Critical review of strategies for CO₂ delivery to large-scale microalgae cultures

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Abstract

Microalgae have great, yet relatively untapped potential as a highly productive crop for the 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. During microalgae cultivation, carbon dioxide (CO₂) is supplied as the carbon source for photosynthesising microalgae. There are a number of potential CO₂ supplies including air, flue gas and purified CO₂. In addition, several strategies have been applied to the delivery of CO₂ to microalgae production systems, including directly bubbling CO₂-rich gas, microbubbles, porous membrane spargers and non-porous membrane contactors. This article provides a comparative analysis of the different CO₂ supply and delivery strategies and how they relate to each other.

Introduction

In 2016, fossil fuel consumption, including oil (34%), natural gas (23%) and coal (28%), accounted for 85% 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 that impose a large carbon footprint, the world is looking to alternative, renewable sources of energy. Biofuels derived from biomass are renewable and near-carbon neutral. They can compensate for the depleting non-renewable fossil fuel resources and reduce global carbon emissions. Microalgae are regarded as a feedstock for 'third generation' biofuels due to their ability to be grown at very high productivity on completely non-arable land^[2, 3]. While this means that microalgae are a promising biofuel feedstock, the costs are currently prohibitively high ^[4]. Technologies to reduce the cost of both producing and processing microalgal biomass are required.

One of the major costs relates to the need to provide a carbon source to facilitate microalgae growth. Current CO₂ sources are atmospheric air, commercial purified CO₂ or raw flue gas. From a flue gas perspective, at least 13 gigatonnes of CO₂ is emitted every year from large point sources, such as power plants, cement processing, the steel industry and gas production^[5]. Effective utilization of such large point CO₂ emissions is an opportunity to reduce global greenhouse gas emissions. Every year, around 350 gigatonnes of atmospheric CO₂ is biologically converted to biomass by photosynthetic organisms ^[6, 7]. Consumption of such point sources would thus require only an additional 4% in world biomass production.

In mass microalgae cultivation, simply relying on diffusion of CO₂ from the atmosphere will mean the cultures 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 to reduce such carbon limitation has been to bubble gases into the microalgae cultures ^[8]. However, in the process, approximately 50% to 90% of the CO₂ delivered to the microalgae pond exits to the atmosphere ^[9]. As CO₂ has been estimated to account for over 50% of the raw material costs in microalgal cultivation ^[10], more effective delivery mechanisms are vital for both efficient microalgae production and reduction of CO₂ emissions. This paper provides a critical analysis of different CO₂ delivery strategies by comparing their efficiency, costs and limitations.

1. The role of CO₂ in microalgae growth

1.1 CO₂ uptake by microalgae

Carbon is a fundamental compositional element of microalgae, representing approximately 50 wt% of the microalgae dry biomass [11]. During photoautotrophic growth, microalgae uptake dissolved inorganic carbon from the surrounding water, and chemically reduce it (via the so-called light-independent reactions) using energy derived from photosynthesis. This reduced carbon goes into central metabolism and from there can be used for production of lipids and biomass. The overall reaction can be summarised as follows [11]:

In eukaryotic algal cells, CO₂ is fixed in the stroma of the chloroplast by the enzyme Ribulose Biphosphate Carboxylase Oxygenase (RuBisCO) within the Calvin-Benson-Bassham (CBB) cycle, as shown in Reaction (2) [12].

RuBisCO has a very slow turnover and a poor specificity for CO₂ over oxygen, a product of photosynthesis. To increase efficiency and to favour carbon fixation over competing photorespiration, most microalgae [13, 14] have evolved CO₂ concentrating mechanisms (CCMs) to increase the CO₂ concentration in the vicinity of RuBisCO. There are a number of different CCMs, including the 'biochemical C4' and the 'CAM' mechanisms of higher plants, and biophysical active transport processes in microalgae, as have been summarized in review papers on this topic [12, 15, 16]. Briefly, the CCMs in microalgae involve a combination of active transport of inorganic carbon from outside the cell into the chloroplast, concentration of CO₂ at the reaction site of RuBisCO, and the use of carbonic anhydrase enzymes to interconvert between different forms of inorganic carbon [17].

