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ARTICLE

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

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This article demonstrates a novel combination of solvent absorption, membrane desorption and microalgal cultivation to capture carbon dioxide and convert it to a 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 CO_2 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.

Broader context

This article shows for the first time that carbon dioxide can be transferred directly from a carbon capture solvent (a simple potassium carbonate solution) into a microalgal culture, via commercially available hollow fibre membranes, *in a single step*. Importantly, this approach eliminates the reboiler that is normally used for solvent regeneration in a capture process thus significantly reducing the energy requirement for delivery of purified carbon dioxide. Further, by delivering rich solvent to the microalgal system, we eliminate the need for gas compression; an additional energy expense in a CO_2 assisted microalgal system. The maximum microalgal biomass productivities achieved using this approach are significantly greater than those presented before, providing a lower cost, more efficient approach to production of biofuels and other bio-derived products.

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 CO_2[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 CO_2 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 CO_2[16].

To improve the energy efficiency of delivering CO_2 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 CO_2 concentrations. In a life cycle analysis completed by Stephenson et al[17], an increase in CO_2 concentration in feed gas from 5% to 12.5%, reduced the

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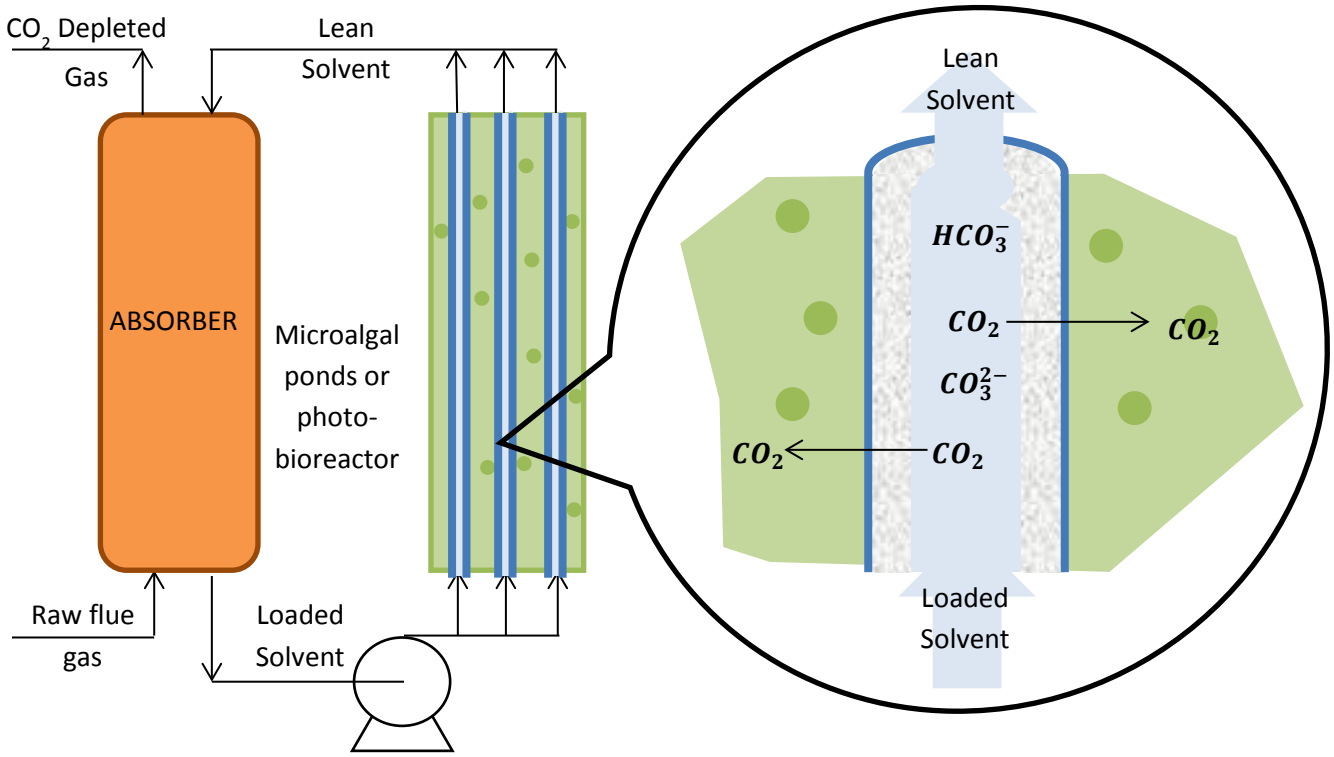

