to improve reaction rate, different reaction promoters such as piperazine \(^{[54]}\), boric acid\(^{[55]}\), amino acid \(^{[56]}\) and carbonic anhydrase (CA)\(^{[57]}\) have been investigated. Thee et al. \(^{[58]}\) showed that the addition of 10 wt% MEA can achieve a 45-fold acceleration compared with simple 30 wt% potassium carbonate. Other practical issues still need to be addressed in the deployment of this solvent. K\(_2\)CO\(_3\) may react with impurities in the flue gas (NO\(_x\) and SO\(_x\)) to produce potassium nitrate and potassium sulphate \(^{[29]}\). In addition, at high CO\(_2\) loading potassium bicarbonate may precipitate, and these salts may block pathways in the absorber column \(^{[29]}\).
### 2.2.3 Amino acid salts

Amino acid salts are also promising alternative solvents to capture carbon dioxide. These amino acid salts have fast reaction kinetics with CO₂ and good chemical and thermal stability [59]. No environmental issues, such as toxic by-products during degradation, have been observed in this application. The negligible vapour pressure of amino acid salts can avoid solvent losses during regeneration [60]. However, amino acid salts usually are more expensive than alkanolamines.

In aqueous solution, at low pH, amino acids exist in a protonated form HOOC-R-NH₃⁺. At neutral to mildly acidic pH, the amino acids are in the neutral form -OOC-R-NH₂⁺, and at high pH, they exist in the deprotonated base form -OOC-R-NH₂⁻ [61]. In order to increase amino acid solubility, the amino acids are usually neutralized with potassium hydroxide or sodium hydroxide to form amino acid salts as Reaction 2.7. Amino acid salts have similar reactions with CO₂ as the primary and secondary alkanolamines. Carbon dioxide firstly reacts with -OOCRNH₂⁻ to form a zwitterion (Reaction 2.8), which is then deprotoned by a base (which can be another alkanolamine molecule or water, Reaction 2.9). The overall reaction is shown in Reaction 2.10. Two moles of amino acid salts react with 1 mole of CO₂ to produce carbamate, via a zwitterionic mechanism.

\[
\text{−OOCRNH}_2^+ + \text{OH}^- \leftrightarrow \text{−OOCRNH}_2 + \text{H}_2\text{O} \quad (2.7)
\]
\[
\text{−OOCRNH}_2 + \text{CO}_2 \leftrightarrow \text{−OOCRNH}_2^+ \text{COO}^- \quad (2.8)
\]
\[
\text{−OOCRNH}_2^+ \text{COO}^- + \text{−OOCRNH}_2 \leftrightarrow \text{−OOCRNHCOO}^- + \text{−OOCRNH}_3^+ \quad (2.9)
\]
\[
\text{CO}_2 + 2\text{−OOCRNH}_2 \leftrightarrow \text{−OOCRNHCOO}^- + \text{−OOCRNH}_3^+ \quad (2.10)
\]

The CO₂ absorption kinetics and physicochemical properties such as density, viscosity and CO₂ solubility of solutions of several amino acid salts has been investigated to provide fundamental information for industrial implementation. These salts include glycine, taurine, alaninate, prolinate, sarcosine, threonate and arginine [59, 60, 62-65]. In industry, the use of amino acid salts has been demonstrated for carbon dioxide capture as the BASF Puratreat Solvent and through Siemens PostCap™ Technology [66]. The latter has been shown to consume regeneration energy of 2.7GJ t⁻¹ CO₂, almost 60% of MEA solvents.
2.2.4 Ammonia

The Chilled Ammonia process (CAP) is another alternative solvent to capture CO$_2$. The overall reaction of CAP is

$$\text{CO}_2 + \text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4\text{HCO}_3$$ \hspace{1cm} (2.11)

Ammonia has high CO$_2$ absorption capacity and can resist oxidative degradation. However, in order to prevent ammonia loss, the operation temperature of the absorber should be limited at a range of 0 to 20°C \cite{67}. Extra energy is consumed to maintain this low temperature \cite{16}.

2.3 Membrane Technology for CO$_2$ separation

Membrane technology has been applied in industrial processes for water filtration and gas purification in decades \cite{68, 69}. In recent years, membrane technologies have attracted more attention for CO$_2$ separation. Membrane technology can be economically competitive with other technologies, for instance chemical absorption, as it avoids the energy penalty associated with solvent regeneration and can be easily scaled up \cite{70}. A brief introduction about current gas separation membrane and membrane gas absorption technology is reviewed here.

2.3.1 Gas separation membranes

Based on the molecular mass of the gas and the membrane pore diameter, different gas diffusion mechanisms can occur in gas separation (Figure 2.5) \cite{71}. For a porous membrane, Knudsen diffusion (Figure 2.5A) occurs, which relies on the different pathways taken by molecules due to their molecular collisions with pore walls \cite{71}. Molecular sieving (Figure 2.5B) is based on size exclusion; large gas molecules will not be able to enter the pores at all, and gases with smaller kinetic diameters can move faster through the pores than those with larger diameters \cite{71}. The solution diffusion mechanism (Figure 2.5C) can describe the gas separation within nonporous or dense membranes \cite{71}. In this case, the CO$_2$ gas dissolves at the surface of the dense membrane, then diffuses through the membrane material as a consequence of the driving force caused by the chemical potential. CO$_2$ desorbs at the opposite surface of the dense membrane \cite{72}. 

The important parameters that define the separation performance of a membrane are permeability and selectivity. Permeance is the gas flux through a certain membrane area and under a specific pressure difference, expressed in unit of GPU (Equation 2.12) \[ \text{GPU} = \frac{10^{-6}}{\frac{\text{cm}^3_{\text{STP}}}{\text{cm}^2 \cdot \text{s} \cdot \text{cmHg}}} \]

Here, cm$^3_{\text{STP}}$ is standard cubic centimetre at standard temperature (273.15 K) and under standard pressure (1 bar)

- $Q$: Gas permeation rate through the membrane, cm$^3_{\text{STP}}$ s$^{-1}$
- $A$: Membrane surface area, cm$^2$
- $\Delta p$: Pressure difference across the membrane, cmHg
\[ \text{Permeability} = \text{Permeance} \times \text{Thickness} \]  
\[ 1 \text{ Barrer} = 10^{-6} \text{ cm}^3_{\text{STP}} \text{ cm} \text{ cm}^{-2} \text{ s cmHg} \]

\[ \alpha = \frac{P_A}{P_B} \]  
(2.14)

\( \alpha \) Selectivity dimensionless
\( P_A \) Permeability of gas A barrer
\( P_B \) Permeability of gas B barrer

Several membranes have been investigated to separate CO\(_2\) from other gases. Inorganic membranes, for instance zeolite based membranes, are inert and can tolerate high temperatures, but inorganic membranes are usually more expensive, limiting their application [75]. Now more research is focused on polymeric membranes, such as cellulose acetate, polycarbonates, polyimide and polysulfone and PDMS [73, 76-79]. Polyimide is a widely used membrane material. It has excellent thermal and chemical stability, and provides good CO\(_2\) permeability and selectivity [80, 81]. Cellulose acetate and polysulfone have reasonable CO\(_2\) permeability and have been implemented more broadly in industrial processes due to their cheap price and resistance to impurities [76, 78]. PDMS is a rubbery polymeric membrane, it has high CO\(_2\) permeability at a range of 2600 to 5400 barrer [82-88], but lower selectivity.

There are other ways to improve membrane performance. A facilitated transport membrane has a carrier agent embedded in the membrane and a gas such as CO\(_2\) reacts reversibly with the carrier agent [89, 90]. In a mixed matrix membrane inorganic particles are added into a polymeric membrane to increase permeability and selectivity [91, 92].
2.3.2 Membrane gas absorption technology

In recent years, membrane gas absorption (MGA) technology has been proposed to capture CO$_2$. In MGA, chemical solvents provide the gas selectivity performance. The membrane provides an interface, preventing solvents coming into direct contact with gases, and eliminating the flooding or foaming in typical absorption column operation [93, 94]. The high interfacial contact area provided by the membrane can reduce column size and capital costs. However, membrane fouling may block the pores and membrane wetting may decrease the gas mass transfer efficiency [95]. During the operation, membrane degradation may affect membrane durability and thus operation costs.

Membranes can be manufactured as flat sheets or in a hollow fibre format. The flat sheet is assembled into a spiral wound module [96]. Several fibres are bundled and combined to form a hollow fibre membrane contactor with a higher membrane area to volume ratio [94]. In 1985, Qi and Cussler [97, 98] were the first to introduce sodium hydroxide into a hollow fibre membrane contactor to absorb CO$_2$. The chemical reaction between CO$_2$ and solvents can suppress the mass transfer resistance on the solvent side and increase CO$_2$ mass transfer. Sodium hydroxide, MEA, amino acid salts, amines and K$_2$CO$_3$ have been investigated as chemical absorbent solvents in hollow fibre membrane contactors [97-102].

The mass transfer in gas liquid membrane contactors can be described by the film theory with three steps (Figure 2.6) [103],

1) Gas transfer from the bulk gas to the membrane surface,
2) Gas diffusion through the membrane,
3) Gas transfer from the membrane-liquid interface into the bulk liquid.
The resistances of gas absorption in a hollow fibre membrane contactor can be divided into three parts, the resistance of the gas side, the membrane, and the solvent side. The overall mass transfer coefficient is given by Equation 2.15,

\[
\frac{1}{K} = \frac{1}{K_g} + \frac{1}{k_m} + \frac{1}{mEk_l}
\]  

\begin{align*}
K &\quad \text{overall mass transfer coefficient} \quad \text{m s}^{-1} \\
K_g &\quad \text{mass transfer coefficient on the gas side} \quad \text{m s}^{-1} \\
k_m &\quad \text{mass transfer coefficient through the membrane} \quad \text{m s}^{-1} \\
k_l &\quad \text{mass transfer coefficient on the solvent side} \quad \text{m s}^{-1} \\
E &\quad \text{Enhancement factor} \quad \text{dimensionless} \\
m &\quad \text{Henry's law constant} \quad \text{dimensionless}
\end{align*}

The fluid dynamics of the membrane contactor on both the tube side and shell side can be generally expressed according to Equation 2.16:

\[
Sh \sim Re^a Sc^b f(\text{geometry})
\]  

Where \( Sh \) is the Sherwood number, \( Re \) is the Reynolds number, \( Sc \) is the Schmidt number. These dimensionless numbers are defined according to following Equations 2.17-19,
\[ Sh = \frac{k d_h}{D} \]  \hspace{2cm} (2.17)  

\[ Re = \frac{\rho \bar{u} L}{\mu} \]  \hspace{2cm} (2.18)  

\[ Sc = \frac{\mu}{\rho D} \]  \hspace{2cm} (2.19)  

And Graetz number used in the following expression, defined as Equation 2.20.

\[ Gz = Re Sc \frac{d_h}{l} \]  \hspace{2cm} (2.20)  

Where \( k \) is mass transfer coefficient \((m \cdot s^{-1})\), \( d_h \) is the hydraulic diameter of membrane contactor \((m)\), \( D \) is the gas diffusivity \((m \cdot s^{-2})\), \( \rho \) is the density \((kg \cdot m^{-3})\), \( u \) is the flow velocity \((m \cdot s^{-1})\), \( L \) is the effective length of the membrane contactor \((m)\), \( \mu \) is the dynamic viscosity \((kg \cdot m^{-1} \cdot s^{-1})\).

Depending on the design of the membrane contactor, correlations based on Equation 2.16 can describe the mass transfer coefficients of tube and shell sides.

The mass transfer coefficient for the tube side flow has been modelled using the Graetz-Leveque correlation \cite{94,106}:

\[ Sh = 1.62 Gz^{1/3} \]  \hspace{2cm} Gz > 4  \hspace{2cm} (2.21)  

Although the mass transfer of the shell side flow has not been fully understood, different correlations have been modified based on various operations \cite{94,106-109}:

\[ Sh = 1.25 \left( \frac{Re d}{l} \right)^{0.93} Sc^{0.33} \]  \hspace{2cm} (2.22) \hspace{1cm} Yang and Cussler \cite{106}  

\[ Sh = 8 \left( \frac{Re d}{l} \right) Sc^{0.33} \]  \hspace{2cm} (2.23) \hspace{1cm} Dahuron et al. \cite{107}  

\[ Sh = 0.019 Gz \]  \hspace{2cm} (2.24) \hspace{1cm} Wickramasinghe et al. \cite{109}  

\[ Sh = (0.53 - 0.56 \varphi) Re^{0.53} Sc^{0.33} \]  \hspace{2cm} (2.25) \hspace{1cm} Costello et al. \cite{108}  

Where \( \varphi \) is the packing density.
2.4 Technology for mass production of microalgae

Microalgae are by definition photosynthetic organisms, harnessing the energy from light to power cellular processes and to reduce inorganic carbon into organic carbon for biosynthesis. While microalgae can also utilise organic carbon sources either exclusively (heterotrophic growth) or in combination with photosynthesis (mixotrophic growth), photoautotrophic production is the most feasible method at a large scale as carbon dioxide is absorbed and solar energy is utilised. In heterotrophic production, microalgae utilise an organic substrate such as glucose as the carbon source in a bioreactor or fermenter [110, 111]. When grown heterotrophically, microalgae can achieve higher volumetric productivities and biomass concentrations, but contamination needs to be strictly controlled [112]. Mixotrophic production is the combination of photoautotrophic and heterotrophic production [113]. One example application is the mixotrophic growth of microalgae on organic carbon in wastewater [114-116]. Some microalgae can grow through either photosynthesis or organic substance utilisation. Photoautotrophic production is most widely used and investigated as it takes full advantage of the photosynthetic capabilities of microalgae. As the technology investigated in this thesis relates to the delivery of the inorganic carbon required for photosynthesis, the discussion here is based on photoautotrophic production.

Microalgae can be grown at large scale in lakes or lagoons [117], for instance *Dunaliella salina* plants located at Whyalla in South Australia [118, 119], or in artificial systems such as open raceway ponds and closed photobioreactors [120-122]. A raceway pond is a shallow pond configured as a loop, around which the algal cultures are circulated, typically using a paddle wheel (Figure 2.7) [123]. The 0.2-0.5m pond depth allows the microalgae to make use of natural sunlight. Nutrients (such as nitrate, phosphorus, trace metals) are introduced into the pond after the paddle wheel. As mass transfer of CO₂ from the atmosphere is insufficient to avoid C-limitation [118], purified CO₂ or air is usually injected into the pond through a sparger at the bottom of the pond [124]. The paddlewheel is operated to circulate and agitate the microalgae broth and nutrients [125]. A raceway pond has relatively low capital cost compared to closed systems [125] and in suitable locations can
maintain up to 25 g m$^{-2}$ d$^{-1}$ biomass productivity [126]. As the raceway ponds are open to the environment, production cultures may be contaminated by competitors or predators [127] and are influenced by various weather conditions, so only some specific species are suitable in this application. Examples of microalgae that can be grown in conditions which favour their growth over contaminants include, *Dunaliella* that can grow in high salinity conditions, *Spirulina* that can tolerate a high alkalinity medium and *Chlorella* that can grow under high nutrient conditions [128].

![Figure 2.7 Raceway pond](image)

Closed photobioreactors are a more costly alternative to open raceway ponds that have been designed to maintain a higher biomass concentration, achieve better gas agitation, high CO$_2$ mass transfer efficiency and higher illumination use efficiency [122]. In order to improve illumination efficiency different designs of photobioreactors have been explored, such as flat-plate photobioreactors, tubular photobioreactors and column photobioreactors. A flat-plate photobioreactor has a 10-25 mm light path [129, 130] and large surface area, maximizing illumination efficiency (Figure 2.8A). Compared with other photobioreactors, its structure is simple, making it easier to clean and to do maintenance. In column photobioreactors gas is injected from the bottom, which can result in good mixing and agitation of the microalgae (Figure 2.8B) [131]. Tubular photobioreactors are arranged as an array of transparent tubes (Figure 2.8C, D). A lot of modified
designs have been applied to further enhance illumination efficiency, such as horizontal tubular and helical tubular photobioreactors \cite{123, 132, 133}. Despite the potential advantages of closed photobioreactors over raceway ponds, the additional capital costs of these systems mean it is difficult for them to be cost competitive at large scale.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{photobioreactor_designs.png}
\caption{Photobioreactor designs}
\end{figure}

\subsection*{2.5 Provision of CO$_2$ to enhance microalgae growth}

Many factors (temperature, illumination, pH, nitrogen and carbon) may effect microalgae growth, which have been summarized in several review papers and research articles \cite{136-140}. The thesis will focus on the influence of CO$_2$ on microalgae growth.
2.5.1 The role of CO₂ in microalgae growth

CO₂ concentrating mechanisms (CCMs)

Microalgae convert CO₂ into reduced carbon that can be used for production of lipids and biomass through photosynthesis, for which the overall reaction can be summarised as follows [141]:

\[
CO_2 + H_2O \xrightarrow{\text{photons (light)}} [CH_2O]_n + O_2 \tag{2.26}
\]

Carbon is a fundamental compositional element of microalgae, representing approximately 50 wt% of the microalgae dry biomass [141]. In eukaryotic algal cells, inorganic carbon is first fixed by Ribulose Bisphosphate Carboxylase Oxygenase (RuBisCO, a CO₂ fixing enzyme) within the Calvin cycle, as shown in Reaction 2.27.

\[
\text{Ribulose-1,5-biphosphate} + CO_2 + H_2O \rightarrow 2 \times \text{glycerate-3-P} \tag{2.27}
\]

However, due to the low affinity of RuBisCO with CO₂, microalgae have evolved CO₂ concentrating mechanisms (CCMs) to increase CO₂ concentration in the vicinity of RuBisCO. There are a number of different CCMs, including the ‘biochemical C4’ and the ‘CAM’ mechanisms, as well as biophysical active transport processes, as have been summarized in review papers on this topic [118, 142]. Figure 2.9 illustrates the process of CO₂ utilization in eukaryotic algal cells [142]. Firstly, inorganic carbon is delivered into the chloroplast through CO₂ diffusion or active transport of CO₂ and HCO₃⁻. Then CO₂ is fixed by RuBisCO in the Calvin cycle.

![Figure 2.9 A schematic model for inorganic carbon transport and CO₂ accumulation processes in eukaryotic algal cells, reproduced from a paper by Giordano et al.][142]
Carbon limitation

Due to CCMs, carbon concentration is unlikely to limit photosynthesis in dilute cell cultures, in which the overall demand for CO₂ is not intense. However, CCMs cannot avoid carbon limitation in dense microalgae cultures in which the overall demand for CO₂ exceeds the supply \[^143, 144\]. To maximise the utilisation of the available light and growth infrastructure carbon limitation needs to be avoided in mass microalgae production. As diffusion of CO₂ from atmospheric air cannot provide CO₂ at a sufficient rate, a higher concentration CO₂ is typically injected into microalgae ponds or photobioreactors, to ensure a sufficient supply of CO₂ is available to fully utilise the available carboxylase activity of RuBisCO to improve microalgae photosynthetic efficiency \[^145\]. However, excessively high CO₂ concentrations can decrease the medium pH and reduce activity of the carbonic extracellular anhydrase (CA), the enzyme required to catalyze the reversible reaction between CO₂ and bicarbonate \[^146\]. This can eventually limit microalgae growth. So it is important to achieve a balance between the CO₂ demand of microalgae growth and the CO₂ supply in microalgae media. Here, the CO₂ demand varies with different microalgae species, the culture density and the photosynthetic rate. On the other hand, the CO₂ supply depends on CO₂ concentration in gas, gas flowrate, CO₂ mass transfer coefficient and contact surface of different delivery technologies.

2.5.2 CO₂ solubility in water

Carbon dioxide dissolved in water (CO₂\(_{aq}\)), reacts to form three carbonate species, carbonic acid (H₂CO₃), bicarbonate ion (HCO₃⁻) and carbonate ion (CO₃²⁻). Due to the low equilibrium constant \(K_m\), carbonic acid (H₂CO₃) is less than 0.3% of CO₂\(_{aq}\). The reactions are as follows\[^147\].

\[
\begin{align*}
CO₂(\text{g}) & \overset{K_m}{\leftrightarrow} CO₂(\text{aq}) \quad (2.28) \\
CO₂(\text{aq}) + H₂O & \overset{K_m}{\leftrightarrow} H₂CO₃ \quad (2.29) \\
H₂CO₃ & \overset{K_1}{\leftrightarrow} HCO₃⁻ + H^+ \quad (2.30)
\end{align*}
\]
\[ HCO_3^- \xleftrightarrow{K_2} CO_3^{2-} + H^+ \]  \hspace{2cm} (2.31)

In reaction 2.29, the relationship between CO₂ in the gas phase and CO₂ dissolved in water can be expressed by Henry's Law (Equation 2.32).

\[ H_{CO_2} = \frac{[CO_2(aq)]}{P_{CO_2}} \]  \hspace{2cm} (2.32)

- \( H_{CO_2} \)  Henry's law constants \( \text{mol L}^{-1} \text{ atm}^{-1} \)
- \([CO_2(aq)]\) Dissolved CO₂ concentration in water \( \text{mol L}^{-1} \)
- \( P_{CO_2} \) CO₂ partial pressure \( \text{atm}^{-1} \)

In Reaction 2.30 and 2.31, carbonate species have equilibrium relationships, according to the following Equations 2.33 and 2.34.

\[ K_1 = \frac{\{H^+\}\{HCO_3^-\}}{\{H_2CO_3\}} = \frac{\gamma_{H^+}[H^+]Y_{HCO_3^-}[HCO_3^-]}{\gamma_{H_2CO_3}[H_2CO_3]} \]  \hspace{2cm} (2.33)

\[ K_2 = \frac{\{H^+\}\{CO_3^{2-}\}}{\{HCO_3^-\}} = \frac{\gamma_{H^+}[H^+]Y_{CO_3^{2-}}[CO_3^{2-}]}{\gamma_{HCO_3^-}[HCO_3^-]} \]  \hspace{2cm} (2.34)

Carbonate concentrations are different in an open system and a closed system. The open system refers to a system which has CO₂ exchange between the liquid phase and a gas phase, and a closed system refers to a single liquid phase. In the open system, the carbonate species are in chemical equilibrium with carbon dioxide in the gas phase, and the total dissolved inorganic carbon (DIC) varies with pH and CO₂ partial pressure. However, in a closed system, as there is no carbon dioxide exchange between the aqueous phase and gas phase, the DIC remains constant, and the proportion of carbonate species (\(H_2CO_3, HCO_3^- \text{ and } CO_3^{2-}\)) varies with pH. The exact carbonate species concentrations can be calculated according to the DIC concentration and pH.