While CO₂ is the substrate for RuBisCO, most algae species have the ability to uptake and utilise both CO₂ and HCO₃⁻ [12]. This is important as most inorganic carbon is present as HCO₃⁻ at the pH values typical of microalgae cultures. There are a number of known pathways of CO₂ transport in eukaryotic algal cells [12] involving CO₂ diffusion and active

transport of CO_2 and HCO_3^- (Figure 1). The affinity for the two carbon species varies from species to species [18]. The difference is largely related to extracellular carbonic anhydrase (CA), the essential enzyme that catalyzes the reversible conversion of HCO_3^- to CO_2 . Only algae capable of using HCO_3^- have been found to express CA [14], which can then maintain the continuous supply of CO_2 to the active transporters by dehydration of HCO_3^- in the periplasmic space [19, 20]. These algae show a higher affinity for HCO_3^- than CO_2 , but the major carbon species entering the cytoplasm is CO_2 . The existence of external CA in different algae has been reviewed [12, 14]. In addition to variations between species, the expression of external CA is also largely influenced by pH and CO_2 concentration [19, 21, 22].

Figure 1. Diagrammatic representation of inorganic carbon uptake processes in eukaryotic algae, reproduced from Raven and Beardall 2016 [23].

1.2 Carbon limitation in microalgae cultures

The productivity of microalgae cultures can be limited by a number of factors, of which light and CO_2 availability are of most practical importance. Fully realising the potential productivity of a microalgae cultivation site requires maximal utilisation of the available light. This means that the cultures must be light-limited, and not limited by CO_2 availability. Due to the CCMs, the availability of inorganic carbon is often not a limit to

photosynthesis in dilute natural systems, 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 of CO₂ that can be provided by diffusion from the atmosphere^[24, 25]. Achieving a typical target biomass productivity of 25 g m⁻² d⁻¹ requires an average of 45.8 gCO₂ m⁻² d⁻¹ to be delivered to the growth ponds (assuming a biomass carbon content of 50% w/w). This is a much greater flux than can be provided to algae ponds via atmospheric diffusion, due to the low concentration of CO₂ in the atmosphere and limited pond surface area. Therefore, to maximise the utilisation of the available light and growth infrastructure, carbon limitation needs to be avoided in mass microalgae production by provision of external CO₂ ^[26]. However, excessively high CO₂ concentrations can decrease the medium pH and reduce the activity of external CA ^[27]. 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.

2. Global CO₂ supply and demand

Global anthropogenic CO₂ emissions were around 33 gigatonnes in 2017, mainly from fossil fuel combustion, industrial processes, residential consumption and transportation^[1]. Although CO₂ emissions are numerous, only the large point sources of CO₂ emissions are amenable for capture using current technology. Understanding the global CO₂ supply gives us information of potential CO₂ sources for microalgae cultivation. As the CO₂ market price depends on the relationship of CO₂ supply and demand, realizing the current and future CO₂ demand helps to evaluate the economic viability of different CO₂ sources for microalgae cultivation.

2.1 CO₂ Supply

The Intergovernmental Panel on Climate Change (IPCC) reported there was in total 13375 Mt CO₂ emissions from large point sources (of more than 0.1 Mt CO₂ per year) in 2002 ^[5]. The largest proportion (10540 Mt) was 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 ^[5]. The United Nations Industrial Development Organization (UNIDO) also reported that 6% of the global

industrial CO₂ emissions was from high purity sources (426 Mt) [28]. 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 [28], respectively.

2.2 CO₂ Demand

Parsons Brinckerhoff [29] investigated the demand for purified CO₂ in 2011 and found that 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 [29].

The CO₂ demand ultimately determines the CO₂ price. In 2010 this was quoted as anywhere from US\$ 3 to US\$ 55 t⁻¹ CO₂ depending upon the source and the location of this source [29] [5]. 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 the costs for CO₂ capture. Rubin *et al.* [30] estimated the CO₂ capture costs of different technologies for fossil fuel combustion power plants to be between US\$ 36 to US\$ 111 t⁻¹ CO₂. The implementation of a carbon tax or other incentives to reduce emissions can partly offset this difference. However, new strategies must be proposed to completely eliminate the gap between the CO₂ market price and carbon capture costs.

3. Types of CO₂ supplies available for microalgae cultivation

As discussed above, CO₂ must be provided to improve microalgae growth such that the available light is fully utilised. But contrary to EOR or other chemical industry processes, it is not necessary to use 100 vol% CO₂ for microalgae cultivation, so atmospheric air and raw flue gas can also be regarded as potential CO₂ sources. Secondly, some impurities (e.g. NO_x and SO_x) present in flue gas, even at low concentration, may detrimentally effect microalgae growth. The following paragraphs compare the different types of CO₂ supplies for microalgae cultivation, including air, raw flue gas, commercial purified CO₂, purified CO₂ from carbon capture facilities and CO₂-containing solvents in relation to CO₂ delivery. The advantages and disadvantages of each type of CO₂ supply is discussed, with a summary provided in Table 2.