Fig. 1 A schematic of the proposed process. Carbon dioxide is absorbed from a combustion flue gas into a potassium carbonate solvent which is then pumped through a microalgal raceway pond or photobioreactor. The carbon dioxide desorbs into the microalgal culture medium and the depleted solvent is returned to the absorber. There is no need for a receiving solution, or a capture stripping operation.

energy requirement for biodiesel production from 23.7 to 6.5 GJ/t of biodiesel. Secondly, there has been a focus on improving the rates of CO_2 mass transfer within the microalgal media. The most common method is to sparge cultures with CO_2 bubbles[18, 19]. 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 CO_2 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 CO_2 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 CO_2 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 CO_2 was then stripped into a sodium carbonate solution to produce a bicarbonate-rich solution. In turn, a CO_2 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 Fig. 1, carbon dioxide is first absorbed from a raw flue gas, or other source of CO_2, into a potassium carbonate solution, via Reactions (1) to (3):

$$CO_{2(g)} \leftrightarrows CO_{2(l)} \quad (1)$$

$$CO_{2(l)} + OH^- \leftrightarrows HCO_3^- \quad (2)$$

$$HCO_3^- + OH^- \leftrightarrows CO_3^{2-} + H_2O \quad (3)$$

Potassium carbonate has been utilized in industry to absorb CO_2 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 CO_2 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 1 to 3 are reversed. Once within the microalgal medium, the carbon dioxide can be absorbed by the microalgal cells directly as CO_2 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 CO_2)[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.

Materials and methods

Materials

The solvent chosen was a 20%wt potassium carbonate solution with different CO_2 loadings prepared by mixing quantities of K_2CO_3 (Senator Chemicals,99.7%) and $KHCO_3$ (Univar,98%) in purified water (Table 1).

The solvent loading is defined as Eq(4):

$$loading = \frac{[HCO_3^-]}{[K^+]} \qquad (4)$$

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 S1. 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.

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_2CO_3 solutions with initial loadings of 0.2, 0.5, 0.7 were pumped though the tube side of hollow fibre PDMS membranes immersed in the microalgal medium (Fig. 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 1 The initial composition of 20%wt K_2CO_3 with different loadings

	$KHCO_3$ (mol L^{-1})	K_2CO_3(mol L^{-1})
$KHCO_3$-20%wt-0.2 loading	0.624	1.34
$KHCO_3$-20%wt-0.5 loading	1.578	0.867
$KHCO_3$-20%wt-0.7 loading	2.285	0.471

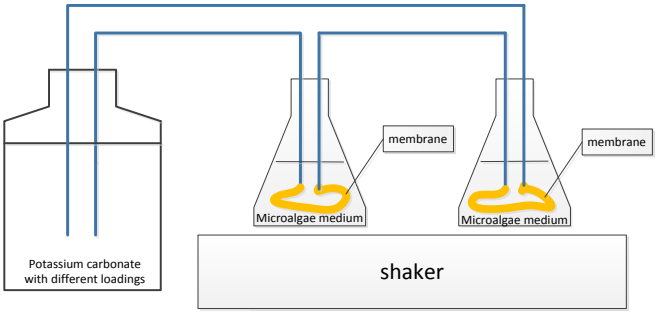

Fig. 2 A schematic of the experimental system

Analysis

Samples (5 mL) of the microalgal 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[27]. 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, R^2 = 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.

Results and discussion

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 (Fig. 3). Significantly, for all CO_2 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}).