In the carbonate system, the DIC needs to balance on a molar (Equation 2.35) and a charge (Equation 2.36) basis.

\[ DIC = [H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] \]  \hspace{2cm} (2.35)
\[ 0 = [H^+] - [HCO_3^-] - 2[CO_3^{2-}] - [OH^-] \]  
(2.36)

In pure water, the activity coefficient \( \gamma \) is 1 and the equations shown above can be simplified so that carbonate speciation can be predicted from Equations 2.37 to 2.39 by using dissociation constants in Table 2.1. Seawater contains different ions such as \((\text{Na}^+, \text{Cl}^-, \text{Mg}^{2+}, \text{SO}_4^{2-}, \text{PO}_4^{3-})\), with a total ionic strength of approximately 0.7 mol kg\(^{-1}\)\(^{[148]}\) and a salinity of 30-35 g salt kg\(^{-1}\)\(^{[149]}\). The activity coefficients \( \gamma \) of ions are lower than 1. The dissociation constants in 30 g salt kg\(^{-1}\) seawater at 25°C are shown in Table 2.1, which incorporate the stoichiometric equilibrium constants with the activity coefficients.

\[
[H_2CO_3] = DIC \times \frac{[H^+]^2}{[H^+]^2 + K_1[H^+] + K_1K_2} \]  
(2.37)

\[
[HCO_3^-] = DIC \times \frac{K_1[H^+]}{[H^+]^2 + K_1[H^+] + K_1K_2} \]  
(2.38)

\[
[CO_3^{2-}] = DIC \times \frac{K_1K_2}{[H^+]^2 + K_1[H^+] + K_1K_2} \]  
(2.39)

Table 2.1 Dissociation constants of carbonic acid in pure water and 30 g salt kg\(^{-1}\) seawater at 25°C

<table>
<thead>
<tr>
<th></th>
<th>pK(_1)</th>
<th>pK(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water (^{[147]})</td>
<td>6.35</td>
<td>10.33</td>
</tr>
<tr>
<td>Seawater (^{[150]}) (30 g salt kg(^{-1}))</td>
<td>5.87</td>
<td>8.97</td>
</tr>
</tbody>
</table>

### 2.5.3 Global CO\(_2\) supply and demand

Global anthropogenic CO\(_2\) emissions were around 36.2 billion tonnes in 2015, mainly from fossil fuel combustion, industrial processes, residential consumption and transportation \(^{[32]}\). Although CO\(_2\) emissions are numerous, only the large point sources of CO\(_2\) emissions are amenable for capture based on the current technology. Understanding the global CO\(_2\) supply gives us information of potential CO\(_2\) sources for microalgae cultivation. As CO\(_2\) market price depends on the relationship of CO\(_2\) supply and demand, realizing the current and future CO\(_2\)
demand helps to evaluate the economic viability of different CO₂ sources for microalgae cultivation.

**CO₂ Supply**

Intergovernmental Panel on Climate Change (IPCC) reported there was in total 13375 Mt CO₂ emissions from large point sources (more than 0.1 Mt CO₂ per year) in 2002. The largest proportion (10540 Mt) is from fossil fuel combustion including coal, natural gas and fuel oil. However, the low CO₂ concentration (3 to 15 vol%) in these sources may lead to high costs for CO₂ capture. Other sources of highly pure CO₂ (above 97 vol%) include the Ammonia production process and ethanol fermentation, which could provide 113 Mt and 17.6 Mt CO₂ in 2002, respectively. The United Nations Industrial Development Organization (UNIDO) also reported that 6% of the global industrial CO₂ emissions was from high purity sources (426 Mt). Ammonia production, gas processing, coal to liquids process and ethylene oxide production provided 240 Mt, 160 Mt, 20 Mt and 6.3 Mt CO₂ in 2010, respectively.

**CO₂ Demand**

Parsons Brinckerhoff investigated the CO₂ demand in 2011 (Figure 2.10). The total CO₂ demand was 80 Mt, in which 50 Mt was for enhanced oil recovery (EOR) and the remaining 30 Mt for beverage carbonation, the food industry, precipitated calcium carbonate and other uses.

![Figure 2.10 Global CO₂ demand in 2011, reproduced from a report by Parsons Brinckerhoff](image_url)
CO₂ Price

The CO₂ price in 2010 has been quoted as US$ 15 to US$ 19 t⁻¹ CO₂ [152]. CO₂ from ammonia production in the US was sold from US$ 3 to US$ 15 t⁻¹ CO₂ depending on the location [152]. The Dakota Gasification Company's Great Plains Synfuels Plant sold CO₂ at US$ 19 t⁻¹ CO₂ in 2009 [152].

Although CO₂ emissions from fossil fuel power plants provide a large potential supply, it is important to notice that there is a gap between the CO₂ market price and costs for CO₂ capture. Rubin et al. [8] estimated the CO₂ capture costs of different technologies for fossil fuel combustion power plant. The costs of post combustion technology, pre-combustion technology and Oxy-combustion technology are US$ 36 to US$ 111 t⁻¹ CO₂, US$ 42 to US$ 87 t⁻¹ CO₂ and US$ 45 to US$ 73 t⁻¹ CO₂ [8], respectively.

Based on the above information, the current high-purity CO₂ sources can maintain the CO₂ demand for EOR or other industrial processes. However, once microalgae cultivation technology becomes mature, the demand for CO₂ will increase. Purified CO₂ from raw flue gas could be a potential CO₂ source for microalgae production, but new strategies must be proposed to eliminate the gap between the CO₂ market price and carbon capture costs.

2.5.4 CO₂ sources for microalgae cultivation

As discussed in section 2.4.1, carbon dioxide must be provided to improve microalgae growth such that the available light is fully utilised. Section 2.4.3 provides general information about CO₂ sources. But different from EOR or other chemical industry processes, microalgae cultivation has its own standards for CO₂ sources. Firstly, it is not necessary to use 100 vol% CO₂, so atmospheric air and raw flue gas can also be regarded as CO₂ sources for microalgae cultivation. Secondly, some impurities (NOₓ and SOₓ) in gas, even at low concentration may influence microalgae growth. The following paragraphs provide information of potential CO₂ sources for microalgae cultivation, including air, raw flue gas, commercial purified CO₂, purified CO₂ from carbon capture facilities and CO₂-containing solvents.
Air

The atmosphere is the most readily available CO$_2$ source for microalgal growth, and is the source for growth of these organisms in natural systems. In this case, there is no need for gas transportation from a CO$_2$ production plant. However, atmospheric air has only about 0.035 vol% CO$_2$. This low concentration means that there is a low driving force for mass transfer into a microalgal growth medium. This fact, combined with the low gas-liquid interfacial area on the surface of ponds, means that relying on passive atmospheric diffusion is not sufficient to maintain high concentrations of biomass. A gas compressor and a pump on site can be used to bubble air through the cultures to improve carbon delivery for microalgae and enhance the agitation of the culture, however the low CO$_2$ concentration both limits mass transfer and greatly increases the total volume of gas that has to be pumped. Jiang et al.\textsuperscript{[153]} showed that with air aeration, \textit{Nannochloropsis} sp. only achieved one third of the biomass concentration of cultures grown using gas containing 15% CO$_2$.

Raw flue gas from fossil fuel combustion

Raw flue gas from fossil fuel combustion accounts for 78% CO$_2$ emissions\textsuperscript{[32]}. The high capture costs associated with low CO$_2$ concentration restrict its usage for EOR and other industrial applications, but raw flue gas can be utilized as the carbon source for microalgae cultivation. Typically it contains several components, such as N$_2$, O$_2$, CO$_2$, CO, NO$_x$, SO$_x$, C$_x$H$_y$, heavy metals and particulate matter\textsuperscript{[154, 155]}. The concentration of these components varies depending on flue gas sources\textsuperscript{[156]}, such as with the CO$_2$ concentration usually in the range 4 to 33 vol%\textsuperscript{[27]}. NO$_x$ can be in a range from 2 to 1500 ppm and SO$_x$ can be in a range from 0 to 1400 ppm\textsuperscript{[155]}. Components, such as NO$_x$ and SO$_x$, have been reported to have a negative effect on microalgae growth\textsuperscript{[27]}. SO$_x$ from flue gases may hydrolyse in the microalgae medium to release H$^+$, causing a pH decrease and inhibit the microalgae growth\textsuperscript{[156]}. NO$_x$ has two forms NO and NO$_2$, that may be oxidized by the oxygen produced by microalgae photosynthesis to form nitrate or nitric acid in the culture medium\textsuperscript{[157]}. Kao et al.\textsuperscript{[156]} showed that flue gas containing less than 100 ppm NO$_x$ with 0.2 vvm aeration rate can be used as an additional nitrogen source for
*Chlorella* sp. MTF-15, which could be used to increase the maximum biomass concentration reached in the cultures.

There are two options for directly using raw flue gas containing NO\textsubscript{x} and SO\textsubscript{x} to enhance microalgal growth at large scale. One approach is to isolate NO\textsubscript{x}- and SO\textsubscript{x}-tolerant microalgae strains. *Chlorella fusca* LEB 111 was isolated by Duarte *et al.* [145] from the ash settling ponds of a thermoelectric plant in Brazil, which can tolerate up to 400 ppm SO\textsubscript{2} and 400 ppm NO, respectively. Radmann *et al.* [158] isolated *Chlorella vulgaris* from the sewage treatment pond of a thermoelectric plant in Brazil which can grow with 12% CO\textsubscript{2}, 60 ppm SO\textsubscript{2} and 100 ppm NO. *Chlorella* sp., *Dunaliella tertiolecta* and *Scenedesmus obliquus* are the most commonly reported species that can tolerate SO\textsubscript{x} and NO\textsubscript{x} [27]. The other option is to remove the SO\textsubscript{x} and NO\textsubscript{x} from the flue gas prior to microalgae use by adding desulfurization and denitrification units [156].

Usually the microalgae pond needs to be located near to the flue gas source to reduce the CO\textsubscript{2} delivery distance. Rubin *et al.* [8] estimated the CO\textsubscript{2} transportation costs through onshore pipeline, which is from US$ 1.3 to 10.9 t\textsuperscript{-1} CO\textsubscript{2} per 250 km depending on the different capacities. For direct flue gas utilization, 6 to 30 fold more volume of gas needs to be delivered than that provided by a pure CO\textsubscript{2} stream. As gas compression and transportation is energy intensive [159], purified CO\textsubscript{2} is chosen by some microalgae plants.

**Purified CO\textsubscript{2}**

For microalgae ponds that do not have flue gas sources nearby, the more economic choice is commercial purified CO\textsubscript{2}. As mentioned above, ammonia production, gas processing, coal to liquids process and ethylene oxide production can provide commercial sources of purified CO\textsubscript{2} [151]. These CO\textsubscript{2} sources only need simple drying and compression, and have CO\textsubscript{2} prices in the range US$ 5- US$ 55 t\textsuperscript{-1} CO\textsubscript{2} [32].

For microalgae ponds that do have flue gas sources nearby, another potential source is purified CO\textsubscript{2} from carbon capture facilities. Research by Kadam [159] compared the supply costs of CO\textsubscript{2} from raw flue gas and purified CO\textsubscript{2} from an MEA extraction process with 100 km pipeline distance. The results exhibited the direct flue gas supply (containing 14% CO\textsubscript{2}) had more expenses in compression, drying
(US$ 46.64 t\textsuperscript{-1} CO\textsubscript{2}) and transportation (US$ 10.58 t\textsuperscript{-1} CO\textsubscript{2}). Including MEA extraction cost (US$ 28.72 t\textsuperscript{-1} CO\textsubscript{2}), purified CO\textsubscript{2} decreases costs to compression, drying (US$ 8.48 t\textsuperscript{-1} CO\textsubscript{2}) and transportation (US$3.30 t\textsuperscript{-1} CO\textsubscript{2}) compared to using raw flue gas. The total cost of directly pumping flue gas was found to be 40% more expensive than supplying purified CO\textsubscript{2} by MEA extraction. And a life cycle analysis completed by Stephenson et al\textsuperscript{[160]} presented that an increase in CO\textsubscript{2} concentration in the feed gas from 5 vol\% to 12.5 vol\% could reduce the energy requirement for biodiesel production from 23.7 to 6.5 GJ t\textsuperscript{-1} of biodiesel.

**CO\textsubscript{2}-containing solvents**

A large amount of energy is required for gas compression and transportation over the vast areas required for large scale microalgae cultivation. Applying CO\textsubscript{2}-containing liquid solvents for microalgae growth could reduce the energy required to transport the CO\textsubscript{2} as liquid does not require compression and is much more efficient to pump. Further, CO\textsubscript{2} might be temporarily stored in the solvents when the microalgae stop photosynthesis at night. Some researchers have tried the direct addition of sodium bicarbonate to the medium to enhance microalgae growth \textsuperscript{[27]}. Pancha et al\textsuperscript{[161]} found that *Scenedesmus* sp. CCNM 1077 with 0.6 g L\textsuperscript{-1} sodium bicarbonate has 23% increased biomass and 21% increase lipid production compared with normal BG11 medium without sodium bicarbonate addition. Nunez and Quigg \textsuperscript{[162]} showed that the growth of *Nannochloropsis salina* was about 3-fold higher with 5 g L\textsuperscript{-1} sodium bicarbonate, compared to the no sodium bicarbonate addition. Usually seawater species can have a higher tolerance to bicarbonate addition than fresh water species, as seawater species are already conditioned to high ionic strengths. Current sodium bicarbonate addition is in a range from 0.1 to 5 g L\textsuperscript{-1} \textsuperscript{[161-164]}, with the highest concentration of 0.60 mol L\textsuperscript{-1} NaHCO\textsubscript{3} for the highly salt-tolerant *Dunaliella salina*\textsuperscript{[164]}. An issue with this approach is that while the bicarbonate is consumed, the sodium concentration within the medium will grow over time, increasing the total ionic strength and the cost of production.
Further, some microalgae strains do not have external carbonic anhydrase, and so can only take up CO₂. For instance *Nannochloris atomus* and *Nannochloris maculata*[^165]. This limits the potential application of this approach.

Based on the above information, Table 2.2 presents the advantages and disadvantages of different CO₂ sources for microalgae cultivation. Although purified CO₂ from flue gas is a potential CO₂ source for mass microalgae cultivation, the unavoidable high capture costs needs to be addressed before implementation.

<table>
<thead>
<tr>
<th>Table 2.2 Comparison of different CO₂ sources for microalgae cultivation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Advantages</strong></td>
</tr>
<tr>
<td>Air</td>
</tr>
<tr>
<td>Raw flue gas</td>
</tr>
<tr>
<td>Reduced costs for CO₂ transportation and compression</td>
</tr>
<tr>
<td>Purified CO₂ from flue gas</td>
</tr>
<tr>
<td>Reduced costs for CO₂ transportation and compression</td>
</tr>
<tr>
<td>CO₂-containing solvents</td>
</tr>
<tr>
<td>Do not require compression</td>
</tr>
<tr>
<td>Cheap costs for transportation</td>
</tr>
<tr>
<td>Temporarily storage of CO₂ in the solvents</td>
</tr>
<tr>
<td></td>
</tr>
</tbody>
</table>

**2.5.5 Carbon dioxide delivery technologies**

As a carbon source, CO₂ is estimated to account for around 56% of the raw materials costs for microalgae production[^166]. Increasing the efficiency of utilization of CO₂ can therefore reduce operation costs. There are several ways to transfer CO₂ to microalgae, including conventional sparging of bubbles, production of microbubbles, use of membrane spargers, and bubbleless membrane contactors.
Conventional sparging

The conventional method for delivering CO₂ to microalgae ponds or photobioreactors is to use a sparger \(^{[167-169]}\), with a diameter of around 1-2 mm \(^{[27]}\). As the microalgae pond typically only has 0.2 - 0.5 m depth, bubbles rise quickly to the pond surface and burst, so that most of the carbon dioxide is lost to the atmosphere (Figure 2.11). To increase retention time, Lundquist \textit{et al.} \(^{[170]}\) introduced a sump (1 meter depth) to form a counter-current flow of gas and water with around 20 second contact time (Figure 2.12), and reduced the CO₂ loss to 50%. But the short retention time is still a limitation of CO₂ utilization efficiency.

Figure 2.11 The difference behaviour of bubble and microbubble, reproduced from a paper by Tskahashi \(^{[171]}\)

Figure 2.12 Schematic diagram for sump for gas delivery in microalgae pond, modified from Lundquist \textit{et al.} \(^{[170]}\)
Microbubbles

Compared to conventional bubbles (with a diameter of 1-2 mm\textsuperscript{[27]}) microbubbles with a diameter of less than 100 µm have a much higher surface to volume ratio and slower rise velocity in the microalgae medium, so more carbon dioxide can dissolve in the medium\textsuperscript{[27,172]}. Compared with the rapid rise of larger bubbles, microbubbles decrease gradually in size as they are dissolved in the water (Figure 2.11)\textsuperscript{[171]}. Several methods have been applied to create microbubbles, such as fluidic oscillation, ultrasound or pressurized gas liquid circulation system\textsuperscript{[172,173]}. Such microbubbles have been applied for O\textsubscript{2} injection for wastewater treatment or oyster cultivation\textsuperscript{[172-174]}. Zimmerman \textit{et al.}\textsuperscript{[169,175]} firstly introduced microbubble into the microalgae cultivation by using the fluidic oscillation diffuser. The bubble size is around 550 to 750µm, bigger compared with the usual definition of microbubbles. The later research by Al-Mashhadani \textit{et al.}\textsuperscript{[176]} showed that with a fluidic oscillation diffuser, 29% increase of CO\textsubscript{2} overall mass transfer coefficient was obtained with 550µm microbubbles compared with normal 1.3 mm bubbles. However, the greater head pressure loss with microbubbles leads to more energy consumption in the process. Further, the strong shear stress effect created by microbubble generation may damage microalgae cells\textsuperscript{[177,178]}.

Porous membrane sparger

Instead of lying on the bottom of the algal bed like a diffuser, a hollow fibre membrane can be submerged in the functional volume of a photobioreactor from the bottom to the top, which can increase the contact surface area between the microalgae medium and the nascent bubbles. The porous membrane can also provide smaller and more uniform CO\textsubscript{2} bubbles (0.2-0.9mm)\textsuperscript{[179]} to improve the mass transfer coefficient compared to direct bubbling. Fan \textit{et al.}\textsuperscript{[180]} tested the performance of PVDF hollow fibre membranes through sparging 1% CO\textsubscript{2}. By introducing a membrane sparger into helical tubular photobioreactor, Fan \textit{et al.}\textsuperscript{[178]} achieved 10 times higher mass transfer coefficient compared to tube bubbling. Cheng \textit{et al.}\textsuperscript{[181]} compared the performance of polypropylene hollow fibre membrane contactor with a bubble photobioreactor, and showed that the CO\textsubscript{2} fixation rate of \textit{Chlorella vulgaris} was enhanced from over 3-fold. Mortezaeikia \textit{et al.}
[179] also used a polypropylene microporous membrane contactor to supply CO₂ bubbles for *Synechococcus elongates* growth.

**Non-porous membrane contactor**

A membrane contactor fabricated with a dense membrane can minimize CO₂ loss by producing bubbleless CO₂ in the aqueous phase [182-184]. In this case, the CO₂ crosses the membrane, as individual molecules in a vapour state through the solution diffusion mechanism (Figure 2.5C). Kumar *et al.*[183] used a composite hollow fibre membrane (a thin dense polyurethane layer sandwiched between two microporous polyolefin layers) to transfer gas containing 2-15% CO₂ to *Spirulina platensis*. A three layer composite membrane (nonporous thin polyurethane membrane sandwiched between two porous polyethylene layers) applied by Kim *et al.*[182] delivered bubbleless CO₂ into a photobioreactor for microalgae growth (Figure 2.13). Another non-porous polypropylene hollow fibre membrane tested by Kim *et al.* demonstrated the ability to use this system to provide CO₂ without any CO₂ loss to the atmosphere [184]. Although the issue of CO₂ loss is solved with a membrane contactor, the gas supply still needs energy for gas compression and transportation.

![Non-porous membrane for bubbless CO₂](image)

Figure 2.13 Non-porous membrane for bubbless CO₂, modified for Kim *et al.*[182]
2.6 Scope of the research

In mass microalgae cultivation, CO₂ must be provided as the carbon source to enhance microalgae growth and ensure full utilisation of the available solar energy. Current CO₂ sources include air, raw flue gas, commercial purified CO₂ and CO₂-containing solvents. However, using air cannot maintain dense microalgae cultures. The use of commercially purified CO₂ (costing between US$ 15 to US$19 t⁻¹ CO₂) greatly increases the operational costs of microalgae cultivation. All CO₂ gas sources require energy for gas compression and transportation. CO₂-containing solvents may eliminate energy associated with compression and transportation, but some species can only absorb CO₂ and cannot take up HCO₃⁻.

Due to its abundance and lack of competing uses, raw flue gas is the best potential CO₂ source for microalgae cultivation. However, the impurities (NOₓ and SOₓ) may inhibit microalgae growth and there is a high energy penalty incurred during the carbon capture process, especially the regeneration process in chemical absorption technology (around 4.2 GJ t⁻¹ CO₂). A strategy to directly use the CO₂ loaded solvents as a CO₂ source can both reduce the energy of gas compression and transportation, and eliminate the energy for solvent regeneration.

Sparging CO₂ bubble into microalgae ponds or photobioreactors is the conventional method used during microalgae mass cultivation. However, most CO₂ is lost to the atmosphere due to the low mass transfer efficiency. To address this problem, various technologies, such as microbubbles and membrane contactors, have been proposed to increase the contact time between gas and medium. However, the utilization of CO₂ gas still consumes large amounts of energy for gas compression and transportation.

In order to find an efficient method to deliver CO₂ to microalgae, this thesis establishes a novel combination system, involving chemical absorption, membrane separation and microalgae cultivation. This method allows CO₂ loaded solvents from a chemical absorption process to be utilized as the CO₂ source. This can be easily achieved from a carbon capture process in a fossil fuel combustion power plant and greatly reduces the energy related to gas compression and transportation. In this system, CO₂ loaded solvents are pumped through a dense
hollow fibre membrane, CO₂ diffuses from the tube side to the medium outside to provide a carbon source for microalgae cultivation. The membrane system can minimize the CO₂ loss into the atmosphere and also eliminates the energy penalty for chemical solvent regeneration.

The effectiveness of this system is tested on different chemical solvents (potassium carbonate, monoethanolamine, potassium glycinate) and various microalgae species (marine species *Chlorella* sp. freshwater species *Chlorella vulgaris*, marine species *Dunaliella tertiolecta*).

The following is a summary of the structure and contents of this thesis:

Chapter 1 - A brief introduction giving the background and context of the project.

Chapter 2 – A critical literature review of carbon dioxide capture technology, membrane technology, microalgae system and different carbon dioxide delivery strategies.