3.1 Air

The atmosphere is the most readily available CO₂ 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 CO₂ production plant. However, atmospheric air has only about 0.035 vol% CO₂. 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 biomass concentrations or productivities. 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 CO₂ concentration still limits mass transfer efficiency due to the low concentration driving force. Jiang *et al.* [31] showed that with air aeration, *Nannochloropsis* sp. only achieved one third of the biomass concentration of cultures grown using gas containing 15% CO₂. Even more importantly, the low concentration of CO₂ means that an enormous volume of gas has to be pumped to provide the required carbon for intensive cultivation (Table 1). These issues mean that air is not a practical source of CO₂ despite being free and highly available.

Table 1. Volume of gas required^a (ton m⁻² d⁻¹) to provide carbon^b for an areal microalgal biomass productivity of 25 g m⁻² d⁻¹ as a function of CO₂ concentration and CO₂ utilisation. CO₂ utilisation is the proportion of CO₂ put into the ponds that is converted to microalgal biomass, and will increase with increasing CO₂ concentration and decreasing bubble size.

CO ₂	CO ₂ concentration (% v/v)				
	Air	Flue gas			Purified
Utilisation		Low	Med.	High	CO ₂
(%)	0.04	3	17	55	95
1	7090	96	18.4	6.9	4.7
5	1420	19.3	3.7	1.4	0.95
20	355	4.8	0.92	0.35	0.24
50	142	1.9	0.37	0.14	0.09
100	71	1.0	0.18	0.07	0.05

a. Assuming an air density of 1.225 kg m⁻³ and a CO₂ density of 1.98 kg m⁻³.

b. Assuming the biomass is 50% w/w carbon.

3.2 Raw flue gas from fossil fuel combustion

Raw flue gas from fossil fuel combustion accounts for 78% of anthropogenic CO₂ emissions [5]. The high capture costs associated with the low CO₂ concentrations in this flue gas restrict its usage for EOR and other industrial applications, but raw flue gas can be utilized as the carbon source for microalgae cultivation. The CO₂ concentration ranges widely, from about 4% for natural gas combustion up to about 33 vol% for cement or steel production [32]. The above-ambient concentrations increase the rate of mass transfer compared to air, and reduce the required volume of gas by orders of magnitude (Table 1).

However, in addition to CO₂, raw flue gas usually contains several other components, such as N₂, O₂, CO, NO_x, SO_x, C_xH_y, heavy metals and particulate matter [33,34]. The concentration of these components varies depending on the flue gas source [35]; 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 [34]. Components, such as NO_x and SO_x, have been reported to have a negative effect on microalgae growth [32, 36]. SO_x from flue gases may hydrolyse in the microalgae medium to release H⁺, causing a pH decrease and inhibit the microalgae growth [35]. NO_x has two forms NO and NO₂, that may be oxidized by the oxygen produced by microalgae photosynthesis to form nitrate or nitric acid in the culture medium [37]. Kao *et al.* [35] showed that flue gas containing less than 100 ppm NO_x with 0.2 l/l/min 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 have been many other studies into the effect of flue gas concentration on microalgae productivity [38-43], as well as some recent investigations into the effects of flue gas on microalgae physiology and biochemistry [44-48]. Broadly, there are two options for directly using raw flue gas containing NO_x and SO_x to enhance microalgal growth at large scale. One approach is to remove the SO_x and NO_x from the flue gas prior to microalgae use by adding desulfurization and denitrification units [35]. However, to avoid the cost of gas processing, another method is to isolate NO_x- and SO_x-tolerant microalgae strains [39]. *Chlorella fusca* LEB 111, which was isolated by Duarte *et al.* [26] from the ash settling ponds of a thermoelectric plant in Brazil, can tolerate up to 400 ppm SO₂ and 400 ppm NO, respectively. Radmann *et al.* [49] isolated *Chlorella vulgaris* from the sewage treatment pond of a thermoelectric plant in Brazil can grow with 12% CO₂, 60 ppm SO₂ and 100 ppm

NO. *Chlorella* sp., *Dunaliella tertiolecta* and *Scenedesmus obliquus* are the most commonly reported species that can tolerate SO_x and NO_x [32].