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 (Figs 4-6, Fig. 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 (Fig. 3), the pH was constant at around 7.5 (Fig. 4) and the nitrate decreased slightly from 80 mgN L^{-1} to 60 mgN L^{-1} (Fig. 5). As there was no artificial carbon addition, the inorganic carbon concentration was constant at around 8 mg L^{-1} (Fig. 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[28,29] according to Eq.(5):

$$X = X_i + \frac{FS_{feed}}{V} Y_{x/C} t \qquad (5)$$

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). According to Anjos et al.[19], the carbon content in *Chlorella vulgaris* biomass is 45.6%. The yield coefficient can then be calculated from Eq.(6):

$$Y_{X/C} = \frac{biomass}{carbon} = \frac{1}{0.456} = 2.193 \qquad (6)$$

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± 0.0006gC 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 (Fig. 3). However, in this period, the pH has a more obvious decline (Fig. 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 (Fig. 6). From Days 1.5 to 4, growth appears unlimited, showing approximately exponential growth (Fig. 3). *Chlorella* sp. has sufficient carbon, nitrogen and light. In this period the specific growth rate μ (d^{-1}) of the microalgae can be determined from Eq.(7):

$$\mu = \frac{lnX_t - lnX_{t0}}{t - t_0} \qquad (7)$$

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 (Fig. 4), revealing that the culture absorbs increasing amounts of carbon as the population grows, until the demand exceeds the

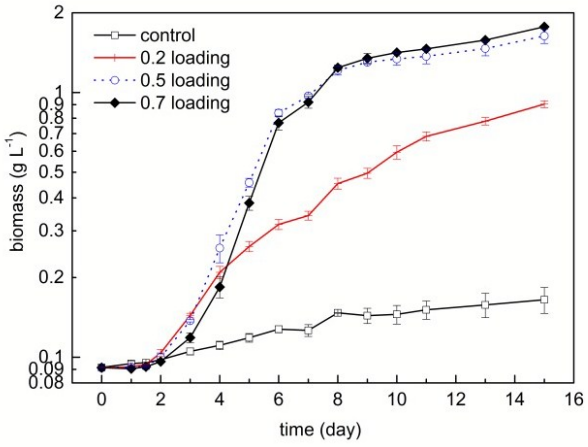

Fig. 3 Growth curves of *Chlorella* sp. cultures supplied with carbon dioxide by membrane delivery at different potassium carbonate loadings, or by atmospheric diffusion only (the control). Errors bars represent the standard deviation of duplicate experiments, measured by optical density.

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 (Fig. 3). The pH becomes stable at around 9.5, consistent with a constant, low concentration of carbon dioxide (Fig. 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 (Fig. 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 *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 (Fig. 4). The reactions occurring are as indicated in Equations 2 and 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 (Fig. 4). However, interestingly, the inorganic carbon in the solution in this period continues to increase (Fig. 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 gC 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 (Fig. 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.

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

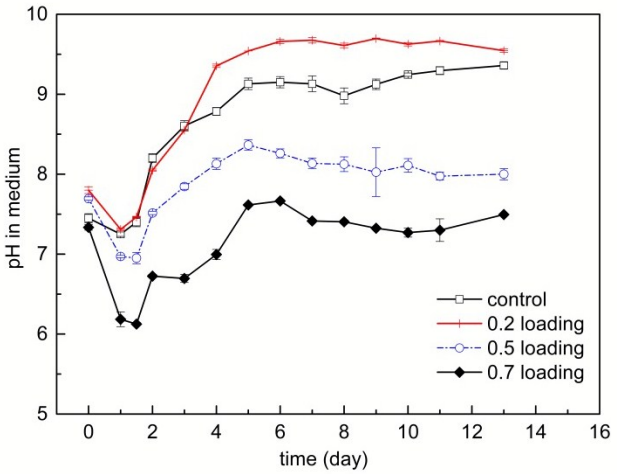

Fig. 4 pH in microalgae medium in different loadings and control, errors bars represent the standard deviation of duplicate experiments.