Chapter 3 – A detailed description of the novel CO₂ delivery system and the materials and methods used in the experimental program.

Chapter 4 – An experimental investigation into the effectiveness and operation of the novel system using potassium carbonate at different CO₂ loadings to efficiently deliver carbon dioxide to marine species *Chlorella* sp. Experiments are performed to determine if potassium carbonate solvents can improve the *Chlorella* sp. growth and lipid production, with consideration to growth limiting factors such as nitrate and carbon concentration.

Chapter 5 – An expansion of the research presented in chapter 4 using different chemical solvents. The relative effectiveness of potassium carbonate, monoethanolamine, potassium glycinate on marine species *Chlorella* sp. is compared. Consideration is given to potential solvent leakage and toxicity.

Chapter 6 – An investigation into the effectiveness of the system using different chemical solvents to produce different microalgae species grown at different salinities (marine strain *Chlorella* sp., freshwater strain *Chlorella vulgaris*, marine
strain *Dunaliella tertiolecta*). The impact of the medium salinity on the operation and performance of this system is studied.

Chapter 7 – An economic assessment of the membrane system is conducted.

Chapter 8 – Conclusions and discussion of future work involving this system.


138. Yeesang, C. and B. Cheirsilp, *Effect of nitrogen, salt, and iron content in the growth medium and light intensity on lipid production by microalgae isolated from*


Chapter 3 Materials and methods

3.1 Materials

3.1.1 Preparation of chemical solvents

In this work, 20 wt% K$_2$CO$_3$, 30 wt% monoethanolamine (MEA) and 20 wt% potassium glycinate (PG) (2 mol L$^{-1}$) were used as the chemical solvents. 30 wt% MEA is the most commonly used concentration of this solvent used in post-combustion carbon capture process [1, 2]. As 30 wt% K$_2$CO$_3$ may form precipitates during CO$_2$ absorption under atmospheric temperature, 20 wt% K$_2$CO$_3$ was utilized in this study, although 30 wt% is often used during post-combustion capture where higher temperatures (30-50$^\circ$C) prevent precipitation [3]. Amino acid salts with the range from 0.5 mol L$^{-1}$ to 6 mol L$^{-1}$ have been investigated to capture CO$_2$ [4-7], 20 wt% PG (2 mol L$^{-1}$) was chosen in this study as it was easily compared with 20 wt% K$_2$CO$_3$.

20 wt% K$_2$CO$_3$ solutions of CO$_2$ loadings from 0.2 to 0.7 were prepared by mixing the required quantities of K$_2$CO$_3$ (Senator Chemicals, 99.7%) and KHCO$_3$ (Univar, 98%) in purified water [8]. The concentrations of KHCO$_3$ and K$_2$CO$_3$ were determined using a Metrohm 905 Titrando autotitrator [9]. The solvent loading for potassium carbonate is defined according to Equation 3.1.

$$\text{CO}_2 \text{ loading in K}_2\text{CO}_3 = \frac{[\text{HCO}_3^-]}{[\text{K}^+]}$$ (3.1)

Both MEA and PG contain a primary amine group, which reacts with CO$_2$ to form a carbamate anion and a protonated amine according to Equation 3.2.

$$2\text{AmH} + \text{CO}_2 \leftrightarrow \text{AmCOO}^- + \text{AmH}_2^+$$ (3.2)

CO$_2$ loaded MEA was prepared by bubbling carbon dioxide gas through 30 wt% MEA (Chem-supply, 99%) for 30 minutes to saturate it with CO$_2$. The carbon dioxide concentration in the solvent was then measured using a coulometer (CM5015 Coulometer, UIC). By mixing CO$_2$-loaded MEA and CO$_2$-free MEA, 30 wt% MEA having loadings of 0.5 and 0.2 was prepared (loading indicates the extent to
which the CO₂ carrying capacity of the solvent is fulfilled). The CO₂ loading for MEA solvents is defined according to Equation 3.3 [10].

\[
\text{CO₂ loading in MEA} = \frac{\text{Moles of all CO₂ carrying species}}{\text{Moles of all MEA carrying species}}
\]

\[
= \frac{[\text{CO}_2] + \text{[HCO}_3^-] + \text{[CO}_3^{2-}] + \text{[HOCH}_2\text{CH}_2\text{NHCOO}^-]}{\text{[HOCH}_2\text{CH}_2\text{NH}_2} + \text{[HOCH}_2\text{CH}_2\text{NH}_3^+] + \text{[HOCH}_2\text{CH}_2\text{NHCOO}^-]}
\] (3.3)

20 wt% PG solution was prepared by adding equimolar amounts of potassium hydroxide (Chem-supply, 99%) to glycine (Chem-supply, 99%) and dissolving into purified water (Millipore Elix)[11]. Carbon dioxide gas was bubbled through the solution for 30 minutes to saturate it with CO₂. The CO₂ concentration in the solvent was measured using a coulometer (CM5015 Coulometer, UIC). By mixing CO₂-loaded PG and CO₂-free PG, 20 wt% PG having CO₂ loadings of 0.2, 0.5, and 0.6 was prepared. As amino acid salts have been detected to achieve CO₂ loading of more than 0.5 [12, 13], the effect of higher CO₂ loading solvents on microalgae growth was determined with PG solution of 0.6 loading. The CO₂ loading for PG solvent is defined according to Equation 3.4[14].

\[
\text{CO₂ loading in PG} =
\]

\[
= \frac{[\text{CO}_2] + \text{[HCO}_3^-] + \text{[CO}_3^{2-}] + \text{[COO}_2\text{CC}_2\text{NHCOO}^-]}{\text{[COO}_2\text{CC}_2\text{NH}_2} + \text{[COO}_2\text{CC}_2\text{NH}_3^+] + \text{[COO}_2\text{CC}_2\text{NHCOO}^-]}
\] (3.4)

### 3.2.2 Membrane parameters

The hollow fibre membrane used in this study was supplied by Airrane (Korea). This composite membrane contained a polysulfone support layer and a thin non-porous PDMS layer coating. Forty fibres of the hollow fibre membrane were bundled together in 4 cm long Nylon tubing (Brotec, Australia) using Selleys Araldite super strength epoxy adhesive (Selleys, NSW, Australia) at each of two ends (Figure 3.1). Table 3.1 shows various parameters of the hollow fibre PDMS membrane used in the current work.
Figure 3.1 The schematic of bundled membranes

Table 3.1 Specifications of the PDMS membrane contactor

<table>
<thead>
<tr>
<th>Membrane Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supplier</td>
<td>Airrane, Korea.</td>
</tr>
<tr>
<td>Membrane type</td>
<td>Composite membrane</td>
</tr>
<tr>
<td>Supporting layer</td>
<td>Polysulfone</td>
</tr>
<tr>
<td>Non-porous layer</td>
<td>PDMS</td>
</tr>
<tr>
<td>Fibre inside diameter (µm)</td>
<td>$d_{in}$, 300</td>
</tr>
<tr>
<td>Fibre outside diameter (µm)</td>
<td>$d_{out}$, 450</td>
</tr>
<tr>
<td>Fibre Wall Thickness (µm)</td>
<td>$L$, 75</td>
</tr>
<tr>
<td></td>
<td>PDMS layer 0.5 µm</td>
</tr>
<tr>
<td>Number of fibres per flask (n)</td>
<td>40</td>
</tr>
<tr>
<td>Membrane surface area per flask (m²)</td>
<td>$A$, 0.0226</td>
</tr>
<tr>
<td>Membrane Length (m)</td>
<td>0.4</td>
</tr>
</tbody>
</table>

### 3.2.3 Microalgae cultivation

Four microalgae strains were used in this study. The first was a marine strain of *Chlorella* sp., which was isolated from the Cooper Creek at Innamincka, SA, Australia[15]. The second was a freshwater *Chlorella vulgaris*, which was obtained from CSIRO, Australia. The third was a strain of marine *Dunaliella tertiolecta*, which was isolated from Port Phillip Bay, VIC, Australia. The fourth was a strain of the fresh water *Haematococcus pluvialis*, which was isolated from a rooftop in the Parkville campus, VIC, Australia.
The marine strains were cultivated in Modified-F (MF) medium and 3% artificial seawater mix \cite{15}. As this research was to supply CO\textsubscript{2} for microalgae medium, the freshwater strain was cultivated in freshwater MLA medium excluding NaHCO\textsubscript{3} addition \cite{16}.

**Modified-F (MF) medium preparation**

Firstly, the primary stock solution and stock solutions was prepared with purified water (Millipore Elix) based on the ingredients in Table 3.2 and 3.3. After sterilization by filtration through Millipore 0.22 µm filters, the solutions were stored in the refrigerator at 4 °C. Then MF medium was prepared by adding 1.0 mL of each of five stock solutions (solutions 2-6) into 1 litre of 3% artificial seawater, then filtering through 0.22 µm Millipore filter. 3% artificial seawater was prepared by adding 30 g ocean salt (Ocean Fish, Prodac International, Italy) into 1 litre purified water. The concentrations of major ions in 3% artificial seawater were presented in Table 3.4, as measured using inductively coupled plasma optical emission spectrometry (ICP-OES 720 ES, Varian) and Ion Chromatography (ICS-1000, Dionex). Note that while the MF medium was prepared with 30 g of ocean salt per litre. The final salt concentration was of the order of 25 g L\textsuperscript{-1} (see Table 3.4). This lower concentration probably results from the loss of some undissolved salts during filtration of prepared seawater solution.

**Table 3.2 Primary stock solution for MF medium**

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 mg L\textsuperscript{-1}</td>
<td>Sigma 99%</td>
</tr>
<tr>
<td>100 mg L\textsuperscript{-1}</td>
<td>Fluka 99%</td>
</tr>
</tbody>
</table>

---

1. Biotin/Vitamin B\textsubscript{12} Primary Stock solution
2. Biotin

---
Table 3.3 Stock solutions for MF medium

<table>
<thead>
<tr>
<th></th>
<th>Concentration</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>NaNO₃</td>
<td>Ajax Finechem 99%</td>
</tr>
<tr>
<td>3</td>
<td>KH₂PO₄·2H₂O</td>
<td>BDH 99.5%</td>
</tr>
<tr>
<td>4</td>
<td>Ferric citrate</td>
<td>Ajax Finechem 18% Fe</td>
</tr>
<tr>
<td></td>
<td>Citric acid</td>
<td>Merck 99.5%</td>
</tr>
<tr>
<td>5</td>
<td>Trace metals</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CuSO₄·5H₂O</td>
<td>Sigma 98%</td>
</tr>
<tr>
<td></td>
<td>ZnSO₄·7H₂O</td>
<td>Fluka 99%</td>
</tr>
<tr>
<td></td>
<td>CoCl₂·6H₂O</td>
<td>Chem-Supply 98%</td>
</tr>
<tr>
<td></td>
<td>MnCl₂·4H₂O</td>
<td>Ajax Finechem 98%</td>
</tr>
<tr>
<td></td>
<td>Na₂MoO₄·2H₂O</td>
<td>Sigma 99.5%</td>
</tr>
<tr>
<td></td>
<td>H₂SeO₃</td>
<td>Sigma 98%</td>
</tr>
<tr>
<td>6</td>
<td>Vitamins</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Biotin/Vitamin B12</td>
<td>Primary Stock solution (1)</td>
</tr>
<tr>
<td></td>
<td>Thiamine HCl</td>
<td>Sigma 99%</td>
</tr>
</tbody>
</table>
Table 3.4 Major ions in 3% artificial seawater

<table>
<thead>
<tr>
<th>Ion</th>
<th>Concentration (mg L(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na(^+)</td>
<td>8460 ± 30</td>
</tr>
<tr>
<td>Mg(^{2+})</td>
<td>860 ± 10</td>
</tr>
<tr>
<td>Ca(^{2+})</td>
<td>280 ± 30</td>
</tr>
<tr>
<td>K(^+)</td>
<td>505 ± 50</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>14410 ± 330</td>
</tr>
<tr>
<td>SO(_4^{2-})</td>
<td>330 ± 200</td>
</tr>
</tbody>
</table>

**MLA medium preparation**

Firstly, the primary stock solutions, stock solutions and 40 times concentrated nutrient solutions were prepared step by step with purified water based on the ingredients in Table 3.5, 3.6 and 3.7. After sterilization through Millipore 0.22 µm filters, these solutions were stored in the refrigerator at 4 °C. Then MLA medium was prepared by adding 25mL of nutrient solutions (solution 8) and 1mL of CaCl\(_2\)·2H\(_2\)O solutions (solution 9) into 960 mL purified water, then filtering through a 0.22 µm Millipore filter.

Table 3.5 Primary stock solutions for MLA medium

<table>
<thead>
<tr>
<th>Primary Stock solution</th>
<th>Concentration</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biotin/Vitamin B12</td>
<td>100 mg L(^{-1})</td>
<td>Sigma 99%</td>
</tr>
<tr>
<td>Biotin</td>
<td>100 mg L(^{-1})</td>
<td>Fluka 99%</td>
</tr>
<tr>
<td>CuSO(_4)·5H(_2)O</td>
<td>1 g L(^{-1})</td>
<td>Sigma 98%</td>
</tr>
<tr>
<td>ZnSO(_4)·7H(_2)O</td>
<td>2.2 g L(^{-1})</td>
<td>Fluka 99%</td>
</tr>
<tr>
<td>CoCl(_2)·6H(_2)O</td>
<td>1.0 g L(^{-1})</td>
<td>Chem-Supply 98%</td>
</tr>
<tr>
<td>Na(_2)MoO(_4)·2H(_2)O</td>
<td>0.6 g L(^{-1})</td>
<td>Sigma 99.5%</td>
</tr>
</tbody>
</table>
Table 3.6 Stock solutions for MLA medium

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>6</strong> Vitamins</td>
<td></td>
</tr>
<tr>
<td>Biotin/Vitamin B12 Primary Stock solution (1)</td>
<td>5 mL L$^{-1}$</td>
</tr>
<tr>
<td>Thiamine HCl</td>
<td>100 mg L$^{-1}$</td>
</tr>
<tr>
<td><strong>7</strong> Micronutrients</td>
<td></td>
</tr>
<tr>
<td>Na$_2$EDTA</td>
<td>4.36 g L$^{-1}$</td>
</tr>
<tr>
<td>FeCl$_3$·6H$_2$O</td>
<td>1.58 g L$^{-1}$</td>
</tr>
<tr>
<td>NaHCO$_3$</td>
<td>0.60 g L$^{-1}$</td>
</tr>
<tr>
<td>MnCl$_2$·4H$_2$O</td>
<td>0.36 g L$^{-1}$</td>
</tr>
<tr>
<td>CuSO$_4$·5H$_2$O (2)</td>
<td>10 mL L$^{-1}$</td>
</tr>
<tr>
<td>ZnSO$_4$·7H$_2$O (3)</td>
<td>10 mL L$^{-1}$</td>
</tr>
<tr>
<td>CoCl$_2$·6H$_2$O (4)</td>
<td>10 mL L$^{-1}$</td>
</tr>
<tr>
<td>Na$_2$MoO$_4$·2H$_2$O (5)</td>
<td>10 mL L$^{-1}$</td>
</tr>
</tbody>
</table>

Table 3.7 40 times concentrated nutrient solutions for MLA medium

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>8</strong> Nutrients</td>
<td></td>
</tr>
<tr>
<td>MgSO$_4$·7H$_2$O</td>
<td>2 g L$^{-1}$</td>
</tr>
<tr>
<td>NaNO$_3$</td>
<td>6.8 L$^{-1}$</td>
</tr>
<tr>
<td>K$_2$HPO$_4$</td>
<td>1.4 L$^{-1}$</td>
</tr>
<tr>
<td>H$_3$BO$_3$</td>
<td>0.1 L$^{-1}$</td>
</tr>
<tr>
<td>H$_2$SeO$_3$</td>
<td>40 mL L$^{-1}$</td>
</tr>
<tr>
<td>Vitamin stock (6)</td>
<td>40 mL L$^{-1}$</td>
</tr>
<tr>
<td>Micronutrient stock (7)</td>
<td>40 mL L$^{-1}$</td>
</tr>
<tr>
<td><strong>9</strong> CaCl$_2$·2H$_2$O</td>
<td>29.4 g L$^{-1}$</td>
</tr>
</tbody>
</table>
Culture inoculation

250 mL of microalgae stock culture was incubated in 175 cm$^2$ angled neck flasks (Corning, USA). After two weeks cultivation, 20 mL of the stock microalgae culture was inoculated into 380 mL newly prepared media in a sterile conical flask. The cultures were cultivated under ambient temperature 25 ±3 °C and continuously exposed to light at an incident intensity of approximately 130 µmol m$^{-2}$ s$^{-1}$[8]. An orbital shaker (SS70, Chiltern Scientific, Australia) was operated at 120 rpm to provide agitation for the culture flasks. A ventilated plastic film was covered over the flask mouth to prevent contamination and water evaporation.

3.2 The novel CO$_2$ delivery system

Experiments were conducted according to the setup shown in Figure 3.2. Solvents were loaded with CO$_2$ prior to each experiment. CO$_2$ rich solvent was sealed in the glass bottle by a rubber stopper with an inlet and an outlet. The platinum-cured silicone tubing (Masterflex, Cole-Parmer, USA) was used to connect two bundled hollow fibre PDMS membranes, and membranes with the inlet and the outlet of solvent bottle. The bundled membranes immersed in 400 mL microalgal media in each of two duplicate conical flasks. CO$_2$ rich solvent (1 litre) in glass bottle was pumped though silicone tubing, then arrived the tube side of hollow fibre PDMS membranes in the flasks, CO$_2$ in the rich solvents was released from the tube side solvent to the medium and provided a carbon source for microalgae growth. After depleting in CO$_2$, the lean solvent was recycled back to the CO$_2$ loaded solvent container. The peristaltic pump (Masterflex, Cole-Parmer, USA) provided solvent flow rate of 10.6 mL min$^{-1}$. No CO$_2$ topped up for the solvents during the experiment. The CO$_2$ concentration in solvents declined over two weeks (by 20%). The decline was always greater than the algal uptake. One reason was water pass through membrane from the medium side to solvent side, which diluted the solvent. CO$_2$ was also lost to the atmosphere directly from the solvent storage container or the platinum-cured silicone tubing.
Figure 3.2 A schematic of the experimental setup developed in the laboratory

3.3 Analysis

3.3.1 Microalgae cultivation

10 mL of microalgae broth was taken out regularly for pH and optical density measurement. Each sample was filtered through a 0.45 µm Millipore syringe filter and the filtrate tested for: different metals (K, Na, Ca, Mg), inorganic elements (phosphorus, boron), NO₃⁻, total nitrogen (TN), total carbon (TC), dissolved inorganic carbon (DIC).

pH

The sample pH was monitored using a pH meter (HI 9125, HANNA, Australia), which was calibrated using standard buffer solutions of pH 4 and 7.

Optical density

Optical density was measured at 750 nm using a Cary 3E UV-Vis absorbance spectrophotometer (Agilent Technologies, Mulgrave, VIC, Australia).

Measurement of ions

The concentrations of metals (K, Na, Ca, Mg) and those of inorganic elements (boron, phosphorus) were determined using inductively coupled plasma optical emission spectrometry (ICP-OES 720 ES, Varian).

In Chapter 4, the NO₃⁻ concentration was determined using Ion Chromatography (ICS-1000, Dionex). In Chapter 6, the NO₃⁻ concentration was estimated using the
absorbance at 275 nm and 220 nm (APHA Method 4500-NO₃⁻ B)[¹⁷] by means of a Cary 3E UV-Vis absorbance spectrophotometer (Agilent Technologies, Mulgrave, VIC, Australia). A comparison of the two methods has been conducted to prove that there was no measurable difference between these two methods.

The concentrations of Cl⁻ and SO₄²⁻ were determined using Ion Chromatography (ICS-1000, Dionex).

**Total nitrogen**

A sample of 4 mL was added to 2 mL digestion reagent, which is the mix of 20.1 g L⁻¹ K₂S₂O₈ (Sigma-Aldrich, 99%) and 3 g L⁻¹ NaOH (Chem-Supply, 97%). Then the combined sample was digested in an autoclave (HIRAYAMA, Japan) at 121 °C for 30 min. After cooling down, the digested sample was mixed with 0.4 mL 1mol L⁻¹ HCl (Merck, 99.8%) and analysed using the absorbance at 275 nm and 220 nm (APHA Method 4500-N C)[¹⁷] by means of a Cary 3E UV-Vis absorbance spectrophotometer (Agilent Technologies, Mulgrave, VIC, Australia).

**Total carbon and dissolved inorganic carbon**

The total carbon (TC) and dissolved inorganic carbon (DIC) in the culture medium were measured using a Total Organic Carbon Analyser (TOC-VCSH, SHIMADZU).

At the end of experiments, samples were taken out for dry weight and lipid measurements.

**Dry weight**

20 mL samples of culture were taken out at the end of the cultivation period and filtered through glass microfiber filters (Whatman GF/C 47mm), which were washed once with 20 mL deionized water and dried at 105 °C for 16 h [¹⁸]. The linear regression relationships of optical density and dry weight for each microalgae strain are presented in Chapters 4, 5 and 6, respectively.

The specific growth rate μ (d⁻¹) of the microalgae in exponential phase is determined using Equation 3.5.
\[ \mu = \frac{\ln X_t - \ln X_{t_0}}{t - t_0} \]  

(3.5)

where \( X_t \) refers to the biomass concentration at the end of exponential phase,

\( X_{t_0} \) refers to the biomass concentration at the beginning of exponential phase,

\( t \) refers to the cultivation day at the end of exponential phase,

\( t_0 \) refers to the cultivation day at the beginning of exponential phase.

The biomass productivity is calculated according to Equation 3.6.

\[ Productivity = \frac{X_t - X_{t_0}}{t - t_0} \]  

(3.6)

**Lipid measurement**

50 mL samples of culture were taken out at the end of the cultivation period, centrifuged at 1400 g for 10 min (Avanti™ 30, Beckman, Australia). The top water phase was discarded, and the remaining biomass was resuspended with 1.2 mL water. Olmstead’s method\[^{15}\] was used for lipid extraction. The method included the following steps.

1) The 1.2 mL sample was mixed with 3 mL methanol and 1.5 mL chloroform.
2) The mixer was vortexed and rotated overnight.
3) Another 1.5 mL of chloroform and 1.5 mL of water were added to the sample.
4) The sample was vortexed and centrifuged at 1400 g for 5 min.
5) The bottom chloroform phase containing the extracted lipid was collected.
6) The top water soluble phase was discarded.
7) The remaining biomass was re-suspended with 1.2 mL water. Steps 1 – 7 were repeated two more times.
8) The collected chloroform phase was dried with nitrogen stripping at 40 °C. The remaining mass was considered to represent the recovered lipids.