Usually the microalgae pond needs to be located near to the flue gas source to reduce the CO₂ delivery costs, but this also limits the potential scale of algae production. While there are many points sources of flue gas, only a small proportion of these will be suitably located for algae production (e.g. suitable climate, proximity to cheap flat land and water)[8]. The distance between the CO₂ point source and algae cultivation site influences the cost and therefore the potential utilisation of this form of CO₂ supply. For example, Quinn et al. [50] estimated that with a baseline maximum distance between the CO₂ source and the algae cultivation site of 4.8 km only 44 million barrels of oil equivalent could be produced from microalgae in the USA. Increasing the CO₂ transportation distance to 80 km would allow the production of 1.8 billion barrels of oil, however the costs of CO₂ transportation would not be economically feasible. Rubin *et al.* [30] estimated the CO₂ transportation costs through onshore pipelines as 1.3 to 10.9 US\$ t⁻¹ CO₂ per 250 km depending on the different capacities. The feasibility of CO₂ transportation is therefore dependent on both the CO₂ concentration of the gas and the required distance. A life cycle analysis completed by Stephenson *et al.*[51] indicated that an increase in CO₂ concentration in the feed gas from 5 vol% to 12.5 vol% could reduce the energy requirement for microalgal biodiesel production from 23.7 to 6.5 GJ t⁻¹ of biodiesel. For direct flue gas utilization, higher volumes of gas need to be delivered than that provided by a pure CO₂ stream (Table 1). As gas compression and transportation is energy intensive[52], purified CO₂ is therefore more preferable for microalgae plants located further from point sources of CO₂.

3.3 Purified CO₂

For microalgae ponds that do not have flue gas sources nearby, the more economic choice may be commercial purified CO₂. As mentioned above, ammonia production, gas processing, coal to liquids process and ethylene oxide production can provide commercial sources of purified CO₂ [28]. Research by Kadam[52] compared the supply costs of CO₂ from raw flue gas and purified CO₂ extracted from the flue gas using monoethanolamine (MEA), with a 100 km pipeline distance between the flue gas source and the microalgal cultivation site. The results showed that the direct flue gas supply (containing 14% CO₂) incurred expenses in compression, drying (US\$ 46.6 t⁻¹ CO₂) and

transportation (US \$10.6 t⁻¹ CO₂). Including MEA extraction added a cost of US \$28.72 t⁻¹ CO₂, but decreased the costs of compression, drying (US \$8.48 t⁻¹ CO₂) and transportation (US\$3.30 t⁻¹ CO₂) due to the smaller volume of the purified stream. For this scenario, the total cost of directly pumping flue gas was thus found to be 40% more expensive than supplying purified CO₂ by MEA extraction.

3.4 Bicarbonate addition

As discussed, a large amount of energy is required for gas compression and transportation over the vast areas required for large scale microalgae cultivation. An alternative is to directly add sodium bicarbonate to the medium to enhance microalgae growth^[32]. This avoids any pumping of gas, however the price of CO₂ via sodium bicarbonate is higher than even purified CO₂ (Table 2).

Enhancement of algae growth using bicarbonate has been demonstrated. Pancha *et al.*^[55] found a 23% and 21% increase in biomass and lipid productivities when *Scenedesmus* sp. CCNM 1077 was supplied with 0.6 g L⁻¹ sodium bicarbonate instead of normal BG11 medium without sodium bicarbonate addition. Nunez and Quigg^[56] showed that the growth of *Nannochloropsis salina* was about 3-fold higher with 5 g L⁻¹ sodium bicarbonate, than without sodium bicarbonate addition. It has also been shown that delivery of gaseous CO₂ can be supplemented by the addition of sodium bicarbonate to increase productivity^[57].

Usually seawater species have a higher tolerance to bicarbonate addition than fresh water species, as seawater species are already conditioned to high ionic strengths. As has been mentioned above, some microalgae strains (for instance, *Nannochloris atomus* and *Nannochloris maculate*^[14]) do not have external carbonic anhydrase, so the major, or only inorganic carbon species taken up is CO₂. This limits the potential application of this approach to species that can utilise bicarbonate. Sodium bicarbonate addition is typically in a range from 0.1 to 5 g L⁻¹ [55, 56, 58, 59], with the highest reported concentration of 0.60 mol L⁻¹ NaHCO₃ being applied to the highly salt-tolerant *Dunaliella salina*^[59]. 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. Nonetheless, it has been shown that there are certain algae present in alkaline natural soda lakes can be highly productive at very high ionic strengths and high

pH (>10)^[60]. The high pH increases the rate of CO₂ mass transfer ^[61] and the high alkalinity provides good buffering capacity. The potential to grow algae suited to cultivation under these extreme conditions is therefore of growing interest ^[62-65].

3.5 CO₂-containing solvents

Using CO₂-containing liquid solvents for microalgae growth could also reduce the energy required to transport the CO₂ as liquid does not require compression and is much more efficient to pump. This could provide a cheaper source of bicarbonate and reduce the energy associated with carbonate regeneration. It would also avoid energy and losses associated with pumping a gas and decouple CO₂ capture and utilisation ^[53, 54]. Noel *et al.*^[66] used a sodium carbonate solution, loaded with CO₂ to form sodium bicarbonate, as a carbon source. The CO₂ was transferred into seawater through contact of the two liquids either side of a non-porous poly dimethyl siloxane (PDMS) membrane. The CO₂ loaded seawater was used as a microalgal medium, while the sodium carbonate solution was recycled.