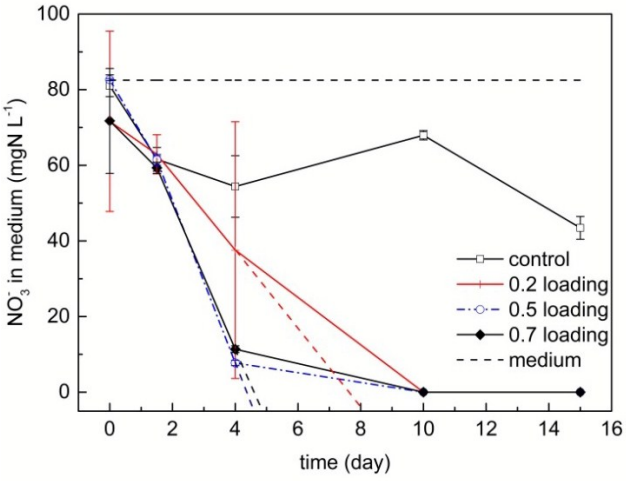

Fig. 5 Nitrate in microalgae medium in different loadings and control, errors bars represent the standard deviation of duplicate experiments.

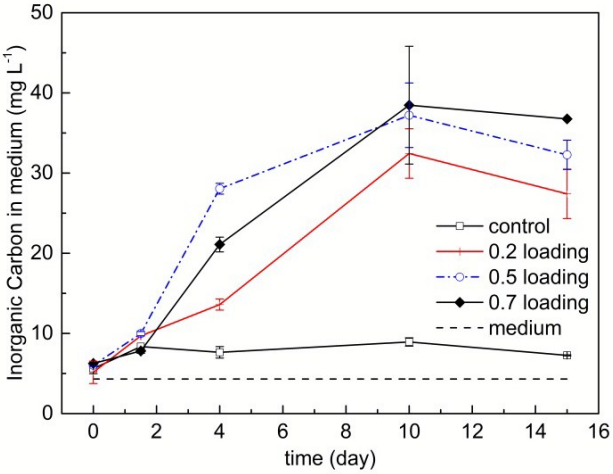

Fig. 6 Inorganic carbon in microalgae medium in different loadings and control, errors bars represent the standard deviation of duplicate experiments.

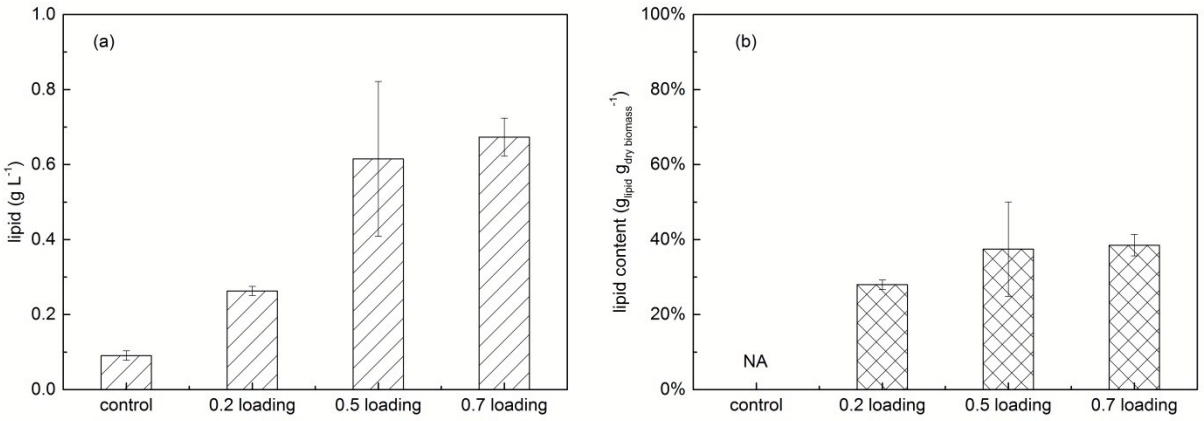

Fig. 7 Concentration of lipid in the *Chlorella* sp. cultures after 15 days growth with different carbon dioxide provision. Errors bars represent the standard deviation of quadruplicate experiments per sample condition (duplicate measurements for each flask, n=4)

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 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.