**3.3.2 Chemical solvents**

**KHCO\textsubscript{3} and K\textsubscript{2}CO\textsubscript{3} concentrations**

A 5 mL sample was diluted with 50 mL purified water. The diluted sample was titrated against 0.4 mol L\textsuperscript{-1} sulphuric acid in the autotitrator (Metrohm 905
Titrando, Switzerland). During the titration, two endpoints were determined by the software. Based on the acid consuming volumes at these two endpoints ($V_1$ and $V_2$), the concentrations of $\text{HCO}_3^-$ and $\text{CO}_3^{2-}$ were calculated using Equations 3.7 and 3.8.

\[
\left[ \text{CO}_3^{2-} \right] = \frac{V_1 \times [\text{H}_2\text{SO}_4] \times 2}{V_{\text{sample}}} \tag{3.7}
\]

\[
\left[ \text{HCO}_3^- \right] = \frac{(V_2-2V_1) \times [\text{H}_2\text{SO}_4] \times 2}{V_{\text{sample}}} \tag{3.8}
\]

**Concentration of inorganic carbon in MEA and PG solutions**

The carbon concentrations in MEA and PG solutions were determined using a CO$_2$ coulometer (CM5015, UIC, USA). Firstly, 200 µL of sample was acidified in the reaction vessel to evolve inorganic carbon. Then, a CO$_2$-free carrier gas swept the evolved CO$_2$ into the CO$_2$ coulometer, where it reacted with MEA to form a titratable acid that caused the colour indicator to fade. The change in colour of the solution was monitored by the photodetector and reported as percentage transmittance (%T). In addition, the titration current was automatically activated to electrochemically regenerate the base at a rate proportional to the %T. Based on the generated current, the carbon concentration was measured.

**3.3.3 Surface image of membrane and microalgae image**

The membrane surface was photographed using a microscope (Prism optical, SciTech, Australia). The microalgae images were taken using an Olympus BX51 microscope (Olympus Optical, Japan).


Chapter 4 Energy efficient transfer of carbon dioxide from flue gases to microalgal systems

4.1 Chapter perspective

A novel system was demonstrated in this chapter. In this system, carbon dioxide can be transferred directly from a potassium carbonate solution into a microalgal culture, via commercially available PDMS hollow fibre membranes. Chemical solvents (20 wt% potassium carbonate with 0.2, 0.5 and 0.7 CO₂ loadings) were evaluated for microalgae growth improvement in this novel system. Some practical issues, such as limitation factors during microalgae growth, ion permance through membrane and membrane fouling, were also investigated in this chapter.

Declaration for a thesis with publication

PhD and MPhil students may include a primary research publication in their thesis in lieu of a chapter if:

- The student contributed greater than 50% of the content in the publication and is the “primary author”, i.e. the student was responsible primarily for the planning, execution and preparation of the work for publication
- It has been peer-reviewed and accepted for publication
- The student has approval to include the publication in their thesis from their Advisory Committee
- It is a primary publication that reports on original research conducted by the student during their enrolment
- The initial draft of the work was written by the student and any subsequent editing in response to co-authors and editors reviews was performed by the student
- The publication is not subject to any obligations or contractual agreements with a third party that would constrain its inclusion in the thesis

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### A. PUBLICATION DETAILS (to be completed by the student)

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<td>Authors</td>
<td>QI Zheng, Gregory J. O. Martin and Sandra E. Kentish</td>
</tr>
<tr>
<td>Student’s contribution (%)</td>
<td>70</td>
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<tr>
<td>Journal or book name</td>
<td>Energy &amp; Environmental Science</td>
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<td>Volume/page numbers</td>
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### B. STUDENT’S DECLARATION

I declare that the publication above meets the requirements to be included in the thesis

**Student’s name**

QI Zheng

**Student’s signature**

15/05/17

### C. PRINCIPAL SUPERVISOR’S DECLARATION

I declare that:

- the information above is accurate
- The advisory committee has met and agreed to the inclusion of this publication in the student’s thesis
- All of the co-authors of the publication have reviewed the above information and have agreed to its veracity
- 'Co-Author Authorisation' forms for each co-author are attached.

**Supervisor’s name**

Sandra E. Kentish

**Supervisor’s signature**

15/05/17
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In cases where all members of a large consortium are listed as authors of a publication, only those that actively collaborated with the student on material contained within the thesis should complete this form. This form is to be used in conjunction with the Declaration for a thesis with publication form.

Students must submit this form, along with the Declaration for thesis with publication form, when the thesis is submitted to the Thesis Examination System: [https://tes.app.unimelb.edu.au/](https://tes.app.unimelb.edu.au/)


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<td>Journal or book name</td>
<td>Energy &amp; Environmental Science</td>
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<td>Status</td>
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## B. CO-AUTHOR’S DECLARATION (to be completed by the collaborator)

I authorise the inclusion of this publication in the student's thesis and certify that:

- the declaration made by the student on the Declaration for a thesis with publication form correctly reflects the extent of the student's contribution to this work;
- the student contributed greater than 50% of the content of the publication and is the "primary author" i.e. the student was responsible primarily for the planning, execution and preparation of the work for publication.

<table>
<thead>
<tr>
<th>Co-author’s name</th>
<th>Co-author’s signature</th>
<th>Date (dd/mm/yyyy)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gregory J.O. Martin</td>
<td></td>
<td>15/05/17</td>
</tr>
</tbody>
</table>
Co-author authorisation form

All co-authors must complete this form. By signing below co-authors agree to the listed publication being included in the student's thesis and that the student contributed greater than 50% of the content of the publication and is the "primary author" i.e. the student was responsible primarily for the planning, execution and preparation of the work for publication.

In cases where all members of a large consortium are listed as authors of a publication, only those that actively collaborated with the student on material contained within the thesis should complete this form. This form is to be used in conjunction with the Declaration for a thesis with publication form.

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B. CO-AUTHOR'S DECLARATION (to be completed by the collaborator)

I authorise the inclusion of this publication in the student’s thesis and certify that:

- the declaration made by the student on the Declaration for a thesis with publication form correctly reflects the extent of the student’s contribution to this work;
- the student contributed greater than 50% of the content of the publication and is the "primary author" i.e. the student was responsible primarily for the planning, execution and preparation of the work for publication.

Co-author's name | Co-author's signature | Date (dd/mm/yyyy)
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<td>Sandra E. Kentish</td>
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The University of Melbourne
CRICOS Provider Number: 00115K

Last Updated 17 August 2015
4.2 Abstract

This article demonstrates a novel combination of solvent absorption, membrane desorption and microalgal cultivation to capture carbon dioxide and convert it to an lipid-rich biomass. In the system, carbon dioxide is absorbed into a potassium carbonate solvent and this gas is desorbed directly into the microalgal medium via a non-porous polydimethyl siloxane (PDMS) hollow fibre membrane. This single step approach provides a paradigm shift in the cost of carbon delivery to the microalgae, as the very large reboiler energy demand of standard carbon capture solvent regeneration is avoided, as is the energy associated with gas compression. Specifically, the use of a 20%wt potassium carbonate solvent with 0.2, 0.5 and 0.7 CO₂ loading was evaluated as a mechanism to deliver carbon dioxide to cultures of a salt tolerant *Chlorella* sp. microalgae. In all cases, accelerated growth of *Chlorella* sp. was observed, relative to a control. The use of carbonate solutions of 0.5 and 0.7 loading resulted in the highest volumetric productivity (0.38 g L⁻¹ d⁻¹) and biomass concentration (1.8 g L⁻¹) by completely avoiding carbon limitation of the cultures. The system has demonstrated potential for the generation of biofuels that utilise carbon dioxide generated from power station flue gases with minimal parasitic energy demand.

4.3 Introduction

There is an ever increasing need to reduce greenhouse gas emissions and to replace our dependency on fossil fuels without impacting on global food supplies. Microalgae can be grown without competing for arable land while capturing carbon dioxide [1]. The biomass produced can then be converted to fuels such as biodiesel and other products such as commodity chemicals, protein feed and nutraceuticals [1].

The cost of cultivating microalgae is a barrier to large scale commercialisation[2]. One of the major costs is the delivery of CO₂ [3] which is required to achieve high productivity and to maximise the use of available solar radiation. In this regard, most research has focused on the delivery of raw flue gas or purified carbon dioxide to microalgae ponds or photobioreactors [4-9]. The carbon dioxide captured from the flue gases of fossil fuel power stations is a direct way to reduce
greenhouse gas emissions. However, delivery in this manner can be highly energy intensive due to the need to capture and compress gas and deliver it over the hectares of land required for raceway pond algal production [10].

The most common process proposed for CO₂ capture from fossil fuel power stations is chemical absorption of the carbon dioxide to form a loaded solvent [11], using solvents such as potassium carbonate [12], MEA [13], MDEA [14] and piperazine [15]. However, the energy associated with the regeneration of this loaded solvent is prohibitive, varying from 2.4 to 4.2 GJ t⁻¹ CO₂ [16].

To improve the energy efficiency of delivering CO₂ to microalgae, two approaches have so far been considered. Firstly, there has been a focus on the isolation of microalgae that are tolerant of high CO₂ concentrations. In a life cycle analysis completed by Stephenson et al. [17], an increase in CO₂ concentration in feed gas from 5% to 12.5%, reduced the energy requirement for biodiesel production from 23.7 to 6.5 GJ t⁻¹ of biodiesel. Secondly, there has been a focus on improving the rates of CO₂ mass transfer within the microalgal media. The most common method is to sparge cultures with CO₂ bubbles [18, 19]. Al-Mashhadani et al. [20] used a fluidic oscillation diffuser to create microbubbles in order to achieve longer retention time, while Fan et al. [8] used a PVDF hollow fiber membrane to form small bubbles. However, in all these approaches, much of the CO₂ may be lost to the atmosphere as gas bubbles, through buoyancy effects.

Alternatively, a number of workers have considered the use of membrane contactors. In this case, the CO₂ is delivered to the algal medium in a dissolved state within the media, rather than as free bubbles, minimizing loss. For example, Kim at al. [21] utilized a sandwich membrane consisting of a dense polyurethane membrane and microporous polyethylene membrane to deliver CO₂ from a pure gas into a medium that was then pumped through the microalgal culture. However, this system still cannot avoid the energy penalty for carbon dioxide gas compression and transportation.

Noel et al. [22] proposed an alternate approach where a solid sorbent was first used to adsorb carbon dioxide. The CO₂ was then stripped into a sodium carbonate solution to produce a bicarbonate-rich solution. In turn, a CO₂ selective membrane
was used to transfer the carbon dioxide, again in a dissolved state into seawater through contact of the two liquids either side of the membrane. This seawater was finally provided to a photobioreactor as a carbon source. Importantly, this approach eliminated the energy impact of solvent regeneration. However, the approach was complicated by a number of inter-related unit operations that would add to capital cost and reduce the efficiency of the operation.

Here, a novel approach that can deliver inorganic carbon to a microalgal population in a single step and with minimum energy demand is proposed. As shown in Figure 1, carbon dioxide is first absorbed from a raw flue gas, or other source of CO₂, into a potassium carbonate solution, via reactions (4.1) to (4.3):

\[
\begin{align*}
    \text{CO}_2(g) & \rightleftharpoons \text{CO}_2(l) \quad (4.1) \\
    \text{CO}_2(l) + \text{OH}^- & \rightleftharpoons \text{HCO}_3^- \quad (4.2) \\
    \text{HCO}_3^- + \text{OH}^- & \rightleftharpoons \text{CO}_3^{2-} + \text{H}_2\text{O} \quad (4.3)
\end{align*}
\]

Potassium carbonate has been utilized in industry to absorb CO₂ for many decades [23] and is used here as a solvent typical of those under consideration for large scale carbon capture.[24]

Importantly, this carbon dioxide loaded solvent is then pumped directly through microalgal raceway ponds or photobioreactors, within CO₂ selective hollow fibre membranes. The carbon dioxide is delivered directly as a dissolved gas into the microalgal medium through contact of the two liquids either side of a non-porous membrane. This transport occurs because the dissolved carbon dioxide concentration in the algal media is lower than in the rich potassium carbonate solution and hence reactions 4.1 to 4.3 are reversed. Once within the microalgal medium, the carbon dioxide can be absorbed by the microalgal cells directly as CO₂ or converted into carbonate or bicarbonate anions for consumption. After depletion, the lean solvent can then be recirculated directly to the absorber.

This approach has several important advantages. Firstly, the energy associated with capture solvent regeneration (2.4-4.2 GJ t⁻¹ CO₂) [16] is avoided. This dramatically reduces the cost of capture, which has been the main barrier to implementation. Secondly, the high energy demand associated with compressing a
gas stream for delivery to microalgal ponds is eliminated and there is no loss of gas through evolution of free bubbles. Finally, the complications implicit in the process proposed by Noel et al. [22] as discussed above, are eliminated. Rather than the use of a receiving solution, the carbon dioxide is delivered directly from loaded solvent to the medium.

Figure 4.1 A schematic of the proposed process. Carbon dioxide is absorbed from a combustion flue gas into a potassium carbonate solvent which is then pumped through a microalgal raceway pond or photobioreactor. The carbon dioxide desorbs into the microalgal culture medium and the depleted solvent is returned to the absorber. There is no need for a receiving solution, or a capture stripping operation.

4.4 Materials and methods

4.4.1 Materials
The solvent chosen was a 20%wt potassium carbonate solution with different CO$_2$ loadings prepared by mixing quantities of K$_2$CO$_3$ (Senator Chemicals, 99.7%) and KHCO$_3$ (Univar, 98%) in purified water (Table 4.1).

The solvent loading is defined as eqn (4.4):

$$loading = \frac{[HCO_3^-]}{[K^+]}$$  \hspace{1cm} (4.4)

A salt tolerant strain of *Chlorella* sp., isolated from Cooper Creek at Innamincka, SA, Australia$^{[25]}$, was used in these experiments. This strain was chosen as it grows well in salt water and can produce lipids suitable for biofuel production$^{[25]}$. The strains were cultured in 3% artificial ocean water mix (Ocean Fish, Prodac International, Italy) and Modified-F medium$^{[25]}$.

Hollow fibre membranes kindly supplied by Airrane (Korea) were used. These are a composite membrane with a polysulfone support layer and a thin non-porous polydimethylsiloxane (PDMS) layer coating as described in Table S4.1. PDMS is a rubbery polymer membrane that has a high selectivity for carbon dioxide $^{[26]}$. Due to its high selectivity, it is widely used in gas separation.

### 4.4.2 Methods

*Chlorella* sp. cultures were grown in 400 mL of modified F-medium$^{[25]}$ in 500 mL Erlenmeyer flasks inoculated with cells harvested in the exponential growth phase to an initial concentration of approximately 0.09 g L$^{-1}$. During cultivation the culture flasks were illuminated at a light intensity of approximately 130 µmol m$^{-2}$ s$^{-1}$, held at ambient temperature (25 ± 3 °C) and agitated at 120 rpm on an orbital shaker (SS70, Chiltern Scientific, Australia). Flask openings were sealed with vented plastic film to limit water evaporation.

20%wt K$_2$CO$_3$ solutions with initial loadings of 0.2, 0.5, 0.7 were pumped through the tube side of hollow fibre PDMS membranes immersed in the microalgal medium (Figure 4.2) in duplicate flasks. This loading fell slightly during the two weeks of the experiment due to some loss of CO$_2$ from the carbonate solvent to the atmosphere. Duplicate control flasks were included in which cultures were grown.
in flasks without any active CO$_2$ delivery via membrane or gas injection. All results are presented as the average of duplicate cultures.

Table 4.1 The initial composition of 20%wt K$_2$CO$_3$ with different loadings

<table>
<thead>
<tr>
<th>KHCO$_3$-20%wt-0.2 loading</th>
<th>KHCO$_3$ (mol L$^{-1}$)</th>
<th>K$_2$CO$_3$ (mol L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.624</td>
<td>1.34</td>
</tr>
<tr>
<td>KHCO$_3$-20%wt-0.5 loading</td>
<td>1.578</td>
<td>0.867</td>
</tr>
<tr>
<td>KHCO$_3$-20%wt-0.7 loading</td>
<td>2.285</td>
<td>0.471</td>
</tr>
</tbody>
</table>

Figure 4.2 A schematic of the experimental system

4.4.3 Analysis

Samples (5 mL) of the microalgae culture medium were taken daily to monitor pH (HI 9125, HANNA, Australia, calibrated using pH 4 and 7 buffer solutions) and optical density. The optical density was monitored using a Cary 3E UV-Vis absorbance spectrophotometer (Agilent Technologies, Mulgrave, VIC, Australia) at an absorbance of 750 nm. An additional 5mL was taken on Days 0, 2, 4, 10 and 15 for determination of inorganic carbon (IC), nitrate and potassium after filtration through a 0.45µm filter. The IC was determined with a Total Organic Carbon Analyser (TOC-VCSH, SHIMADZU) while nitrate was measured by Ion Chromatography (ICS-1000, Dionex). Potassium was determined after dilution using inductively coupled plasma optical emission spectrometry (ICP-OES 720 ES, Varian). In 15 days, a total of 100 mL sample volume was taken from each culture flask. The composition of the potassium carbonate solvent was also monitored.
throughout the experiment by titration (905 Titrando autotitrator, Metrohm) and ICP-OES analysis.

At the end of the culture period, the dry weight of cells in each flask was determined in duplicate by taking 20 mL samples of the culture, which were filtered through Whatman GF/C 47 mm glass microfiber filters and washed with 20 mL deionized water. The filter was then dried at 105°C for 16 h. There was a strong linear correlation between the measured optical density and dry cell weight (dry cell weight (g L⁻¹) = 0.2298 × optical density + 0.0886, R² = 0.994), confirming the accuracy of both approaches.

The lipid extraction method from Olmstead et al. [25] was used, which included the following steps: a 1.2 mL sample is mixed with 3 mL methanol and 1.5 mL chloroform and then vortexed and rotated overnight. Another 1.5 mL chloroform and 1.5 mL water are then added to the sample, vortexed and centrifuged at 1400 g for 5 min. The chloroform phase containing the extracted lipid is separated and collected. The remaining biomass is re-suspended with 1.2 mL water and processed two more times according to the previous procedures. All the chloroform phases thus obtained are dried with nitrogen stripping at 40°C. The remaining mass is considered to represent the recovered lipids.

4.5 Results and discussion

4.5.1 Effect of loading on Chlorella sp. growth

The growth of Chlorella sp. was compared for cultures supplied with carbon dioxide by the membrane process using 0.2, 0.5, 0.7 loadings of potassium carbonate to a control culture which relied solely on atmospheric diffusion of carbon dioxide (Figure 4.3). Significantly, for all CO₂ loadings, Chlorella sp. showed enhanced growth relative to the control, as indicated by greater biomass concentration. A considerable improvement in rate was observed for the 0.2 loading relative to the control throughout the duration of the experiment. An increased biomass concentration in the cultures with 0.5 and 0.7 loadings compared to the 0.2 loading was evident after approximately 5 days. The growth curve of the 0.7 loading culture was identical to that at 0.5 within error. After 15
days of growth, excellent biomass concentrations (1.63 ± 0.10 and 1.77 ± 0.02 g L\(^{-1}\) respectively) were achieved for the 0.5 and 0.7 loadings, significantly higher than with 0.2 loading (0.90 ± 0.03 g L\(^{-1}\)) and much higher still than the control (0.16 ± 0.02 g L\(^{-1}\)).

Figure 4.3 Growth curves measured by optical density of *Chlorella* sp. supplied with carbon dioxide by membrane delivery at different potassium carbonate loadings or by atmospheric diffusion only (the control). Results are the mean of duplicate experiments and error bars show the range of the duplicates.

### 4.5.2 Limitation factors during *Chlorella* sp. growth

In order to understand more about the performance of *Chlorella* sp. during operation with different solvents, growth limiting factors such as pH, nitrate, inorganic carbon (IC) were also measured (Figure 4.4-4.6, Figure 4.S1). For the control experiment, from Day 0 to 1.5, *Chlorella* sp. was in a lag phase. In this period, the biomass concentration increased slowly (Figure 4.3), the pH was constant at around 7.5 (Figure 4.4) and the nitrate decreased slightly from 80 mgN L\(^{-1}\) to 60 mgN L\(^{-1}\) (Figure 4.5). As there was no artificial carbon addition, the inorganic carbon concentration was constant at around 8 mg L\(^{-1}\) (Figure 4.6) during the lag period.

For this control experiment, from day 1.5 to 15, *Chlorella* sp. was in a carbon limited growth stage. The microalgae utilizes carbon dioxide from the medium,
resulting in a pH increase. As the medium cannot provide the photosynthesising cells with adequate carbon, the biomass concentration can only increase at a slow rate, proportional to the rate of carbon delivery. This results in approximately linear growth that can be described by a fixed-volume fed-batch growth model which can be used to determine the carbon uptake rate by the microalgae\cite{28,29} according to eqn(4.5):

\[
X = X_i + \frac{FS_{feed}}{V} Y_{X/c} t
\]  

(4.5)

Where \(X_i\) represents the initial biomass concentration, \(FS_{feed}\) is the substrate feed rate (in this case assumed equivalent to the carbon uptake rate) (g L\(^{-1}\) d\(^{-1}\)) and \(V\) is the culture volume which is fixed (L) and \(Y_{X/c}\) is the yield coefficient. According to Anjos et al.\cite{19}, the carbon content in *Chlorella vulgaris* biomass is 45.6\%. The yield coefficient can then be calculated from eqn(4.6):

\[
Y_{X/c} = \frac{\text{biomass}}{\text{carbon}} = \frac{1}{0.456} = 2.193
\]  

(4.6)

Accordingly, in the control experiment the microalgae could only absorb a small amount of carbon dioxide sourced from the atmosphere, which equated to a carbon delivery rate of about 0.0025 ± 0.0006 gC L\(^{-1}\) d\(^{-1}\).