An alternative approach developed by our own group is to capture the carbon dioxide into a solvent such as MEA and to circulate this solvent directly throughout the algal bed within similar PDMS non-porous membranes^[67, 68]. The CO₂ desorbs from the solvent into the algal media, allowing this liquid to be directly recycled to the capture process to absorb more CO₂. Assuming a pressure drop of 300 kPa across a 100km delivery distance, and a pump efficiency of 75%, the energy penalty of pumping is only 0.02 GJ t⁻¹ CO₂, significantly reducing the energy penalty for CO₂ delivery. Aside from the reduction in compression costs, this approach also significantly reduces the cost of the CO₂ capture step. When purified CO₂ is obtained from a typical chemical absorption process in a power plant, the energy penalty for CO₂ regeneration is 2.4-4.2 GJ t⁻¹ CO₂^[69]. By contrast, when the membrane system is implemented to deliver a CO₂-loaded chemical solvent, the energy penalties for CO₂ regeneration are avoided. Further, with this approach, CO₂ might be temporarily stored in the solvents when the microalgae stop photosynthesis at night, allowing the capture process to continue operating on a continuous basis and avoiding the need for any gas storage. Conversely, a large membrane area is required within the ponds and this can add significantly to the capital costs (see Table 1). We estimate that a

membrane cost of under US\$10 per square meter is needed to ensure a competitive process.

3.6 Comparison of types of CO₂ supplies

A comparative summary of information relating to different types of CO₂ supplies is shown in Table 2. While air is free, practically unlimited in volume, and available on-site without requiring transportation, its low CO₂ concentration means that it is not a feasible option due to enormous volumes of air that have to be injected into the microalgae cultivation ponds.

The use of purified CO₂, flue gas, and CO₂-loaded solvents are all dependent on the availability of point sources of CO₂ and their proximity to land suitable for large scale microalgae production. To further explore the topic of CO₂ supply, the reader is referred to a number of detailed analyses of the availability, location and overall potential of point CO₂ sources for microalgae cultivation in the USA [50, 70, 71]. Briefly, flue gas is widely available and has limited commercial value. However, it also contains impurities that may inhibit microalgae. Purified CO₂ has the advantage of higher mass transfer, utilisation and transportation efficiencies, but has a commercial value and is more limited in availability than flue gas.

While the gas CO₂ supplies require considerable energy for compression and transportation, the energy needed to deliver bicarbonates or CO₂-loaded solvents is much lower. The price of bicarbonates is higher than even purified CO₂, and is more limited in availability than flue gas. In addition, not all species of algae can uptake bicarbonates. The use of CO₂-loaded solvents would require co-location with a CO₂ capture plant, but in doing so would reduce the cost and energy required for solvent regeneration. While this approach appears to have potential, it is still an emerging technology. Ultimately, the selection between flue gas, purified CO₂ and bicarbonate addition will be made on a site-by-site basis according to the relative economics.

Table 2. Comparison of different types of CO₂ supplies for microalgae cultivation

	CO ₂ concentration	CO ₂ utilisation/mass transfer efficiency	Gas volume required	Availability	Cost of CO ₂ (US\$ t ⁻¹)	Compression & transportation energy	Pond injection energy
Air	~0.035 vol.%	Very low	Extremely high	Unlimited	0	None required (available on site)	Very high (extremely large volumes of gas)
Raw flue gas	4-33 vol.%	Moderate	Moderate	High	0	High (compression of high volumes of gas)	High (large volumes of gas)
Commercial purified CO ₂	>95 vol.% [72]	High	Low	Low	3 - 55 ^[29] [5]	Moderate (compression of low volumes of gas)	Moderate (moderate volumes of gas)
Purified CO ₂ from flue gas	>95 vol.% [72]	High	Low	High	29-111 ^[30, 52]	Moderate (compression of low volumes of gas)	Moderate (moderate volumes of gas)
Bicarbonate addition	0.1~5g/L NaHCO ₃	Very high	None	Moderate	380 ^[57]	Low (no compression required)	Low (small volumes of solids)
CO ₂ containing solvents	0.5 mols CO ₂ /mol solvent in a 20wt% aqueous solution	Very high	None	Moderate	10 – 35 ^a	Low (no compression required)	Low (moderate volumes of liquid)

a. Assuming that the stripper operation is 70% of the capture cost.

4. Comparison of CO₂ delivery technologies

4.1 CO₂ delivery requirements

At typical microalgal growth conditions, only about 0.8 mmol/L of inorganic carbon can be stored in seawater^[8]. For an areal biomass productivity of 25 g m⁻² d⁻¹ this CO₂ would be consumed in an average of about 5.5 hour. As such, inorganic carbon must be frequently replenished throughout the cultures. It is important to realise that areal productivity targets (e.g. 25 g m⁻² d⁻¹) are averaged over a year. CO₂ supply during peak photosynthetic periods (e.g. the middle of a sunny day in summer) will many times higher than the average, while night time demand will be zero. CO₂ delivery strategies must be able to cope with fluctuating demands, both seasonally and diurnally, and ensure that inorganic carbon is available throughout the cultures. For very large cultivation ponds, multiple CO₂ injection points will be required, the spacing of which will be determined by the rate at which CO₂ supplies are depleted from the cultures^[8].

4.2 Conventional CO₂ delivery by sparging

Microalgae can be grown in artificial systems such as open raceway ponds and closed photobioreactors ^[73-75]. The conventional method for delivering CO₂ to microalgae ponds or photobioreactors is to use a sparger or diffuser ^[76-78]. For large scale production, microalgae are typically cultivated in open raceway ponds^[8]. 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) ^[79]. The shallow 0.2-0.5m pond depth allows the microalgae to best utilize the available light, by minimizing the effects of self-shading. 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 ^[15], purified CO₂ or air is usually injected into the pond through a sparger at the bottom of the pond ^[80]. The paddlewheel is operated to circulate and agitate CO₂, the microalgae broth and nutrients ^[81].

Figure 2. A typical raceway pond configuration for algae production.^[79]

4.3 CO₂ utilisation efficiency

As a carbon source, CO₂ has been estimated to account for around 66% of the raw material costs (including CO₂, fertilizers and water) for microalgae production in a large scale plant using sparged tubular photobioreactors^[10]. Increasing the efficiency of utilization of CO₂ can therefore significantly reduce operating costs. CO₂ utilisation efficiency is defined as the proportion of CO₂ injected into the ponds that is converted into microalgal biomass, rather than lost to the atmosphere. As shown in Table 1, the rate of gas delivery is directly dependent on the CO₂ utilisation efficiency. For gaseous forms of CO₂ supplies (i.e. air, flue gas, purified CO₂), the efficiency of CO₂ utilisation in microalgae cultures is dependent on the rate of CO₂ mass transfer from the gas to the liquid relative to the retention times of the gas in the liquid.

The mass transfer of CO₂ from a gas bubble to an algae cell involves a number of processes (Figure 3), which are described below. In an ideal system with a CO₂- containing gas over water, there will be an equilibrium state according to the following:

Figure 3. Schematic of CO₂ mass transfer pathways from a gas bubble to an algae cell. The important steps are identified by numbers in parentheses and are explained in the text.

In an algae culture the transfer of CO₂ from a gas bubble represents a non-equilibrium state in which CO₂ is pulled through by photosynthetic consumption of the CO_{2(aq)} and HCO₃⁻. The overall driving force for mass transfer is the difference between the concentration of CO₂ in the gas bubble and the concentration of CO_{2(aq)} and HCO₃⁻ that remains in solution despite uptake by the algae cells. CO₂ mass transfer is a multi-step process (Figure 3). (1) CO_{2(g)} must first be solubilised across the liquid film layer to form CO_{2(aq)}, the equilibrium concentration of which is dependent on the CO_{2(g)} concentration in the gas bubble according to Henry's Law (Table 3). The rate of CO₂ mass transfer is dependent on the resistance to mass transfer in the liquid film layer and the concentration driving force. The concentration driving force is the difference between the equilibrium CO_{2(aq)} concentration as determined by Henry's law, and the CO_{2(aq)} concentration in the bulk liquid. A sufficiently high CO_{2(aq)} concentration has to be maintained in the bulk liquid in order to drive mass transfer through to the algae either directly (2) or via HCO₃⁻ (3), (4), (5), (6). This means a high equilibrium CO_{2(aq)} from a concentrated CO₂ supply is needed to maintain a sufficient concentration driving force for efficient CO₂ mass transfer.

4.4 Gas delivery sumps

To achieve high efficiencies of CO₂ utilisation, CO₂ must be rapidly transferred out of the gas bubbles and into solution before the gas bubbles reach the surface of the ponds. The retention time of gas bubbles has a cubic dependency on the bubble diameter and linear dependency on the pond depth. As microalgae ponds are typically only about 0.2 - 0.5 m in depth, large bubbles can rise so quickly to the pond surface that most of the CO₂ is lost to the atmosphere. To increase the retention time of the bubbles, Lundquist *et al.* [8] introduced a sump (1 meter depth) in the raceway pond at the point of gas injection. In addition to increasing the depth for bubble rise, by placing the diffuser below the downward stream the effective contact time can be further increased. For bubbles with a rise velocity of 0.30 m s⁻¹, and a downward water velocity of 0.25 m s⁻¹, the contact time of gas and water could be increased from 1 second to around 20 seconds (Figure 4), and the CO₂ loss reduced. Nonetheless, it was assumed that CO₂ utilization would still be limited to about 50% for a flue gas using this design [8].