The growth of microalgae through which potassium carbonate solution of 0.2 loading was circulated can be divided into four phases. As with the control, the experiment commences with a lag phase (Figure 4.3). However, in this period, the pH has a more obvious decline (Figure 4.4), indicating that carbon dioxide was transferring from the solvent, through the membrane and into the medium. This transfer is also confirmed by the IC increase during this period (Figure 4.6). From days 1.5 to 4, growth appears unlimited, showing approximately exponential growth (Figure 4.3). *Chlorella* sp. has sufficient carbon, nitrogen and light. In this period the specific growth rate \(\mu\) (d\(^{-1}\)) of the microalgae can be determined from eqn(4.7):

\[
\mu = \frac{\ln X_t - \ln X_{t0}}{t - t_0}
\]  

(4.7)
where \( X \) is the microalgae biomass concentration (g L\(^{-1}\)), \( t \) is time and \( t_0 \) is the beginning of the exponential growth stage. Accordingly, over this period the maximum specific growth rate was 0.32 ± 0.02 d\(^{-1}\). The pH shows a steep increase (Figure 4.4), revealing that the culture absorbs increasing amounts of carbon as the population grows, until the demand exceeds the supply at approximately day 4. From day 4 to 8, growth appears carbon limited. As the carbon dioxide delivery rate provided by the 0.2 loaded solvent is now insufficient to meet the microalgae demand, the increase in Chlorella sp. biomass becomes approximately linear with time as it is dependent on the constant supply of carbon dioxide (Figure 4.3). The pH becomes stable at around 9.5, consistent with a constant, low concentration of carbon dioxide (Figure 4.4). Finally, from day 8 to 15, growth appears nitrogen limited. Nitrate concentration was about 40 mgN L\(^{-1}\) on Day 4 and dropped to zero when next measured at day 10 (Figure 4.5). As shown by the dashed line, the nitrate may indeed have already been zero on day 8. So in this stage, nitrogen is no longer available to the cells preventing \textit{de novo} synthesis of protein, limiting cell division and population growth. The cells are still able to photosynthesise and utilise the carbon dioxide provided to them, however they now produce storage lipids instead of new cells\(^{25}\).

Similar phenomena are observed for the 0.5, 0.7 loading cases, except in this cases the carbon demand appears to be able to be met by the increased carbon dioxide transfer rate provided by these higher loadings. Firstly, from day 0 to 1.5, the microalgae culture is in a lag phase. There is carbon transfer from the CO\(_2\) loaded solvent to the microalgae medium. However, as the microalgae density is low, the microalgae cannot absorb all the carbon. Thus CO\(_2\) accumulates in the medium as carbonate and bicarbonate anions, causing the pH to fall sharply (Figure 4.4). The reactions occurring are as indicated in eqn (4.2) and (4.3).

From day 1.5 to 5, the microalgal growth is in an unlimited, exponential phase, with a specific growth rate of 0.46 ± 0.01 d\(^{-1}\) and 0.41 ± 0.01 d\(^{-1}\) at 0.5 and 0.7 loading respectively. It is not clear why the growth rate is higher during this period for the 0.5 and 0.7 loading than for the 0.2 loading, and is possibly not significant within experimental uncertainty. The CO\(_2\) being transferred into the medium is
consumed and the pH in the medium increases (Figure 4.4). However, interestingly, the inorganic carbon in the solution in this period continues to increase (Figure 4.6). Although never reaching carbon limitation, the carbon uptake rate at the end of this period was estimated to be 0.173 and 0.176 g C L\(^{-1}\) d\(^{-1}\) for the 0.5 and 0.7 loadings respectively. This is considerably higher than the 0.2 loading and higher still than the control, demonstrating the effectiveness of this approach in preventing carbon limitation even in dense microalgal cultures.

From day 5 to 8, growth appears nitrogen limited, with a steep decline in the nitrate concentration (Figure 4.5). As the dashed line shows, nitrate may already be 0 at day 5. In this stage, the microalgae reach a stationary phase, with the microalgal growth, pH, IC all stabilizing. After day 8, there appears to be little further growth. Both nitrogen and/or light may be limiting factors in this stage, with the duration of nitrogen starvation likely to have resulted in highly stressed cells.

Figure 4.4 pH in microalgae medium in different loadings and control. Results are the mean of duplicate experiments and error bars show the range of the duplicates.
4.5.3 Effect of loading on biomass and lipid production

The productivity of microalgal cultures is critical to cost efficient biomass production. In this regard it is important that cultures are provided enough carbon to fully utilise the available light, which is the key resource for an outdoor culture. The average and maximal volumetric productivity of the 15 d cultures were greatly improved using this approach (Table 4.2). The further improvement of the 0.5
compared with the 0.2 loading indicates the value of increasing the loading in the solvent, but the approximately equal performance of the 0.5 and 0.7 loading show there is an upper limit, which translates to meeting the carbon demand of the culture.

Table 4.2 Comparison of volumetric productivity (g L⁻¹ d⁻¹) of *Chlorella* sp. with different loadings

<table>
<thead>
<tr>
<th></th>
<th>Average</th>
<th>Maximum</th>
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<tbody>
<tr>
<td>Control</td>
<td>0.0054±0.0013</td>
<td>0.021±0.01</td>
</tr>
<tr>
<td>0.2 loading</td>
<td>0.058±0.002</td>
<td>0.11±0.01</td>
</tr>
<tr>
<td>0.5 loading</td>
<td>0.126±0.005</td>
<td>0.38±0.01</td>
</tr>
<tr>
<td>0.7 loading</td>
<td>0.137±0.002</td>
<td>0.39±0.02</td>
</tr>
</tbody>
</table>

The improvement in productivity resulting from provision of carbon dioxide seen here is significantly better than other studies in which carbon dioxide was delivered using other approaches (a summary of other work is shown in Table S4.2). In other research into CO₂ delivery to microalgae via sparging with air containing 10% CO₂, cultures of *Chlorella pyrenoidosa*[^4] and *Chlorella vulgaris*[^30] achieved maximum biomass productivities of 0.144 g L⁻¹ d⁻¹ and 0.104 g L⁻¹ d⁻¹ respectively. *Chlorella vulgaris*[^31] achieved 0.14 g L⁻¹ d⁻¹ maximum biomass productivity in vertical tubular photobioreactors and *Chlorella kessleri*[^5] achieved 0.087 g L⁻¹ d⁻¹ maximum biomass productivity in conical flask when sparging with air containing 6% CO₂. Compared to conventional CO₂ delivery systems, using CO₂ loaded solvents can thus increase microalgae biomass productivity while importantly avoiding loss of large amounts of CO₂ to the atmosphere.

As a source of “green energy”, biofuels produced from the lipid content of microalgae have attracted much attention. In order to evaluate the lipid content in the present case, the microalgae was harvested after 15 days. As shown in Figure 4.7, the lipid yield was significantly higher when a 0.5 and 0.7 loaded solvent was used (0.62 ± 0.21, 0.67± 0.05 g L⁻¹ medium respectively) relative to the control.
The lipid fraction of the total biomass also appears to slightly improve as the loading increases, although the error is significant. This is likely the consequence of nitrogen starvation during which this strain of *Chlorella* sp. has been shown to accumulate triacylglyceride lipids\cite{25}. Due to the low lipid and biomass yield, it was not possible to measure the lipid fraction of the control, but our past work with this strain has shown the basal lipid content under nitrogen replete conditions to be approximately 15% (w/w) using the identical lipid extraction protocol\cite{25}. Thin layer chromatography\cite{32} confirmed that the lipid in the algae grown with 0.2 loading had a higher proportion of polar lipids and chlorophyll than 0.5 and 0.7 loading, which had a greater proportion of neutral lipids. A detailed analysis of the fatty acid and lipid profiles of this strain under both nitrogen replete and nitrogen starved conditions has been previously reported\cite{33].

Figure 4.7 Concentration of lipid in the *Chlorella* sp. cultures (a) and gravimetric lipid content of the cells (b) after 15 days growth with different carbon dioxide provision. Errors bars represent the standard deviation of quadruplicate experiments per sample condition (duplicate measurements for each flask, n=4)

4.5.4 Ion leakage

During the experiment, there was some loss of water through the PDMS membrane from the medium side into the solvent. This reflects the difference in osmotic pressure between the medium and the 20 wt% solvent. The total increase in volume on the solvent side over 15 days is shown in Table 4.3. A comparable volume was lost from the medium side, once sample volumes are taken into
account. This equates to a water loss of around 0.9% per day, which would need to be added to the medium and removed from the solvent in an upscaled process.

Table 4.3 Water addition volume

<table>
<thead>
<tr>
<th>Water addition volume (mL)</th>
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</thead>
<tbody>
<tr>
<td>0.2 loading</td>
</tr>
<tr>
<td>0.5 loading</td>
</tr>
<tr>
<td>0.7 loading</td>
</tr>
</tbody>
</table>

There is a need to confirm that the carbon is transferring to the medium as CO$_2$ through the non-porous membrane and not in an ionic form, or as bulk solvent passing through defects. If the carbon was crossing the membrane as CO$_3^{2-}$, then each mole would drive two moles of K$^+$ along with it.

After 15 days, this would equate to a 1600 to 2700 mg L$^{-1}$ increase in K$^+$ concentration in the medium. If the carbon was crossing as HCO$_3^-$ this would be a 800 to 1350 mg L$^{-1}$ increase in K$^+$ concentration. As shown in Figure 4.8(b), the increase in K$^+$ is clearly less than this and is more readily explained by the loss of water from the medium over this period.

As shown in Figure 4.8(a), the Na$^+$ concentration on the solvent side of the membrane also did not increase during the experiment, again confirming that ion transport across the membrane was limited. In fact, there was a slight decline in this concentration, because of the water flow described above.
Figure 4.8 Na⁺ (a) within the solvent and K⁺ within the medium after filtration to remove cell biomass (b) during the course of the experiment. Results for Figure 4.8(b) are the mean of duplicate experiments and error bars show the range of the duplicates.

4.5.5 Other Issues

Membrane fouling caused by biofilm formation can be a critical issue in membrane processes. In these experiments, the microalgae were not tightly attached to the membrane and could be removed easily when water was used to flush the membrane surface (see Figure 4.52). This indicates that biofilm formation is unlikely to be a significant concern during scale-up.

In a true flue gas capture operation, the feed gas may contain significant quantities of both sulphur compounds (SOₓ) and nitrogen compounds (NOₓ) in addition to carbon dioxide. The sulphur impurities are detrimental to algal growth, restricting the use of raw flue gas as a source of carbon [34]. However, these compounds are known to sorb irreversibly into capture solvents to form heat stable salts [35, 36]. This provides an additional advantage of the process provided here, as the sulphur compounds will not be transferred to the algal medium, but will accumulate in the solvent. This accumulation is well understood in solvent capture processes and a separate process, such as thermal reclamation or electrodialysis can be used to eliminate the solvent contamination[12, 37].

In the classical CO₂ capture process, the energy penalty from the reboiler is 2.4-4.2 GJ t⁻¹ CO₂[16]. A further 400 MJ t⁻¹ CO₂ is needed to compress the carbon dioxide to
a supercritical state (15 MPa) and a further 8 MJ t-1 CO₂ is required for transportation to a geological storage site (assumed to be 100km away) [38]. Thus the total energy penalty for classical CO₂ capture and geological storage is around 2.8-4.6 GJ t-1 CO₂. Alternatively, using the present approach, the energy penalty for CO₂ storage as biomass is only the energy required to circulate the loaded solvent. Assuming the solvent loading falls from 0.5 to 0.2 during circulation, a pressure drop of 300kPa and a pump efficiency of 75% suggests an energy penalty of only 20 MJ t⁻¹ CO₂.

The fossil energy requirement for biodiesel produced from microalgae grown in open pond culture is estimated by a range of authors as between 6.5 and 68 GJ t⁻¹ biodiesel (Table 4.S3). This fuel demand includes the use of flue gas being pressurized and transferred to the microalgae ponds. The literature also indicates that delivery of raw flue gas to the open ponds incurs an energy penalty of 80-530 MJ t⁻¹ CO₂ [2, 17, 39]. Thus, when CO₂ loaded solvent is utilized in the system presented here to replace the CO₂ transfer process, it can save anywhere between 60 - 510 MJ t⁻¹ CO₂; or between 0.40 and 3.4 GJ t⁻¹ biodiesel (if 1 tonne biodiesel requires 6.7 ton CO₂[17]). This is between 0.6 and 53% of the fossil energy demand. The large variation in these numbers reflects differences in the flue gas pressure and flue gas quality used in the literature work. These workers all assume that the algal ponds are adjacent to the power plant – increasing this distance will add further benefits to the current approach.

The greenhouse gas emissions for fossil derived diesel are about 3.7 ton CO₂-e per t[17] while for biodiesel derived from microalgae grown in open pond culture, the emissions are calculated as between 0.7 and 4.8 ton CO₂-e per t diesel (Table S4.3). [17][17]Eliminating the need for gas compression would reduce this by between 0.09 and 0.76 ton CO₂-e per t diesel based on the above analysis, again a significant saving in many cases.

The system has the potential to be scaled up for practical implementation. Based on the results and experimental conditions reported here (0.4 L microalgal cultures with 0.0226m² hollow fibre membrane achieving 0.38 g·L⁻¹·d⁻¹ maximum biomass productivity), a microalgae pond of 0.3m depth and 25 g m⁻² d⁻¹ areal
productivity, would require approximately 4 mmembrane\(^2\) marea\(^2\) to ensure adequate provision of carbon to the cultures through the membrane. Cost estimates for hollow fibre membranes vary from around US$2 to $8 per square metre of membrane material\(^{[40,41]}\), leading to capital costs of US$ 8 to $32 marea\(^2\).

4.6 Conclusions

This work has shown that carbon dioxide can be effectively delivered to a microalgal medium using liquid-liquid contact with a carbon capture solvent across a PDMS membrane. The approach is significantly more energy efficient than other approaches thus reducing the total energy demand of microalgal culture and biofuel production. Further, it results in significantly greater maximum biomass growth rates and would appear to be resistant to contamination by sulphur impurities in the gas supply.

While this work used potassium carbonate solution as the solvent, it should be possible to use other solvents and this will be the focus of our ongoing work. The productivity of *Chlorella* sp. cultures were highest when a potassium carbonate solvent of 0.5 or 0.7 loading was used. As the loading in a commercial carbon capture operation using potassium carbonate rarely exceeds a loading of 0.5, this level is recommended for further study.

*Chlorella* sp. growth was ultimately restricted by nitrate and light limitations in the later phase. Higher biomass productivities could be achieved through the addition of a nitrogen source and enhanced illumination.

Acknowledgements

The authors acknowledge the Particulate Fluids Processing Centre at The University of Melbourne, a Special Research Centre of the Australian Research Council for access to equipment. We acknowledge the University of Melbourne for providing a Melbourne International Engagement Award scholarship for Ms. Zheng.


**Supplementary information**

Table S4.1 Specifications of the PDMS membrane contactors

<table>
<thead>
<tr>
<th>Membrane Material</th>
<th>PDMS (Silicone)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Supplier</td>
<td>Airrane</td>
</tr>
<tr>
<td>Membrane type</td>
<td>Composite membrane</td>
</tr>
<tr>
<td>Supporting layer</td>
<td>Polysulfone</td>
</tr>
<tr>
<td>Fibre inside diameter (µm)</td>
<td>$d_{in}$</td>
</tr>
<tr>
<td></td>
<td>300</td>
</tr>
<tr>
<td>Fibre outside diameter (µm)</td>
<td>$d_{out}$</td>
</tr>
<tr>
<td></td>
<td>450</td>
</tr>
<tr>
<td>Fibre Wall Thickness (µm)</td>
<td>$l$</td>
</tr>
<tr>
<td></td>
<td>PDMS layer 0.5µm</td>
</tr>
<tr>
<td>Number of fibres per flask (n)</td>
<td>40</td>
</tr>
<tr>
<td>Membrane surface area per flask (m²)</td>
<td>$A$</td>
</tr>
<tr>
<td></td>
<td>0.0226</td>
</tr>
<tr>
<td>Membrane Length (m)</td>
<td>0.4</td>
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</table>
Table S4.2: Microalgae growth rates reported in the literature.

<table>
<thead>
<tr>
<th>Microalgae species</th>
<th>Reactor types</th>
<th>Gas transfer type</th>
<th>CO₂ loading (CO₂ concentration (%))</th>
<th>Max. biomass concentration (g L⁻¹)</th>
<th>Maximum dry weight biomass productivity (Pmax) (g L⁻¹ d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>Chlorella sp.</td>
<td>500 mL conical flask</td>
<td>CO₂ loaded solvent through PDMS membrane</td>
<td>0.03</td>
<td>1.05</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
<td>1.14</td>
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<td></td>
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<td>0.5</td>
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<td>0.7</td>
<td>1.11</td>
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<td></td>
<td></td>
<td>0.1</td>
<td>1.14</td>
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<td></td>
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<td></td>
<td>0.2</td>
<td>1.14</td>
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<td>0.3</td>
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<td>0.4</td>
<td>1.14</td>
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</tbody>
</table>

**References**

<table>
<thead>
<tr>
<th>Microalgae species</th>
<th>Reactor types</th>
<th>Gas transfer type</th>
<th>CO₂ loading (CO₂ concentration (%))</th>
<th>Max. biomass concentration (g L⁻¹)</th>
<th>Maximum dry weight biomass productivity (Pmax) (g L⁻¹ d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scenedesmus obliquus SJTU-3</td>
<td>modified Erlenmeyer flask</td>
<td>200 mL min⁻¹, gas distributor</td>
<td>0.03</td>
<td>1.05</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
<td>1.14</td>
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<td></td>
<td></td>
<td>0.7</td>
<td>1.11</td>
</tr>
<tr>
<td>Scenedesmus obliquus[2]</td>
<td>2L conical flask photobioreactor</td>
<td>540 mL min⁻¹</td>
<td>0.038</td>
<td>1.14</td>
<td>0.076</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1</td>
<td>1.14</td>
</tr>
<tr>
<td>Scenedesmus sp.[3]</td>
<td>Bioreactor</td>
<td>flue gas</td>
<td>0.03</td>
<td>1.14</td>
<td>0.077</td>
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<th>Maximum dry weight biomass productivity (Pmax) (g L⁻¹ d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorella pyrenoidosa LJU-2[1]</td>
<td>modified Erlenmeyer flask</td>
<td>200 mL min⁻¹, gas distributor</td>
<td>0.03</td>
<td>1.05</td>
<td>0.083</td>
</tr>
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<td>0.7</td>
<td>1.11</td>
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<tr>
<td>Chlorella kessleri[2]</td>
<td>2L conical flask photobioreactor</td>
<td>540 mL min⁻¹</td>
<td>0.038</td>
<td>1.14</td>
<td>0.076</td>
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<th>Gas transfer type</th>
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<th>Max. biomass concentration (g L⁻¹)</th>
<th>Maximum dry weight biomass productivity (Pmax) (g L⁻¹ d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorella vulgaris LE-10[4]</td>
<td>11L BioFlo Fermenter</td>
<td>a ring sparger</td>
<td>0.03</td>
<td>1.05</td>
<td>0.083</td>
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<td>1.14</td>
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<td>0.7</td>
<td>1.11</td>
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<tr>
<td>Chlorella vulgaris[3]</td>
<td>Bioreactor</td>
<td>flue gas</td>
<td>0.03</td>
<td>1.05</td>
<td>0.083</td>
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<td></td>
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<td>0.7</td>
<td>1.11</td>
</tr>
<tr>
<td>Botryococcus braunii[3]</td>
<td>Bioreactor</td>
<td>flue gas</td>
<td>0.03</td>
<td>1.05</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
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<td>0.2</td>
<td>1.14</td>
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<td>0.7</td>
<td>1.11</td>
</tr>
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<table>
<thead>
<tr>
<th>Microalgae species</th>
<th>Reactor types</th>
<th>Gas transfer type</th>
<th>CO₂ loading (CO₂ concentration (%))</th>
<th>Max. biomass concentration (g L⁻¹)</th>
<th>Maximum dry weight biomass productivity (Pmax) (g L⁻¹ d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dunaliella tertiolecta SAG-13.86[4]</td>
<td>11L Bioflo Fermenter</td>
<td>a ring sparger</td>
<td>0.03</td>
<td>1.05</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
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<td>0.2</td>
<td>1.14</td>
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<td>0.5</td>
<td>1.12</td>
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<td></td>
<td></td>
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<td>0.7</td>
<td>1.11</td>
</tr>
</tbody>
</table>

87
Figure S4.1 The factors influencing microalgae growth in different loadings (a) control, (b) 0.2 loading, (c) 0.5 loading, (d) 0.7 loading. Different shading indicates different growth phases. Lag phase (grey shadow), ‘unlimited’ (no shading), carbon limited (backslash), nitrogen limited (grey shadow with slash), nitrogen and light limited (diamond line). Results are the mean of duplicate experiments and error bars show the range of the duplicates.
Figure S4.2 Images of a hollow fibre membrane (a) unused; (b) after exposure to algal growth for 16 days, with potassium carbonate 0.5 loading on the lumen side; (c) after algal growth and then washing with water
Table S4.3 Life cycle energy and greenhouse gas emission in other published studies.

<table>
<thead>
<tr>
<th>Fuel source</th>
<th>Authors</th>
<th>Fossil energy requirement (MJ/MJ diesel)</th>
<th>Fossil energy requirement (GJ/ton diesel)</th>
<th>GHG emission (gCO₂-e/MJ diesel)</th>
<th>GHG emission (ton CO₂-e/ton diesel)</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algae derived biodiesel</td>
<td>Stephenson et al.[6]</td>
<td>0.17</td>
<td>6.5</td>
<td>19.3</td>
<td>0.713</td>
<td>Open pond, anaerobic digestion of residual algal biomass</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.4</td>
<td>199.5</td>
<td>320</td>
<td>11.919</td>
<td>Air lift Tubular Bioreactor, anaerobic digestion of residual algal biomass</td>
</tr>
<tr>
<td>Algae derived biodiesel</td>
<td>Gao et al.[7]</td>
<td>1.3</td>
<td>48.4</td>
<td>80</td>
<td>2.98</td>
<td>Open ponds, anaerobic digestion of residual algal biomass</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.7</td>
<td>26</td>
<td>33</td>
<td>1.23</td>
<td>Open pond, hydrothermal liquefaction of residual algal biomass</td>
</tr>
<tr>
<td></td>
<td>Liu et al.[8]</td>
<td>0.37-1.83</td>
<td>13.6-68.2</td>
<td>60.8-129</td>
<td>2.26-4.8</td>
<td>Open pond, using virgin CO₂ from reforming of hydrocarbons</td>
</tr>
</tbody>
</table>

Biodiesel high heat value 37.2MJ/kg[^6] was used in the table to normalize the functional unit.


Chapter 5 The use of monoethanolamine and potassium glycinate solvents for CO\(_2\) delivery to microalgae through a membrane system

5.1 Chapter perspective

Chapter 4 demonstrated a novel system involving solvent absorption, membrane separation and microalgal cultivation, which can effectively provide carbon dioxide for microalgae growth by using CO\(_2\) loaded potassium carbonate. In this chapter, this novel system was expanded with another two chemical solvents, 30 wt% monoethanolamine (MEA) and 20 wt% potassium glycinate (PG). Microalgae were cultivated in this novel system by using MEA with CO\(_2\) loadings of 0.2, 0.5 and PG with CO\(_2\) loadings of 0.2, 0.5, 0.6, respectively. The results were compared with potassium carbonate with a CO\(_2\) loading of 0.5. Solvent permeation and toxicity on microalgae were also determined as fundamental information for solvents selection during industrial implementation.