Figure 4. Schematic diagram of a sump for gas delivery in microalgae ponds, modified from Lundquist *et al.* [8]

4.5 Microbubbles

Reducing the bubble size is another approach to improving CO₂ utilisation efficiency. Compared to conventional bubbles (with a diameter of 1-2 mm [32]) 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 CO₂ can dissolve in the medium [32, 82] (Table 3).

Table 3. Influence of bubble size on key factors affecting CO₂ utilisation efficiency: residence time and specific surface area.

Bubble type	Bubble diameter (mm)	Rising velocity (m/s) ^a	Residence time (s) ^b	Specific surface area (m ² /m ³)	Bubble Formation Energy (kJ/m ³) ^c
Small microbubble	0.02	0.00022	1380	300,000	43
Large microbubble	0.1	0.0054	55	60,000	8.6
Small conventional bubble	1	0.54	0.55	6000	0.86
Large conventional bubble	5	13.6	0.022	1200	0.17

a. Calculated based on Stokes law assuming an air density of 1.225 kg m⁻³, a fluid density of 1000 kg m⁻³, and a fluid viscosity of 0.001 kg m⁻¹ s⁻¹.

b. Average residence time based on rising velocity assuming a pond depth of 0.3 m.

c. Calculated according to equation (4) assuming an air-water surface tension of 72 mJ/m².

Compared with the rapid rise of larger bubbles, microbubbles can reside for much longer periods (Table 3). The difference in residence times between large bubbles and microbubbles can be even greater than predicted by Stokes law owing to the likely coalescence of large bubbles and the ability of micro-turbulence to entrain microbubbles. Further, microbubbles of purified CO₂ can actually decrease gradually in size as they are dissolved in the water (Figure 5) [83]. Several methods have been applied to create microbubbles, such as fluidic oscillation, ultrasound or pressurized gas liquid circulation system [82, 84]. Such microbubbles have been applied for O₂ injection for wastewater treatment or oyster cultivation [82, 84, 85]. Zimmerman *et al.* [78, 86] first introduced microbubbles into microalgae cultivation by using a fluidic oscillation diffuser. The bubble size was around 550 to 750 µm, larger than the usual definition of microbubbles. Later research by Al-Mashhadani *et al.* [87] showed that with a fluidic oscillation diffuser, a 29% increase in the CO₂ overall mass transfer coefficient was obtained with 550 µm microbubbles compared with 1.3 mm bubbles (see Table 2).

Although microbubbles can greatly increase CO₂ utilisation efficiency, there is also a much greater head pressure loss associated with generating microbubbles that leads to

an increased energy consumption compared to conventional sparging. The energy associated with forming bubbles is given by the need to create new surface:

$$Energy = \frac{6\sigma}{R} \quad J/m^3 \quad (4)$$

Where R is the bubble radius and σ is the surface tension, which for air-water systems at ambient temperature is 72 mJ/m². This energy clearly increases as the bubble radius (R) decreases (Table 3). To minimise energy loss through microbubble generation, purified CO₂ supplies are preferable over flue gas as much lower volumes of gas need to be pumped (Table 1). An additional limitation this approach is that the strong shear stress effect created by microbubble generation may damage less robust microalgae cells [88, 89].

Figure 5. Effect of CO₂ delivery technology and supply type on bubble size and mass transfer and resulting CO₂ utilisation efficiency for microalgae cultivation. Depth of shading indicates the concentration of CO₂ in the gas. Not drawn to scale.

4.6 Porous membrane sparger

Porous membranes are another technology that can be used to generate small bubbles in order to maximise CO₂ utilisation efficiency. The porous membrane can provide smaller and more uniform CO₂ bubbles (0.2-0.9 mm) ^[90] than conventional sparging, but is not able to generate microbubbles. Fan *et al.* ^[91] ^[89] tested the performance of PVDF hollow fibre membranes through sparging 1% CO₂ into a helical tubular photobioreactor and achieved a tenfold higher mass transfer coefficient compared to tube bubbling. Cheng *et al.* ^[92] compared the performance of a polypropylene hollow fibre membrane contactor with a bubble photobioreactor, and showed that the CO₂ fixation rate of *Chlorella vulgaris* was enhanced over threefold. Mortezaeikia *et al.* ^[90] also used a polypropylene microporous membrane contactor to supply CO₂ bubbles for *Synechococcus elongates* growth. Similar to microbubble generation, porous membrane sparging results in greater pressure losses and therefore energy consumption than conventional sparging. In addition, the use of porous membranes imposes additional capital and maintenance costs that have to be factored into any design decisions.

4.7 Non-porous membrane contactor

The delivery of molecular CO₂ directly rather than via bubbles has been investigated as a means ensure complete CO₂ utilisation in microalgae cultures. A membrane contactor fabricated with a dense membrane can minimize CO₂ loss by producing bubbleless CO₂ in the aqueous phase ^[93-95]. In this case, the CO₂ crosses the membrane as individual molecules in a vapour state through the solution diffusion mechanism. This eliminates the surface energy required to form a bubble (Equation 1) and thus significantly reduces the compressor demand. Kumar *et al.* ^[94] used a composite hollow fibre membrane composed of a thin, dense polyurethane layer sandwiched between two microporous polyolefin layers to transfer gas containing 2-15% CO₂ to *Spirulina platensis*. A similar three layer composite membrane was used by Kim *et al.* ^[93] ^[95] (Figure 6).

Figure 6. Non-porous membrane for bubbleless CO₂, modified from Kim *et al.*^[93]

As described above, both Noel *et al.* ^[66] and Zheng *et al.* ^[67] have used a similar thin film composite hollow fibre membrane composed of a thin, dense PDMS layer and a microporous support layer to deliver CO₂ from CO₂-loaded solvents. With solutions containing 0.5 mols CO₂ per mol of solvent, a 16 to 20 fold increase in volumetric productivity was achieved compared with simple air diffusion^[96]. This approach not only eliminates the surface energy requirement for bubble formation, but also eliminates the need for gas compression and transport, replacing this with the pumping of a liquid phase, which is less energy intensive.

4.8 Comparative summary

A comparative summary of the various CO₂ delivery technologies is provided in Table 4. Each of the CO₂ delivery technologies differ in their inherent capabilities, limitations, and energy requirements. They also differ in terms of their suitability to different CO₂ supplies. In particular, sparging technologies will result in incomplete utilisation of the CO₂ supply and are therefore less suited to purified CO₂ sources that cost money to purchase. Conversely, microbubble generation and porous membrane sparging are less suited to flue gas due to the high energy requirements for pumping large volumes of gas. The selection of CO₂ delivery technology is complex and site specific, depending on the type and price of CO₂ supply.

Table 4. Qualitative comparative assessment of the different strategies for delivering CO₂ to microalgae.

CO ₂ delivery technology	Relative utilisation efficiency	Relative cost of delivery device	Applicable CO ₂ supplies	Relative pumping energy requirements
Conventional sparging	Low	Low	Flue gas (inadequate utilisation of purified CO ₂)	High (large volumes of gas due to low utilisation efficiency)
Sparging with a sump	Moderate	Low	Flue gas (inadequate utilisation of purified CO ₂)	High (large volumes of gas due to low utilisation efficiency)
Microbubble generation	Very high	Moderate	Purified CO ₂ (excessive pumping energy for flue gas)	High (pumping gas with high pressure losses)
Porous membrane sparger	High	High	Purified CO ₂ (excessive pumping energy for flue gas)	High (pumping gas with high pressure losses)
Non-porous membrane contactor	Complete	High	Purified (captured) CO ₂	Low (pumping a liquid)
Direct bicarbonate dosing	Complete	Very low	Sodium bicarbonate	Nil

7. Conclusion

This paper has described a range of CO₂ supplies and CO₂ delivery strategies for microalgae systems to enhance microalgae growth. As the largest proportion of CO₂ emissions is from large point sources, flue gas is a potential supplement to commercial purified CO₂. While flue gas is cheap, the use of purified CO₂ can greatly reduce gas volumes and pumping energy and increase mass transfer efficiency. However, the gap between CO₂ market price and carbon capture costs has to be narrowed. The energy costs of CO₂ delivery and the loss of CO₂ to the atmosphere are important contributors to the viability of gaseous delivery approaches. The use of concentrated CO₂ supplies and the generation of smaller bubbles can improve utilisation efficiency, however they come at a cost. The use of microbubble generators or the delivery of CO₂ through porous hollow fibre membranes spargers can achieve higher CO₂ utilisation than sparging, but require considerable energy for bubble formation. The use of CO₂ containing solvents, delivered through non-porous membranes offers another approach that ensures low CO₂ loss and avoids gas compression and transportation energy. However, the capital costs associated with the membrane installation can be high.

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