5.2 Abstract

Aqueous solutions of monoethanolamine (MEA) and potassium glycinate (PG) for membrane desorption of CO\(_2\) were evaluated and compared with potassium carbonate. Enhanced growth of *Chlorella* sp. was observed with 20 wt% potassium glycinate with a CO\(_2\) loading of 0.5, yielding a maximum volumetric productivity of 0.23 g L\(^{-1}\) d\(^{-1}\), almost 26 times greater than control cultures that only received CO\(_2\) via atmospheric diffusion (0.0089 g L\(^{-1}\) d\(^{-1}\)). For potassium glycinate with a CO\(_2\) loading of 0.2, *Chlorella* sp. exhibited similar growth rates to the control. The reduced effectiveness of PG at low loadings is due to a significantly decreased CO\(_2\) partial pressure in equilibrium with this solvent and thus a reduced driving force for mass transfer across the membrane. For MEA, algal growth was accelerated at 0.5 loading but was in fact inhibited relative to the control at 0.2 loading. This is due to permeation of MEA across the membrane, which was found to be toxic to the algae. Considering the CO\(_2\) absorption kinetics into the solvent, the improvement of microalgal growth and the system stability in case of solvent
permeation, amino acids such as potassium glycinate can be a better alternative to potassium carbonate or MEA as a solvent for this application.

5.3 Introduction

Chapter 4 proposed an approach to provide an energy efficient means of regenerating CO₂ capture solvents [1]. The system was able to achieve outstanding productivities of up to 0.38 g L⁻¹ d⁻¹ by avoiding carbon limitation in dense cultures using a 20 wt% potassium carbonate solution with a CO₂ loading of 0.5 or 0.7. While this approach proved highly effective for microalgal growth, the reaction rate of potassium carbonate with carbon dioxide is slow [2] and this can mean that the upstream absorption operation becomes difficult. In chemical absorption operations, other solvents such as MEA (monoethanolamine) and amino acid salts (e.g. potassium glycinate (PG)) have been shown to capture carbon dioxide at a greater reaction rate, making them more practical for this absorption step [3]. MEA is the most widely used chemical solvent for carbon dioxide capture due to its rapid reaction rate and low cost [4]. Amino acid salts have also been used in commercial capture operations within the Siemens POSTCAP and the BASF Puratreat and Alkazid formulations; and have attracted research interest due to their fast reaction rate, high cyclic loading capacity, low volatility and degradation stability [5-10].

In this chapter, these two solvents were compared to potassium carbonate to determine whether they might be as effective for microalgal growth. This would allow the combined system to operate with maximum effectiveness.

5.4 Methods

*Chlorella* sp. was cultivated with exposure to only atmospheric CO₂ (control) and in contact with membranes circulating MEA, PG or K₂CO₃ solvents at various loadings as described in Chapter 3. 30 wt% MEA is the most commonly used solvent concentration in post-combustion carbon capture process [11, 12]. As 30 wt% K₂CO₃ may form precipitation during CO₂ absorption under atmospheric temperature, 20 wt% K₂CO₃ was utilized in this study. Amino acid salts with the range from 0.5 mol L⁻¹ to 6 mol L⁻¹ have been investigated to capture CO₂ [13-16], 20 wt% PG (2 mol L⁻¹)
was chosen in this study as it was easily compared with 20 wt% K₂CO₃. As amino acid salts have been detected to achieve CO₂ loading of more than 0.5 \[17, 18\], the effect of higher CO₂ loading solvents on microalgae growth was determined with PG solution of 0.6 loading.

The biomass and total nitrogen (TN) concentration (Figure 5.1), and the pH, dissolved inorganic carbon (DIC) and total carbon (TC) (Figure 5.2) were measured during the experiments, as previously described in Chapter 3. The linear correlation between the measured optical density and dry cell weight is dry cell weight (g L⁻¹) = 0.2727 × optical density + 0.1772, R² = 0.972.

### 5.5 Effect of different CO₂ loaded solvents on *Chlorella* sp. growth

The cultures that were provided CO₂ using any of the solvents at 0.5 loading had significantly improved biomass growth over the control (Figure 5.1A and B). Growth in the culture with 0.5 loading MEA was comparable with 0.5 loading K₂CO₃ for the first three days, after which it progressively fell behind (Figure 5.1A). The cultures with 0.5 loading PG experienced similar growth rate to cultures with 0.5 loading K₂CO₃ (Figure 5.1B).

The cultures with PG at 0.6 loading also grew faster than the control, but slower than at 0.5 loading (Figure 5.1B). However, the use of PG at 0.2 loading did not noticeably enhance microalgae growth, while the cultures grown with MEA at 0.2 loading solvent appeared to be inhibited relative to the control. The maximum specific growth rate µ (d⁻¹) during the initial period of pseudo-exponential growth (i.e. before significant self-shading occur) and the average and maximum volumetric productivities were determined according to chapter 4\[1\] (Table 5.1). The maximum specific growth rate and volumetric productivity of the cultures using K₂CO₃ at 0.5 loading solvent were comparable with chapter 4\[1\].
Figure 5.1 Biomass concentration (A and B) and total nitrogen (TN) (C and D) in cultures of *Chlorella* sp. with carbon dioxide by membrane delivery at potassium carbonate of 0.5 loading, MEA of 0.2 loading, 0.5 loading, potassium glycinate (PG) of 0.6, 0.5, 0.2 loading or by atmospheric diffusion only (the control). Error bars represent the standard deviation of duplicate flasks.
Table 5.1 Comparison of the maximum specific growth rate, $\mu_{\text{max}}$ (d$^{-1}$) and volumetric productivity (g L$^{-1}$ d$^{-1}$) of *Chlorella* sp. cultures grown with different sources of CO$_2$

<table>
<thead>
<tr>
<th>Source</th>
<th>$\mu_{\text{max}}$</th>
<th>Average volumetric productivity</th>
<th>Maximum volumetric productivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>0.026±0.002</td>
<td>0.0062±0.0005</td>
<td>0.009±0.002</td>
</tr>
<tr>
<td>K$_2$CO$_3$-0.5 loading</td>
<td>0.464±0.002</td>
<td>0.126±0.007</td>
<td>0.257±0.008</td>
</tr>
<tr>
<td>MEA-0.5 loading</td>
<td>0.37±0.04</td>
<td>0.10±0.01</td>
<td>0.18±0.03</td>
</tr>
<tr>
<td>MEA-0.2 loading</td>
<td>n/a</td>
<td>0.002±0.003</td>
<td>0.002±0.001</td>
</tr>
<tr>
<td>PG-0.5 loading</td>
<td>0.34±0.001</td>
<td>0.106±0.001</td>
<td>0.23±0.04</td>
</tr>
<tr>
<td>PG-0.6 loading</td>
<td>0.33±0.003</td>
<td>0.080±0.003</td>
<td>0.23±0.01</td>
</tr>
<tr>
<td>PG-0.2 loading</td>
<td>0.05±0.01</td>
<td>0.007±0.001</td>
<td>0.011±0.004</td>
</tr>
</tbody>
</table>

As carbon dioxide crosses the membrane in the vapor state according to the solution diffusion model, it is the CO$_2$ partial pressure that determines the driving force for mass transfer into the algal medium. To better understand the capacity of the different solvents to deliver CO$_2$ to the algal cultures at different loadings, the CO$_2$ partial pressures above 30 wt% MEA, 20 wt% K$_2$CO$_3$ and 20 wt% PG were determined as a function of loading at 25 °C (Figure 5.2). The CO$_2$ partial pressures in all three solvents at 0.5 loading are similar in magnitude (around 10$^3$ Pa). With PG at this loading, the DIC increased from an initial 3.8 mg L$^{-1}$ to 39 mg L$^{-1}$ at day 14 (Figure 5.3D). With K$_2$CO$_3$, the DIC increased continuously from 1.8 mg L$^{-1}$ to 30 mg L$^{-1}$ after 16 days, and with MEA at 0.5 loading, the DIC increased from 1.5 mg L$^{-1}$ to 30 mg L$^{-1}$ at day 16 (Figure 5.3C). This excess of inorganic carbon and the relatively low media pH (Figure 5.3A and 3B) indicates that the supply of CO$_2$ exceeded the culture demands (i.e. it can be considered carbon-unlimited). For these 0.5 loaded solvents, the pH of the microalgae medium fell significantly during the initial lag period (Figure 5.3A and 3B), as more CO$_2$ was delivered to the
medium than could be consumed. Once biomass growth accelerated, the pH of the microalgae medium increased to around 7 to 8; a suitable range for microalgae growth\[19\].

With a CO₂ partial pressure of around $10^4$ Pa in the 0.6 loading PG solvent (Figure 5.2), the rapid transfer of CO₂ to the medium in this lag phase, sharply decreased the pH from 8.4 to 5.6 in the first half day (Figure 5.3B). As the cultures grew, the demand for CO₂ increased so that the pH increased from 5.6 to 6.1 at day 2, and to 7.0 at day 4. However, the low pH during the first two days resulted in a prolonged lag phase compared with that occurring with the PG solvent at 0.5 loading (Figure 5.1B). After the lag phase, the cultures with PG-0.6 loading and PG-0.5 loading grew at a similar specific growth rate (0.33 d⁻¹, 0.34 d⁻¹). This suggests that without a means of providing external pH control, there is likely an upper limit in the CO₂ loading of PG that can be applied to avoid a lag in culture growth due to oversupply of CO₂.

The vertical dashed lines in Figure 5.2 show the minimum CO₂ loadings required to achieve a positive driving force for CO₂ mass transfer into the medium to be 0.42, 0.16 and 0.34 for the 30 wt% MEA, 20 wt% K₂CO₃ and 20 wt% PG solvents respectively.

![CO₂ partial pressure graph](image)

**Figure 5.2 CO₂ partial pressure of 30wt% MEA, 20wt% K₂CO₃ and 20 wt% PG of different loadings, compared to seawater at 25°C and pH 8.3. The seawater [20] and...**
the MEA \textsuperscript{[21]} data are from the published literature. The K$_2$CO$_3$ and PG data is simulated within Aspen Plus™ with the e-NRTL fluid package as modified by Lee \textsuperscript{[22]}

At 0.2 loading the PG solvent initially provides a very low CO$_2$ partial pressure (around 6 Pa) (Figure 5.2) which is below the CO$_2$ partial pressure of sea water at pH 8.3 (around 39 Pa \textsuperscript{[20]}). Hence in the first day, CO$_2$ transfer could in fact be in the opposite direction, out of the growth media and into the solvent. Correspondingly, in the first two days with PG solvent at 0.2 loading the DIC concentration in the cultures decreased slightly, as the CO$_2$ transfer rate could not meet the rate required for microalgae growth. Concomitantly the pH rapidly increased to 9, which is above the optimum value for microalgae growth. However, this higher pH could have increased the CO$_2$ solubility, hence allowing CO$_2$ transfer from the solvent to the medium. In the following days, as carbon dioxide was continuously transferred to the medium, the low carbon dioxide transfer rate limited growth and the DIC remained around 10 mg L$^{-1}$, a similar level to the control. In this case, the CO$_2$ that was made available to the algae may also have come from the atmosphere above the cultures, as with the control, rather than through the membrane.

The cultures with MEA at 0.2 loading appeared to exhibit close to no growth. As with PG, MEA also provides a very low CO$_2$ partial pressure (around 2 Pa) (Figure 5.2) to drive mass transfer. If this had resulted in an absence of CO$_2$ in the growth media, it might explain a reduced rate of growth in the cultures using this solvent. However, the cultures exhibited no growth whatsoever, and measurements of DIC concentration (Figure 5.3C) indicate that CO$_2$ was available but that it was not consumed by the algae.
Figure 5.3 pH (A and B), dissolved inorganic carbon (C and D) and total carbon (E and F) in the microalgae medium with carbon dioxide supplied by different CO₂ loaded solvents or by atmospheric diffusion only (the control). Error bars represent the standard deviation of duplicate flasks.

5.6 Solvent permeation

The complete lack of growth exhibited by the cultures using the MEA solvent at 0.2 loading could not be explained by unavailability of a carbon source. Another
possibility is that MEA was able to pass across the membrane and inhibit the algae. Consistent with an accumulation of MEA in the growth media, the total nitrogen (TN) and total carbon (TC) were both seen to increase markedly when this solvent was used (Figures 5.1C and 5.2E respectively). In contrast, the TN in the K\textsubscript{2}CO\textsubscript{3} and PG solvents at 0.5 loading and the control culture decreased (Figure 5.1D) due to uptake by the algae in accordance with the previous study\textsuperscript{[11]}. In the control culture, this TN only decreased slightly from 37 mgN L\textsuperscript{-1} to 27 mgN L\textsuperscript{-1} reflecting the limited uptake of nitrate associated with the slight increase in biomass concentration. The TN for the 0.2 loaded PG solvent also increased only slightly from 35 to 45 mgN L\textsuperscript{-1}. With K\textsubscript{2}CO\textsubscript{3} at 0.5 loading, the TN was depleted after 5 days. With the PG solvent at 0.5 loading, the TN was exhausted at Day6, while with 0.6 loading it was exhausted at Day10.

Conversely with the 0.2 loaded MEA solvent, the TN in the microalgae medium increased rapidly, from an initial 27 mgN L\textsuperscript{-1} to 203 mgN L\textsuperscript{-1} at Day16 (Figure 5.1C). With the MEA at 0.5 loading, the TN in microalgae medium decreased from 35 mgN L\textsuperscript{-1} to 9 mgN L\textsuperscript{-1} in the first 8 days, but increased to 27 mgN L\textsuperscript{-1} at Day16. These observations are consistent with MEA passing through the PDMS membrane from the CO\textsubscript{2} loaded solvent side to the microalgae medium side. TC (176 mg L\textsuperscript{-1}) in the microalgae medium with MEA-0.2 loading solvent was also much higher than TC (91 mg L\textsuperscript{-1}) with K\textsubscript{2}CO\textsubscript{3}-0.5 loading solvent (Figure 5.2E), again consistent with this hypothesis.

MEA is a volatile solvent with unloaded 30wt% MEA having a vapour pressure of 2800 Pa at 25 ℃\textsuperscript{[21]}. The 0.2 loaded MEA solvent has 60% free, uncharged MEA, which is volatile, and can pass though the PDMS membrane through the solution diffusion mechanism causing the TN and TC concentrations in the microalgae medium to increase. In contrast, in an ideal 0.5 loaded MEA solvent, the MEA should be completely in the charged form (HOCH\textsubscript{2}CH\textsubscript{2}NH\textsubscript{3}\textsuperscript{+} and HOCH\textsubscript{2}CH\textsubscript{2}NHCOO\textsuperscript{-}, as per Reaction 2.4). Only through the reversal of Reaction 2.4 can a small amount of uncharged MEA be released in the MEA-CO\textsubscript{2}-H\textsubscript{2}O system.

To determine the rate of MEA permeance through the PDMS membrane, MEA solvents of variable loading were pumped through the tube side of membranes.
submerged in RO water. The TN concentration in the RO water increased with time, with higher rates observed at decreased solvent loadings (Figure 5.4A). With loadings of 0.2 and 0.5, the average rates were 4.3 mgN L\(^{-1}\) d\(^{-1}\) and 0.9 mgN L\(^{-1}\) d\(^{-1}\), respectively. The permeation from potassium glycinate solvents were also determined (Figure 5.4B). With these solvents at 0.2 and 0.5 loading solvent, the average rates were 0.9 mgN L\(^{-1}\) d\(^{-1}\) and 0.2 mgN L\(^{-1}\) d\(^{-1}\), respectively, which are much lower. The higher rate of permeation with the 0.2 loaded potassium glycinate solvent is consistent with a slight increase in TN observed during microalgae growth (Figure 5.1D), and can be explained by small concentrations of free glycine at the solution at a pH of 10.8\(^{[7]}\).

Figure 5.4 Total nitrogen in RO water when MEA (A) and potassium glycinate (B) solvents of variable loading are passed though the tube side of the immersed PDMS membranes

5.7 Effect of MEA and PG toxicity on Chlorella sp. growth

The results presented above indicate that free MEA, present at low loadings, can pass through PDMS membranes and accumulate in the algal growth medium. Some studies have shown that low concentrations (up to 300 ppm) of MEA can be used as a CO\(_2\) absorbent in the medium to enhance CO\(_2\) solubility and eventually improve the growth of various microalgae (Scenedesmus sp., Spirulina sp.) \(^{[23, 24]}\). However, MEA is generally considered a toxic chemical. If present at high enough concentration, this may presumably be the agent responsible for the lack of growth observed in the MEA-0.2 loaded cultures. To confirm this possibility, MEA was
added directly to microalgae cultures (with no added CO₂ and an initial biomass concentration of 0.18 g L⁻¹) on a daily basis at rates corresponding to the rates of MEA permeation through the membrane system determined above (Figure 5.4A) (0.9 mgN L⁻¹ d⁻¹, 2.6 mgN L⁻¹ d⁻¹ and 4.3 mgN L⁻¹ d⁻¹). *Chlorella* sp. growth was inhibited compared to the control even at the lowest rate of MEA addition, and at the higher rates algal death occurred (Figure 5.5A), demonstrating the toxicity of MEA to *Chlorella* sp. In the previous results *Chlorella* sp. growth was enhanced when MEA of 0.5 loading was used (Figure 5.1A), despite the transfer of toxic MEA into the growth medium. However, in this case the culture was not CO₂ limited and therefore able to grow rapidly, presumably utilising some of the MEA as a nitrogen source, enabling the concentration of MEA in the media to be kept below toxic levels. The relatively constant TN in the MEA 0.5 loading culture (Figure 5.1C) is consistent with this, as is the rising level of TN in the 0.2 loading MEA culture (Figure 5.1C) which was inhibited (Figure 5.1A).

To determine if glycine is also toxic to *Chlorella* sp., glycine and CO₂ loaded potassium glycine were added directly to microalgae cultures (with no added CO₂ and an initial biomass concentration of 0.28 g L⁻¹) on a daily basis at rates corresponding to the rates of glycine permeation through the membrane system determined above (Figure 5.4B), 0.2 mgN L⁻¹ d⁻¹ and 0.9 mgN L⁻¹ d⁻¹. To compare with MEA, the highest rate of 4.3 mgN L⁻¹ d⁻¹ was also chosen. Rather than being inhibited, the growth of *Chlorella* sp. was found to be improved with added glycine and CO₂ loaded potassium glycinate. This suggests that rather than being toxic to the algae, these two solvents can be utilised as carbon and nitrogen sources for microalgae growth[25].
Figure 5.5 Growth curve of *Chlorella* sp. cultures when pure MEA (A), pure glycine (B), or CO₂-loaded potassium glycinate (C) are added directly to the medium. Error bars represent the standard deviation of duplicate experiments.

5.8 Discussion and Conclusions

The enhancement of microalgae growth though liquid-liquid contact of a CO₂ loaded solvent and a microalgae medium by PDMS hollow fibre membranes has considerable promise. In this work, we have investigated the applicability of MEA and PG as alternative CO₂ carrying solvents to potassium carbonate. At 0.5 loading
Potassium glycinate was found to be equally as effective as potassium carbonate; increasing the maximal volumetric productivity of Chlorella sp. cultures by almost 26-fold over control cultures that relied on atmospheric CO₂. At decreased loading the performance of PG declined more sharply than for potassium carbonate due to a more sharply decreasing partial pressure. At 0.5 loading MEA was reasonably effective at delivering CO₂ and enhancing microalgal growth, but less so than either PG or potassium carbonate.

As a chemical absorption solvent, potassium carbonate has several advantages. It has less human toxicity and eco-toxicity compared with MEA [26]. Potassium carbonate does not degrade with oxygen and impurities (NOₓ, SOₓ) in the flue gas and requires less energy for solvent regeneration [26]. However, potassium carbonate has slow reaction rates with carbon dioxide which inhibits its practical implementation [10]. As a carbon source for microalgae, both rich solvent (K₂CO₃-0.5 loading) and lean solvent (K₂CO₃-0.2 loading) can improve microalgal growth as shown in our previous study [1]. Further, as a charged compound, potassium carbonate does not permeate through the membrane, which means it cannot contaminate or be lost to the medium.

MEA is widely used in carbon dioxide capture due to its fast reaction rate. However, MEA is corrosive and can be degraded through irreversible reactions with oxygen, NOₓ and SOₓ in the flue gas [27]. As solvent loss occurs via evaporation and these degradation reactions, 1.6 kg MEA/tCO₂captured make-up is needed in the system [28]. Formaldehyde and nitrosamines, which are products of MEA degradation, are known to be carcinogenic [26]. As a carbon source for microalgae, the rich solvent (MEA-0.5 loading) enhanced microalgal growth, while the lean solvent (MEA-0.2 loading) inhibited microalgal growth due to MEA permeation through membrane, which is toxic to microalgae. Further, in a practical system, membrane failure may occur, causing localised high levels of this solvent, which would also cause the culture to die.

Potassium glycinate has a similar reaction rate towards carbon dioxide with MEA, low oxidative degradation, is less volatile and has less environment impact [10]. As a carbon source, PG solvents at 0.5 loading can result in strong microalgal growth.
when used in the present arrangement. Implementation will require consideration of the optimal range of loadings with which to operate to avoid a low-pH-induced lag at too high a loading (e.g. 0.6 loading here), or suboptimal growth at too low a loading (e.g. 0.2 loading here). The valid range of loadings could presumably be increased by operating in a counter-current mode in which the supply is better matched to the demand (e.g. the inlet solvent with the highest CO$_2$ loading is used in the ponds with the highest concentration of algae and vice versa). Further, the low rate of permeation of PG solvent into the media at low loadings did not have a harmful effect on the microalgae. Rather the permeated solvent actually slightly improved microalgae growth by serving as a carbon and nitrogen source. Based on this discussion, potassium glycinate, or comparable amino acids, would appear as the most suitable solvents for this process, due to their low volatility, low toxicity and their rapid reaction rate with carbon dioxide.


Chapter 6 The effect of CO₂ loaded solvents on different microalgae species

6.1 Chapter perspective

In Chapter 4 it was shown that CO₂ could be efficiently transferred to microalgae through the membrane system via K₂CO₃ solvents with different CO₂ loadings. In Chapter 5 the effectiveness of this system was investigated further with another two chemical solvents, monoethanolamine and potassium glycinate. The above research was performed using only one microalgae strain, marine Chlorella sp. In this chapter, another two microalgae strains were chosen, one is a freshwater strain, Chlorella vulgaris, and the other is a marine strain, Dunaliella tertiolecta. These two microalgae growth were investigated with K₂CO₃, MEA and PG with a CO₂ loading of 0.5, and compared with marine strain Chlorella sp. discussed in chapter 5. In addition, the different behaviour of the marine (MF) medium and freshwater (MLA) medium were investigated.

6.2 Abstract

Three microalgae strains, freshwater Chlorella vulgaris, a marine strain of Chlorella sp. and the marine Dunaliella tertiolecta, were cultivated in the novel system using three chemical solvents (K₂CO₃, PG and MEA of 0.5 CO₂ loading). All these three strains exhibited enhanced growth with chemical solvents compared with a control (only air diffusion). The maximum volumetric productivity of Chlorella vulgaris with MEA was the highest (0.192 g L⁻¹ d⁻¹), which is slightly higher than with PG (0.164 g L⁻¹ d⁻¹) and K₂CO₃ (0.15 g L⁻¹ d⁻¹), and 10 fold of the control (0.019 g L⁻¹ d⁻¹). The maximum volumetric productivities of Chlorella sp. with three chemical solvents were in the same magnitude and about 20 times greater than the control. The maximum volumetric productivities of Dunaliella tertiolecta with three chemical solvents were 0.095 g L⁻¹ d⁻¹ with K₂CO₃, 0.11 g L⁻¹ d⁻¹ with MEA and 0.13 g L⁻¹ d⁻¹ with PG.

The marine (MF) medium dissolved more CO₂ (from initial 2.5 mg L⁻¹ to around 30 mg L⁻¹ in day14) compared with freshwater (MLA) medium (from 1.0 mg L⁻¹ to around 20 mg L⁻¹ in day14). In addition, due to the higher osmotic pressure of salt...
water (MF) medium, less water loss was observed than that of the freshwater (MLA) medium.

6.3 Introduction

Chapter 4 and Chapter 5 were conducted with a marine strain of *Chlorella* sp. This strain was chosen as it grows well in saline and marine conditions, which reduces the risk of contamination. Since different microalgae species have various growth characteristics and requirements, it is necessary to test this system on different microalgae strains. In particular, different microalgae prefer to grow in water of different salinities, from fresh water all the way through to hyper-saline environments. The osmotic pressure across the membrane and the chemical equilibria will vary as a function of the level of salinity in the growth media, and this will affect the media pH and CO₂ solubility. Thus it is necessary to examine the effects of this on the performance of the membrane systems. Also, as solvent permeation was seen to occur (Chapter 5), which for MEA inhibited the growth of the marine *Chlorella* sp. and for potassium glycinate provided a nutrient for growth, it is of interest to explore the variability of these effects amongst different species.

This is of interest, as it has a bearing on whether this technology can be applied more broadly across a range of microalgae, regardless of their preferred growth media. There are several applications for microalgae, and these vary in relation to the salinity of the water used to grow the algae. Microalgae with high lipid content can be used to produce biodiesel as a renewable energy source[1]. To make meaningful volumes of these fuels, the microalgae would have to be grown at very large scale, at which is it generally more practical to use saline water to avoid consumption of large amounts of fresh water. Microalgae containing high levels of protein can also be produced as a food additive for humans, or a bulk feed for aquaculture or farm animals[2]. For these applications suitable strains can be grown in either fresh or salt water. Some specific microalgal strains can produce higher value substances, in particular omega-3 fatty acids, pigments and carotenoids. Among these microalgae, *Chlorella* and *Dunaliella* have been established in large-scale production[2]. *Chlorella* was firstly introduced to the market as a health food, containing essential amino acids and omega-3 fatty acids.
Dunaliella salina has been commercialized for the production of natural β-carotene, which can reach up to 14% of its dry weight\(^{[3]}\). β-carotene is a pigment and a vitamin A precursor with applications in food and cosmetics\(^{[4]}\), with a market price from US$ 300 to 3000 kg\(^{-1}\)\(^{[5]}\). Commerically, Dunaliella is produced in hyper-saline lakes, in which it is difficult for potential contaminant organisms to become established. Another high value product is natural astaxanthin produced by Haematococcus pluvialis. Astaxanthin has been used as a pigmentation source in aquaculture, with an average price of US$ 2500 kg\(^{-1}\)\(^{[6]}\). In contrast to Dunaliella, Haematococcus pluvialis is a fresh water species, which is typically grown in photobioreactors or raceway ponds that can be more controlled to avoid contamination.

This chapter focused on the system reliability and effectiveness in improving the growth of different selected microalgae strains. Two microalgae strains were chosen, one is a freshwater strain, Chlorella vulgaris, and the other is a marine strain, Dunaliella tertiolecta. Chlorella vulgaris was chosen as a direct counterpoint to the marine Chlorella used in the previous studies. Dunaliella tertiolecta was chosen as another marine strain. A freshwater species, Haematococcus pluvialis, was also investigated. However, due to difficulties involved in culturing this organism, which is highly sensitive to contamination and growth conditions, only preliminary results were obtained. As such, these preliminary results have been presented and discussed separately in the appendix. The performance of the membrane systems using different solvents was investigated in relation to the growth of these two species and compared with the marine strain Chlorella sp. discussed in other chapters.

### 6.4 Methods

Three microalgae strains (freshwater Chlorella vulgaris, a marine strain of Chlorella sp. and a strain of the marine species Dunaliella tertiolecta) (Figure 6.1) were cultivated in the membrane system (as described in Chapter 3) with only atmospheric CO\(_2\) (control) and CO\(_2\) supplied by 0.5 loading of MEA, PG and K\(_2\)CO\(_3\) solvents. The Chlorella vulgaris cultures were grown in a freshwater medium described in Chapter 3. The marine Chlorella sp. and Dunaliella tertiolecta cultures
were grown in a medium with a salinity of 25 g salt kg\(^{-1}\) as described in Chapter 3. The biomass concentration, total carbon (TC), pH, dissolved inorganic carbon (DIC) and total nitrogen (TN) were measured during the experiment for these three strains, as previously described in Chapter 3.

For marine *Chlorella* sp., the linear correlation between the measured optical density and dry cell weight is dry cell weight (g L\(^{-1}\)) = 0.2727 × optical density + 0.1772, \(R^2 = 0.972\). For freshwater *Chlorella vulgaris*, the linear correlation between the measured optical density and dry cell weight is dry cell weight (g L\(^{-1}\)) = 0.227 × optical density + 0.003, \(R^2 = 0.994\). For *Dunaliella tertiolecta*, the linear correlation between the measured optical density and dry cell weight is dry cell weight (g L\(^{-1}\)) = 0.273 × optical density - 0.0037, \(R^2 = 0.978\).

Figure 6.1 Images of different microalgae strains
6.5 Effect of CO₂ loaded solvents on different microalgae strains growth

All of the freshwater *Chlorella vulgaris* cultures grown with CO₂-loaded solvents showed enhanced growth compared with the control (Figure 6.2A). With MEA-0.5 loading solvent, a slightly higher final biomass concentration was reached than with PG or K₂CO₃. *Dunaliella tertiolecta* (Figure 6.2C) cultures with CO₂ loaded solvents were enhanced in relation to the controls. Chapter 5 has shown the result of marine *Chlorella* sp. with CO₂ loaded solvents and control. Here, culture growth of marine *Chlorella* sp. with MEA-0.5 loading (obtained from Figure 5.1A), K₂CO₃-0.5 loading (obtained from Figure 5.1A) and with PG-0.5 loading (obtained from Figure 5.1B) are shown in Figure 6.2B as reference. With CO₂ loaded solvents, marine *Chlorella* sp. cultures were enhanced compared to the controls, with K₂CO₃ and PG shown slightly higher biomass concentration compared with MEA. The maximum specific growth rate $\mu_{\text{max}}$ (d⁻¹) during the exponential growth phase, and the average and maximum volumetric productivities were determined (Table 6.1). All three strains exhibited higher maximum specific growth rates, average volumetric productivities, and maximum volumetric productivities with CO₂ loaded solvents than for the control, demonstrating that the membrane system can work well on these three strains.
Figure 6.2 Dry weight biomass of cultures of freshwater *Chlorella vulgaris* (A), marine *Chlorella* sp. (B) and marine *Dunaliella tertiolecta* (C) provided carbon dioxide by membrane delivery from potassium carbonate, MEA, potassium glycinate (PG) at 0.5 loading, or by atmospheric diffusion only (the control). Error bars represent the standard deviation of duplicate flasks.
Table 6.1 Comparison of the maximum specific growth rate, $\mu_{\text{max}}$ (d$^{-1}$) and volumetric productivity (g L$^{-1}$ d$^{-1}$) of *Chlorella vulgaris*, *Chlorella* sp. and *Dunaliella tertiolecta* grown with different sources of CO$_2$

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<th>Maximum volumetric productivity</th>
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</table>

6.6 Comparison of freshwater and marine systems

The accelerated growth of the cultures showed that the membrane system can be implemented in both fresh water and marine environments. However, differences between the freshwater and marine cultures were observed that warrant discussion.

6.6.1 Culture pH

Figure 6.3 shows that with CO$_2$ loaded solvents the pH of the media dropped sharply in the first half day. This is due to the high rate of CO$_2$ delivery, which
exceeded the demands of the low-density algae cultures that were still in the lag-phase. In the following days as the microalgae began to grow, the rate of CO₂ consumption increased such that the pH increased to reach reasonably stable values in the range 7-9. With only atmospheric CO₂ (control), the pH of the *Chlorella vulgaris* culture grown in a fresh water medium increased from 7.5 to 10.5 in 14 days (Figure 6.3A). However, the pH of *Chlorella* sp. and *Dunaliella tertiolecta* cultures grown in saline media increased from 7.5 to only 9 (Figure 6.3B, 6.3C). Compared with the fresh water (MLA) medium made from a base of pure RO water, the salt water (Modified-F) medium made with artificial ocean salt is an aqueous electrolyte. The ionic species present in the salt water medium (such as CO₃²⁻, B(OH)₄⁻, HPO₄²⁻, PO₄³⁻) can act as proton acceptors and contribute to the alkalinity, or pH buffering capacity of the solution. Dickson expressed the alkalinity in seawater as follows:\(^7\),

\[
\text{Total alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] + [\text{HPO}_4^{2-}] + 2[\text{PO}_3^{2-}] + [\text{SiO(OH)}_3^-] + [\text{HS}^-] + [\text{NH}_3] - [\text{H}^+] - [\text{H}_2\text{PO}_4^-] - [\text{HSO}_4^-] - [\text{HF}] - [\text{H}_3\text{PO}_4^-] \tag{6.1}
\]

The practical definition of alkalinity can be simplified to\(^8\),

\[
\text{Total alkalinity} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + [\text{OH}^-] - [\text{H}^+] \tag{6.2}
\]

Table 6.2 presents the concentrations of the main elements in the two media. It shows that the saltwater (MF) medium has slightly higher concentrations of boron and dissolved inorganic carbon (carbonate and bicarbonate). Freshwater (MLA) medium has higher phosphorus concentration. During the cultures, these proton accept species acted as pH buffering agents, reducing the pH change in the marine cultures compared to that in the freshwater cultures (Figure 6.3). Table 6.2 showed the pH of newly prepared media, after 20 mL microalgal culture inoculation, the pH slightly increased from 7.8 to 8.5 for MF media, and from 7.1 to 7.5 for MLA media.
Figure 6.3 The pH of *Chlorella vulgaris* (A), *Chlorella* sp. (B) and *Dunaliella tertiolecta* (C) cultures provided carbon dioxide by membrane delivery at potassium carbonate of 0.5 loading, MEA of 0.5 loading, potassium glycinate (PG) of 0.5 loading or by atmospheric diffusion only (the control). Error bars represent the standard deviation of duplicate flasks.
Table 6.2 Composition of the MF (with 3% artificial seawater) and MLA media

<table>
<thead>
<tr>
<th></th>
<th>Concentration (mg L⁻¹ MF)</th>
<th>Concentration (mg L⁻¹ MLA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>8510 ± 30</td>
<td>49 ± 0.1</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>860 ± 10</td>
<td>4.6 ± 0.2</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>280 ± 30</td>
<td>7.6 ± 0.7</td>
</tr>
<tr>
<td>K⁺</td>
<td>510 ± 50</td>
<td>16.1 ± 0.1</td>
</tr>
<tr>
<td>phosphorus</td>
<td>3.7 ± 0.8</td>
<td>7.2 ± 0.1</td>
</tr>
<tr>
<td>boron</td>
<td>3.2 ± 0.3</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td>DIC</td>
<td>2.5 ± 0.2</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>pH</td>
<td>7.8</td>
<td>7.1</td>
</tr>
</tbody>
</table>

6.6.2 DIC difference

The carbonate-water system is complex. When carbon dioxide (CO₂(g)) is dissolved in water, it first reacts with H₂O and then develops equilibria between four carbonate species: carbon dioxide (CO₂(aq)), carbonic acid (H₂CO₃), bicarbonate ion (HCO₃⁻) and carbonate ion (CO₃²⁻). The equilibrium reactions are as follows[9].

\[
\begin{align*}
\text{CO}_2(g) & \underset{K_H}{\rightleftharpoons} \text{CO}_2(aq) \quad (6.3) \\
\text{CO}_2(aq) + \text{H}_2\text{O} & \underset{K_m}{\rightleftharpoons} \text{H}_2\text{CO}_3 \quad (6.4) \\
\text{H}_2\text{CO}_3 & \underset{K_1}{\rightleftharpoons} \text{HCO}_3^- + \text{H}^+ \quad (6.5) \\
\text{HCO}_3^- & \underset{K_2}{\rightleftharpoons} \text{CO}_3^{2-} + \text{H}^+ \quad (6.6)
\end{align*}
\]

The marine medium has high concentrations of other ions such as Na⁺, Cl⁻, Mg²⁺, PO₄³⁻, with an overall ionic strength of approximately 0.5 mol kg⁻¹, which causes a ‘salting out’ effect, reducing the CO₂ solubility in marine medium. Based on the equation introduced by Weiss in 1974[10], the CO₂ solubility coefficient (Kᵦ) at 25 °C and 1 atm pressure to be 3.406×10⁻² mole kg⁻¹ atm⁻¹ for pure water and 2.991×10⁻² mole kg⁻¹ atm⁻¹ for seawater (25 g salt kg⁻¹ seawater). The ionic strength of seawater also impacts the dissociation constants of carbonic acid. Roy et al.[11]
determined the dissociation constants of carbonic acid in seawater (25 g salt kg\(^{-1}\) seawater) (pK\(_1^*\)=5.8896 and pK\(_2^*\)=9.0332 at 25°C) and pure water (pK\(_1\)=6.35 and pK\(_2\)=10.33).

The dissolved inorganic carbon (DIC) concentrations were calculated for seawater and pure water at pH 7, assuming an atmospheric CO\(_2\) concentration of 400ppm and the above equilibrium constants. The results, presented in Table 6.3, show that seawater has a higher DIC concentration (2.1 mg L\(^{-1}\)) than pure water (0.9 mg L\(^{-1}\)), which is due to the higher pK\(_2^*\) that pushes HCO\(_3^-\) dissociation to produce more CO\(_3^{2-}\). The DIC concentrations also vary with pH, for instance, at pH 8 and the same 400 ppm atmospheric CO\(_2\) concentration, DIC concentration is 21 mg L\(^{-1}\) for seawater and 7.5 mg L\(^{-1}\) for pure water.

Table 6.3 Equilibrium dissolved inorganic carbon concentration in pure water and seawater at pH 7 and 400ppm CO\(_2\) in atmosphere estimated based on the coefficients determined from Weiss \textit{et al.}\[10]\ and Roy \textit{et al.}\[11]\)

<table>
<thead>
<tr>
<th>(mg L(^{-1}))</th>
<th>CO(_2)</th>
<th>HCO(_3^-)</th>
<th>CO(_3^{2-})</th>
<th>DIC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure water</td>
<td>0.16</td>
<td>0.73</td>
<td>0.0003</td>
<td>0.9</td>
</tr>
<tr>
<td>Seawater</td>
<td>0.15</td>
<td>1.89</td>
<td>0.02</td>
<td>2.1</td>
</tr>
</tbody>
</table>

The measured DIC concentration of the initial marine (MF) medium is 2.5 mg L\(^{-1}\) and of the initial freshwater (MLA) media is 1.0 mg L\(^{-1}\) (Table 6.2). This trend, higher DIC of marine medium than of freshwater medium, is consistent with the calculations presented in Table 6.3. The DIC data from the culturing experiments (Figure 6.4B, C) also showed that the DIC in the marine medium (around 30 mg L\(^{-1}\)) was slightly higher than in fresh water (around 25 mg L\(^{-1}\)) (Figure 6.4A) during the growth phase. However, the microalgae medium is a more complex system that contains extracellular polymeric substances (EPS) (mainly polysaccharides, proteins, nucleic acids and lipids) that are produced during microalgae growth. The EPS may absorb organic compounds and inorganic ions\[12]\ and also be freely available in the medium as a total carbon source.
The total carbon concentration in the growth medium increased during microalgae cultivation at a much greater rate for the cultures with the membrane systems than for the controls (Figure 6.4D, E, F). The TC in the medium of the *Dunaliella tertiolecta* cultures (Figure 6.4F) were much higher (250 to 380 mg L\(^{-1}\)) than *Chlorella vulgaris* (Figure 6.4D) (60 to 80 mg L\(^{-1}\)) or *Chlorella* sp. (Figure 6.4E) (80 to 100 mg L\(^{-1}\)). During cultivation, microalgae can produce algae organic matter (AOM)\(^{13, 14}\). AOM consists of a range of biomolecules including carbohydrates, proteins, amino acids, and lipids\(^{13, 14}\), and comprises intracellular organic matter (IOM) and extracellular polymeric substances (EPS). The intracellular organic matter may be released into the external medium through simple diffusion or permeation from dead cells under extreme conditions\(^{13}\). The greater amount of TC in the *Dunaliella tertiolecta* cultures compared to the other two strains, is likely just a characteristic of *Dunaliella tertiolecta*. It is noteworthy that the greatest TC is for the MEA solvent. So it is possible that passage of MEA into this medium increased the concentration of dead cells and hence of EPS.
Figure 6.4 Dissolved inorganic carbon (DIC) and total nitrogen (TC) concentration in cultures of *Chlorella vulgaris* (A, D), *Chlorella* sp. (B, E) and *Dunaliella tertiolecta* (C, F), provided with carbon dioxide by membrane delivery at potassium carbonate of 0.5 loading, MEA of 0.5 loading, potassium glycinate (PG) of 0.5 loading or by atmospheric diffusion only (the control). Error bars represent the standard deviation of duplicate flasks.
6.6.3 Osmotic pressure difference

During microalgae cultivation water passed from the medium side to chemical solvent side of the membrane in response to the osmotic pressure gradient.

As shown in Figure 6.5A, the marine (MF) medium had less water pass into the solvents than from the freshwater (MLA) medium, due to its higher ionic strength (around 0.5 mol kg\(^{-1}\)) reducing the osmotic pressure driving force. According to simulations kindly conducted by Yue Wu using the software package Aspen\textsuperscript{TM}, 30 wt\% MEA has the highest osmotic pressure among the three solvents (Figure 6.5B). The trend in the osmotic pressure differences between these chemical solvents and the growth media is consistent with the trend in the volume of water passed through the membranes.

![Figure 6.5 Water addition volume in solvents side (A) and osmotic pressure of solvents and medium (B)](image)

When the cultures were provide CO\(_2\) using K\(_2\)CO\(_3\) and PG solvent, the total nitrogen (TN) in the medium was depleted within 5 or 6 days for all three strains (Figure 6.6). This reflects the utilisation of nitrate by the microalgae as a nitrogen source for growth. In contrast, the control cultures, which grew much more slowly due to carbon limitation, did not fully utilise the nitrate during the cultivation period.

However, when provided CO\(_2\) via the MEA solvent, the TN concentrations showed different behaviour, particularly for \textit{Dunaliella tertiolecta} (Figure 6.6C). In order to clarify the nitrogen utilization, NO\(_3^-\) concentration was also measured for the three strains with MEA-0.5 loading solvent (Figure 6.6D). The TN concentration in
freshwater (MLA) medium of *Chlorella vulgaris* was exhausted at day 5 (Figure 6.6A), as was the NO\textsubscript{3}\textsuperscript{-} concentration (Figure 6.6D). The TN concentration in the salt water (MF) medium of *Chlorella* sp. decreased in first 8 days, before starting to rise, reaching 20 mgN L\textsuperscript{-1} at day 16 (Figure 6.6B). However, NO\textsubscript{3}\textsuperscript{-} continuously decreased to day 16 (Figure 6.6D). The difference in those concentrations indicated that MEA was leaking through the membrane as described in Chapter 5. Given the higher osmotic pressure difference between the chemical solvents and the freshwater MLA medium, the greater passage of water from the medium side to solvent side may partially reduce MEA permeance from solvent side to medium side for this freshwater MLA medium.

For *Dunaliella tertiolecta*, the TN concentration in the salt water (MF) medium decreased in the first 6 days, before rising to 60 mgN L\textsuperscript{-1} by day 14 (Figure 6.6C) for the MEA system. The TN increase may come from MEA permeation, and also was caused by the AOM or IOM release when *Dunaliella tertiolecta* under MEA stress. Nevertheless, the NO\textsubscript{3}\textsuperscript{-} concentration decreased in first 6 days and became constant at around 20 mgN L\textsuperscript{-1} at day 14. These results probably different from the *Chlorella* sp. case due to *Dunaliella tertiolecta* reaching a stationary phase earlier (Day 6 versus Day 12 (Figure 6.2C)).
Figure 6.6 Total nitrogen (TN) concentration in cultures of *Chlorella vulgaris* (A), *Chlorella* sp. (B) and *Dunaliella tertiolecta* (C) provided with carbon dioxide by membrane delivery at potassium carbonate of 0.5 loading, MEA of 0.5 loading, potassium glycinate (PG) of 0.5 loading or by atmospheric diffusion only (the control). NO₃⁻ concentrations in three cultures with MEA of 0.5 loading solvents (D). Error bars represent the standard deviation of duplicate flasks.

**6.7 Conclusions**

The performance of different microalgae strains (freshwater *Chlorella vulgaris*, a marine strain of *Chlorella* sp. and the marine *Dunaliella tertiolecta*) was investigated in relation to the membrane system using three chemical solvents (K₂CO₃, PG and MEA). All three strains presented enhanced growth with K₂CO₃, PG and MEA of 0.5 CO₂ loading.
The salt water (MF) medium had better buffering capacity than the freshwater (MLA) medium, as the DIC, boron and other ions present could act as proton acceptors to moderate the alkalinity of the salt water (MF) medium. The saltwater (MF) medium could also dissolve more CO$_2$ than the freshwater (MLA) medium.

The concentrated chemical solvents exert an osmotic pressure across the membrane. As the salt water (MF) medium has a higher osmotic pressure, the driving force for water loss is less than that of the freshwater (MLA) medium, leading to more stable media concentrations.

In conclusion, while the membrane delivery of CO$_2$ is possible for both salt water and fresh media, the system is more effective in a salt water system.


Chapter 7 Economic assessment of membrane system

7.1 Chapter perspective

The attraction of this membrane system is that it can efficiently use CO$_2$ from the CO$_2$ loaded solvent. The potential trade-off is that implementing the membrane system may incur extra capital costs compared to conventional capture solvent regeneration and/or CO$_2$-to-pond delivery systems. In addition, this is an energy demand for this system that needs to be considered. It is necessary to better understand the capital costs and energy requirements of this membrane system. A preliminary economic analysis of the cost of the membranes was provided in Chapter 4. Here, this analysis is extended.

7.2 The cost of implementing a membrane system in a large-scale microalgae open pond

To understand the microalgae system, a coal combustion power plant with a capacity of 500 MW$^1$ is introduced in the following calculation. The specifications are listed in Table 7.1. Two scenarios have been investigated.

Table 7.1 Specifications of two scenarios used to assess the cost of implementing the membrane system

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Best case</th>
<th>Worst case</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power plant</td>
<td>500 MW</td>
<td>500 MW</td>
</tr>
<tr>
<td>Plant type</td>
<td>Coal-fired</td>
<td>Coal-fired</td>
</tr>
<tr>
<td>Flue gas flow rate (m$^3$ d$^{-1}$)</td>
<td>3.2×10$^7$</td>
<td>3.2×10$^7$</td>
</tr>
<tr>
<td>CO$_2$ concentration (vol %)</td>
<td>14$^1$</td>
<td>14$^1$</td>
</tr>
<tr>
<td>CO$_2$ captured by MEA absorption (%)</td>
<td>88.6$^1$</td>
<td>88.6$^1$</td>
</tr>
<tr>
<td>Microalgae pond productivity (g m$^{-2}$ pond d$^{-1}$)</td>
<td>25$^2$</td>
<td>25$^2$</td>
</tr>
<tr>
<td>Membrane permeance (GPU)</td>
<td>600$^a$</td>
<td>11$^b$</td>
</tr>
<tr>
<td>Membrane price (US$ m^{-2}$ membrane)</td>
<td>2$^c$</td>
<td>26.9$^d$</td>
</tr>
<tr>
<td>CO$_2$ conversion efficiency (%)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>CO$_2$ supply for microalgae pond (g CO$_2$ m$^{-2}$ pond d$^{-1}$)</td>
<td>41.8$^e$</td>
<td>41.8$^e$</td>
</tr>
</tbody>
</table>

a. The theoretical membrane permeance was kindly provided by Airrane (Korea).
b. This value of membrane permeance was calculated based on the experimental results in Chapter 4.

c. The membrane price is based on the information in Chapter 4.

d. The membrane price was kindly provided by Airrane (Korea).

e. The carbon content in *Chlorella vulgaris* biomass is assumed to be 45.6\%[3]. Based on this, a microalgae pond with an areal productivity of 25 g biomass m\(^{-2}\) pond d\(^{-1}\), requires 41.8 g CO\(_2\) m\(^{-2}\) pond d\(^{-1}\).

As in Chapter 4, a 20 wt\% K\(_2\)CO\(_3\) solution of 0.5 CO\(_2\) loading is used as the base case solvent. In Chapter 4, the membrane permeability was determined from the experimental results (0.4 L microalgal cultures with 0.0226 m\(^2\) hollow fibre membrane area achieving 0.38 g L\(^{-1}\)d\(^{-1}\) maximum biomass productivity). On this basis, the membrane permeability is 11GPU. This estimate is very conservative, as it assumes that this maximum biomass productivity is limited by the membrane permeability, rather than other factors such as light exposure. Conversely, the membrane supplier (Airrane) has provided a membrane permeability estimate of 600 GPU. This will be a highly optimistic value, as it assumes that the porous support of the membrane remains gas filled and that there is no resistance to CO\(_2\) transfer in the boundary layers either side of the membrane. In the analysis below, a ‘best case’ scenario is provided with a permeability of 600 GPU and a worst case is provided with a permeability of 11 GPU. In reality, the economics will lie somewhere between these two options. The capital cost of membrane is calculated as equation 7.1.

Capital cost of membrane (Million US$)

\[
= \text{membrane price} \times \text{microalgae pond area} \times \text{driving force} \times \text{CO}_2 \text{ supply for microalgae pond} \div \text{membrane permeance} \tag{7.1}
\]

When 100\% of the CO\(_2\) exiting from the power plant is used by microalgae in a membrane system, this system requires 1.85\(\times\)10\(^8\) m\(^2\) (18,500 ha) of microalgae pond area. Assuming a single microalgae open pond has an area of 1.25 ha\(^4\), 14800 open ponds would be required. For perspective, the area of the largest
natural lagoon used for cultivating microalgae is 3200 ha (the Hutt Lagoon culturing *Dunaliella* in West Australia [5]). In the best-case scenario, 26 Million US$ of membranes are required, however, in the worst scenario, 18.5 Billion US$ of membranes are required (Table 7.2). Given the cost and the extensive area of land required, is seems unlikely that capturing the entire CO2 emissions from a power station would be realistic.

More realistically, if only 10% of CO2 exiting from the power plant is used in a microalgae membrane system, the microalgae pond and membrane costs are reduced 10-fold (Table 7.2). In this case, the membrane system serves a supplementary way to utilize carbon dioxide from a power plant.

Table 7.2 Capital cost of membranes required for a 500 MW power station

<table>
<thead>
<tr>
<th></th>
<th>100% of the CO2 used</th>
<th>10% of the CO2 used</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Best case</td>
<td>Worst case</td>
</tr>
<tr>
<td>Driving force (Pa)a</td>
<td>771</td>
<td>771</td>
</tr>
<tr>
<td>Microalgae pond area (m²)</td>
<td>1.85×10⁸</td>
<td>1.85×10⁸</td>
</tr>
<tr>
<td>Membrane cost (US$ m⁻² pond)</td>
<td>0.14</td>
<td>99.8</td>
</tr>
<tr>
<td>Membrane capital cost (Million US$)</td>
<td>26</td>
<td>18465</td>
</tr>
</tbody>
</table>

a. The CO₂ partial pressure of 20 wt% K₂CO₃ of 0.5 CO₂ loading is 810 Pa based on an Aspen Plus™ simulation with the e-NRTL fluid package as modified by Lee [6]. The CO₂ partial pressure of sea water is 39 Pa from the published literature [7].

This thesis has studied different chemical solvents, including K₂CO₃, MEA and PG. Different chemical solvents have different CO₂ partial pressures, resulting in different amounts of required membrane areas and costs. Here, the cost of using different chemical solvents with a 0.5 CO₂ loading are compared. Table 7.3 lists the capital cost of membrane when 100% CO₂ utilized by microalgae.
Table 7.3 Capital cost of membrane with different chemical solvents, for 100% CO₂ utilization from a 500 MW power station

<table>
<thead>
<tr>
<th></th>
<th>20 wt% K₂CO₃</th>
<th>20 wt% PG</th>
<th>30 wt% MEA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Best case</td>
<td>Worst case</td>
<td>Best case</td>
</tr>
<tr>
<td>Driving force (Pa)</td>
<td>771</td>
<td>771</td>
<td>771</td>
</tr>
<tr>
<td>Microalgae pond area (m²)</td>
<td>1.85×10⁸</td>
<td>1.85×10⁸</td>
<td>1.85×10⁸</td>
</tr>
<tr>
<td>Membrane cost (US$ m⁻²)</td>
<td>0.14</td>
<td>99.8</td>
<td>0.14</td>
</tr>
<tr>
<td>Membrane capital cost (Million US$)</td>
<td>26</td>
<td>18465</td>
<td>26</td>
</tr>
</tbody>
</table>

Based on the study by Kadam[1], an MEA extraction process for a 500MW power station would account for 112 Million US$ of capital cost, in which it might be assumed as a rough estimate that 50% is for the absorption part (56 Million US$). In the best case then, 82 Million US$ capital cost is required for the column absorption and membrane desorption system. In the worst case, 31.2 Billion US$ capital cost is required.

In the same study by Kadam[1], the total capital cost of MEA absorption and desorption and delivery of the resulting CO₂ to microalgal ponds is 209 Million US$. The capital cost for raw flue gas delivery is 430 Million US$. The capital cost of the membrane system in the best case scenario is thus less than delivery of either pure CO₂ gas or raw flue gas, but the capital cost of membrane system in the worst case scenario is far more than the gas delivery.

### 7.3 Energy penalty for CO₂ capture and Delivery

In a typical chemical absorption process, the energy penalty for CO₂ regeneration, CO₂ compression and CO₂ transportation across 100 km are 2.4-4.2 GJ t⁻¹ CO₂[8], 0.4 GJ t⁻¹ CO₂ and 0.008 GJ t⁻¹ CO₂[9], respectively. In the following analysis, it is
assumed that the CO₂ regeneration is provided by natural gas combustion, while the compression and transportation energy is provided by electricity.

When the membrane system is implemented in this system, the energy penalties for CO₂ regeneration, compression and gaseous CO₂ transportation are avoided, but there is an energy penalty from the pumping of solvent to the site. Assuming a pressure drop of 300 kPa and a pump efficiency of 75%, the energy penalty of this pumping is only 0.02 GJ t⁻¹ CO₂, significantly reducing the energy penalty for CO₂ delivery (see Chapter 4).

Based on the gas market price of 8.6 A$ GJ⁻¹ and an electricity cost of 53 A$ MWh⁻¹ in 2016 in Victoria, Australia[10], Table 7.4 lists the operating costs of pure CO₂ delivery with an MEA extraction system and CO₂ loaded solvent delivery with the membrane system. With the membrane system, the operating costs are dramatically reduced from 59-93 Million US$ per year to less than 1 Million US$ per year.

Table 7.4 Comparison of operating costs of pure CO₂ delivery from an MEA extraction system and CO₂ loaded solvent delivery from the membrane desorption system, considering 100% utilization of the CO₂ from a 500 MW power station

<table>
<thead>
<tr>
<th></th>
<th>MEA extraction</th>
<th>Membrane system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent regeneration (A$ t⁻¹ CO₂)</td>
<td>20.6-36.1</td>
<td></td>
</tr>
<tr>
<td>Compression (A$ t⁻¹ CO₂)</td>
<td>5.9</td>
<td></td>
</tr>
<tr>
<td>Transportation (A$ t⁻¹ CO₂)</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>In total (A$ t⁻¹ CO₂)</td>
<td>27-42</td>
<td>0.3</td>
</tr>
<tr>
<td>In total (US$ t⁻¹ CO₂)</td>
<td>21-33</td>
<td>0.2</td>
</tr>
<tr>
<td>In total (Million US$ per year)</td>
<td>59-93</td>
<td>0.57</td>
</tr>
</tbody>
</table>
7.4 Present value

In order to compare the cost of two systems, net present values are calculated with a 5% discount rate. Here, it is assumed that the capital costs are incurred in the first year and that the system operates for 20 years. With 169 kt biomass produced per year and a biomass market price of 500 US$ per tonne\textsuperscript{[11]}, the revenue from the biomass produced is 84.8 Million US$ per year. The net present value is calculated as equation 7.2.

Net present value (Million US$) =

\[ \text{present value of revenue} - \text{present value of operating cost} - \text{present value of capital cost} \] (7.2)

In the power plant studied by Kadam\textsuperscript{[1]}, the capital cost of pure CO\textsubscript{2} delivery from an MEA extraction system is 209 Million US$\textsuperscript{[1]}. With 59 to 93 Million US$ of operating cost every year and 84.8 Million US$ of revenue per year, the net present value of pure CO\textsubscript{2} delivery from an MEA extraction system is between -299 to 107 Million US$.

In membrane desorption system, the capital cost of membrane varies based on the membrane permeance and membrane price, as equation 7.3. With the operating cost of 0.57 Million US$ per year and revenue of 84.8 Million US$ per year, the net present value of the membrane system is calculated as equation 7.4.

Capital cost of membrane (Million US$)

\[ = \text{membrane price} \times \text{microalgae pond area} \times \text{driving force} \times \text{CO}_2 \text{ supply for microalgae pond} \div \text{membrane permeance} \] (7.3)

\[ = 13218 \times \frac{\text{membrane price (US$ m^{-2} \text{membrane})}}{\text{membrane permeance (GPU)}} \]

Net present value of membrane system (Million US$) =

\[ \frac{\text{present value of revenue} - \text{present value of operating cost} - \text{Capital cost of membrane + Capital cost of MEA absorption}}{(1 + \text{discount rate})} \] (7.4)
Figure 7.1 shows the net present value of the membrane system (red surface) as a function of the membrane permeance and membrane price. The blue surface shows the 0 US$ net present value. With higher membrane permeance and lower membrane price, the present value of the membrane system could be higher than pure CO₂ delivery by an MEA extraction system. With a fixed membrane permeance of 100 GPU, in order to achieve higher present value, the membrane price needs to be less than 6 to 10 US$ (Figure 7.2). With a fixed membrane price of 10 US$, the membrane permeance needs to be greater than 100 to 150 GPU (Figure 7.3).

Figure 7.1 Net present value of the membrane system, the red surface is the net present value of membrane system, the blue surface is net present value of 0 US$. 

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Figure 7.2 Net present value of the membrane system, assuming a membrane permeance of 100 GPU

Figure 7.3 Net present value of the membrane system, assuming a membrane price of 10 US$ m\(^{-2}\)
7.5 Limitations of this study

The mass balance, and in particular the carbon balance, is vital in this system. However, due to the water permeation from the medium side to solvent side discussed in chapter 4, the CO₂ concentrations on the solvent side were diluted. Further, there was some loss of CO₂ from the solvent storage flask to the atmosphere over the course of the experiment. With the small amount of carbon uptake by microalgae and the high CO₂ concentrations in this solvent, the carbon utilization cannot be accurately calculated at this stage. Once this system is implemented on a large scale in the future, more accurate calculation of the CO₂ utilization and estimation of the costs can be performed.

7.5 Conclusions

The membrane system is unlikely to be able to deal with all the CO₂ emissions from a large power plant due to the extensive microalgae pond area required. However, it can be used as a supplementary mechanism for carbon dioxide utilization in a power plant due to the dramatically reduced operating cost. As an alternative way to delivery carbon dioxide to microalgae ponds, this membrane system would significantly reduce the energy penalty for biodiesel production. With a membrane permeance higher than 100 to 150 GPU (assuming a membrane price of 10 US$ m⁻²) and a membrane price lower than US$6-10 (assuming a membrane permeance of 100 GPU), the net present value of the membrane system would be higher than pure CO₂ delivery from an MEA extraction system.


Chapter 8 Conclusions and suggestions

8.1 Conclusions

This thesis demonstrated the effectiveness of a novel system, consisting of chemical absorption, membrane separation and microalgae growth, to efficiently separate and transport CO₂ from flue gas to microalgae. In the proposed system, carbon dioxide can be effectively delivered to microalgae ponds using a liquid-liquid contact between a carbon capture solvent and the microalgae medium across a PDMS membrane. CO₂ transfers between the two liquids in a gaseous state, through the solution diffusion mechanism.

The system was investigated using potassium carbonate, MEA and potassium glycinate as the chemical solvents. As a carbon source for microalgae, potassium carbonate of both high (0.5, 0.7) and low loadings (0.2) accelerated the growth of microalgae. Due to this reason, it is more suitable when low loadings are required for feed to the CO₂ absorber. As implemented in the microalgae ponds, the lean potassium carbonate solvent could maintain a sufficient supply of carbon dioxide to the microalgae before it was recycled back to capture further carbon dioxide.

MEA is widely utilized for capturing carbon dioxide due to its fast reaction kinetics with carbon dioxide. In the novel CO₂ delivery system, MEA with a CO₂ loading of 0.5 enhanced the growth of *Chlorella* sp. However, MEA with a CO₂ loading of 0.2 inhibited the *Chlorella* sp. growth. Furthermore, MEA, especially with low CO₂ loadings, passed through the PDMS membrane into the microalgae medium. This permeation severely inhibited the growth of the microalgae.

Amino acid salts have also been commercialized to capture carbon dioxide due to their fast reaction kinetics with CO₂. Potassium glycinate (PG) is an amino acid salt, which was investigated in the novel CO₂ delivery system. PG having a loading of 0.5 improved the growth of *Chlorella* sp. Furthermore, PG with a loading of 0.2 exhibited similar growth of *Chlorella* sp. as that of the control. A relatively small permeation across the membrane was also observed for PG. However, the toxicity tests showed that the small amount permeance did not inhibit the growth of
microalgae and that it can instead be utilized by microalgae as a source of carbon and nitrogen. This solvent was the optimum solvent of the three tested.

Different microalgae strains (freshwater *Chlorella vulgaris*, a marine strain of *Chlorella* sp. and marine *Dunaliella tertiolecta*) were investigated using the proposed novel CO$_2$ delivery system. All three strains presented enhanced growth with K$_2$CO$_3$, PG and MEA solvents having CO$_2$ loading of 0.5.

The marine (MF) medium showed different performance characteristics compared with the freshwater (MLA) medium. The marine (MF) medium had better pH buffering capacity than the freshwater (MLA) medium, as the DIC, boron and other ions present in marine MF medium could act as proton acceptors to moderate the alkalinity of the salt water medium. The saltwater MF medium also had higher CO$_2$ capacity than the freshwater MLA medium.

The concentrated chemical solvents exerted an osmotic pressure across the membrane. Since the marine (MF) medium has a higher osmotic pressure than the fresh water, the driving force for water loss is less than that of the freshwater (MLA) medium, which resulted in more stable media concentrations.

The novel CO$_2$ delivery system has been verified with different chemical solvents and various microalgae strains. With this approach, carbon dioxide can be delivered to a microalgae system without the losses and with low energy requirement (around 20 MJ t$^{-1}$ CO$_2$), compared with the high energy consumption associated with direct bubbling (80 to 530 MJ t$^{-1}$ CO$_2$). Further, the energy consumption (2.4-4.2 GJ t$^{-1}$ CO$_2$) of regenerating the solvent is eliminated. The costs of CO$_2$ captured from flue gas in power plant (around US$ 36 to 111 t$^{-1}$ CO$_2$) substantially reduced. Ultimately this means that the CO$_2$ can be supplied to microalgae in large volumes at a much lower net price than currently possible (US$ 15 to US$ 19 t$^{-1}$ CO$_2$).

The economic assessment shows that membrane system can be utilized as supplementary way to utilize carbon dioxide in power plant. Estimates of the capital cost of the membrane process have been calculated to be in the range from 26 to 31158 Million US$. The operating cost of the membrane system is only 0.57
Million US$ per year, which is around 0.6% to 1% of the operating cost of pure CO₂ delivery from an MEA extraction system. A membrane permeance higher than 100-150 GPU (assuming a membrane price of 10 US$ m⁻²) and a membrane price lower than US$6-10 (assuming a membrane permeance of 100 GPU) results in a net present value of this membrane system that is higher than that of a comparable system with pure CO₂ delivery.

8.2 Suggestions and future work

The proposed system still needs some future work to further enhance its operability and efficiency.

When microalgae were firstly inoculated in this system, a lag phase (around 2 to 4 days) was observed, as the CO₂ delivery exceeded the microalgae demand. If the equilibrium between the CO₂ delivery rate and microalgae demand is determined through experiments and modelling, delivery of solvent can be moderated to maintain the demand of microalgae which would ensure reasonable microalgae growth at an optimum pH.

The novel CO₂ delivery system was tested in conical flasks at a laboratory scale. There are a number of practical engineering and design issues that will need to be investigated in relation to implementing this system in large scale microalgae ponds. Optimization of the operational conditions and the configuration, such as the use of counter-current flow, can further enhance the efficiency of proposed system. This may solve the lag phase problems and also improve the use of solvents.

Potassium carbonate has slow reaction kinetics with carbon dioxide, whereas potassium glycinate acts as a promoter, due to which, it can accelerate the CO₂ reaction rate. The system has been tested with either potassium carbonate or potassium glycinate. It is expected that a combination of potassium carbonate and potassium glycinate will exhibit good performance, if employed in the proposed system. However, such a modification in the proposed process would require more information and research.
Appendix

This appendix includes the results obtained from a limited series of experiments investigating the application of the novel CO₂ delivery system on a fresh water algae, *Haematococcus pluvialis*. This freshwater microalgal strain has been commercially cultivated to produce astaxanthin, which is a pigment for aquaculture feeding[1]. As *Haematococcus pluvialis* is very sensitive to illumination, pH and nutrient concentration, the results varied with slight fluctuations in illumination, initial biomass concentration and medium pH. In addition, *Haematococcus pluvialis* exhibits a “green vegetative phase” and “red non motile phase” during its cultivation [2], which makes analysis complex. More replicate experiments conducted with a more finely-tuned control system would be required to comprehensively understand the behaviour of *Haematococcus pluvialis*. The following graphs from one trial give simple information about *Haematococcus pluvialis*. The linear correction between dry weight and optical density is dry cell weight (g L⁻¹) = 0.6557 × optical density, R² = 0.991.

*Haematococcus pluvialis* exhibited similar behaviour with previously studied microalgae species. With K₂CO₃, MEA and PG of 0.5 CO₂ loading, *Haematococcus pluvialis* achieved enhanced growth compared with the control, both in terms of dry weight and cell number (Figure A.1A and A.1B). PG- 0.5 loading exhibited a longer lag phase compared with K₂CO₃ and MEA, as the pH sharply dropped in first two days (Figure A.2A). The DIC in the microalgae media with K₂CO₃, MEA and PG solvents reached around 30 mg L⁻¹ in day 18, higher than that of control (13 mg L⁻¹) (Figure A.2B). The increase of TC and TN in the microalgae medium with MEA showed the permeance of MEA through the PDMS membrane (Figure A2.C and A2.D). Due to the microalgae assimilation, TN with K₂CO₃ and PG was exhausted in day 6 and day 12 (Figure A2.C), respectively.
Figure A.1 Dry weight biomass (A) and cell number (B) of freshwater *Haematococcus pluvialis* provided carbon dioxide by membrane delivery from potassium carbonate, MEA, potassium glycinate (PG) at 0.5 loading, or by atmospheric diffusion only (the control). Error bars represent the standard deviation of duplicate flasks.
Figure A.2 pH (A), DIC (B), TN (C) and TC (D) of freshwater *Haematococcus pluvialis* provided carbon dioxide by membrane delivery from potassium carbonate, MEA, potassium glycinate (PG) at 0.5 loading, or by atmospheric diffusion only (the control). Error bars represent the standard deviation of duplicate flasks.

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