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 S.2). In other research into CO_2 delivery to microalgae via sparging with air containing 10% CO_2, 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% CO_2. Compared to conventional CO_2 delivery systems, using CO_2 loaded solvents can thus increase microalgae biomass productivity while importantly avoiding loss of large amounts of CO_2 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 Fig. 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 (0.09 ± 0.01 g L^{-1} medium) and 0.2 loading (0.26 ± 0.01 g L^{-1}). 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[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[25]. Thin layer chromatography[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[33].

Table 2 Comparison of volumetric productivity (g L^{-1} d^{-1}) of *Chlorella* sp. with different loadings

	Average	Maximum
control	0.0054±0.0013	0.021±0.01
0.2 loading	0.058±0.002	0.11±0.01
0.5 loading	0.126±0.005	0.38±0.01
0.7 loading	0.137±0.002	0.39±0.02

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 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.

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.

Table 3 Water addition volume

	Water addition volume (mL)
0.2 loading	125
0.5 loading	125
0.7 loading	144

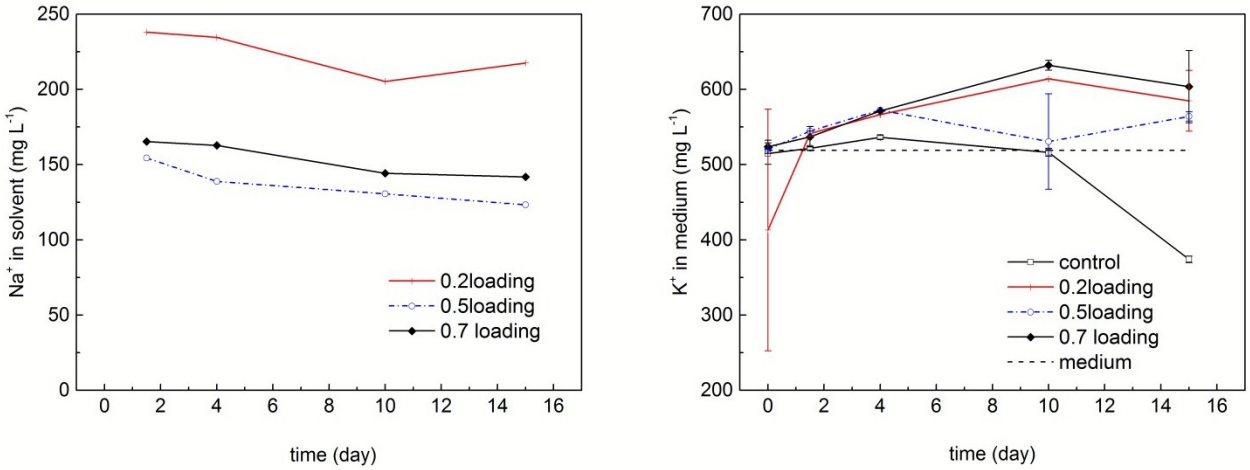

Fig. 8 Na^+(a) within the solvent and K^+ (b) on the medium after filtration to remove cell biomass side during the course of the experiment. Errors bars for Fig. 8(b) represent the standard deviation of duplicate experiments

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 Fig. 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 Fig. 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.

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 Fig. S2). 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 CO_2 capture process, the energy penalty from the reboiler is 2.4-4.2 GJ/t CO_2[16]. A further 400 MJ/t CO_2 is needed to compress the carbon dioxide to a supercritical state (15 MPa) and a further 8 MJ/t CO_2 is required for transportation to a geological storage site (assumed to be 100km away).[38] Thus the total energy penalty for classical CO_2 capture and geological storage is around 2.8-4.6 GJ/t CO_2. Alternatively, using the present approach, the energy penalty for CO_2 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 CO_2.

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 biodiesel (Table 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 CO_2[2, 17, 39]. Thus, when CO_2 loaded solvent is utilized in the system presented here to replace the CO_2 transfer process, it can save anywhere between 60 - 510 MJ/t CO_2; or between 0.40 and 3.4 GJ/t biodiesel (if 1 tonne biodiesel requires 6.7 ton CO_2[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 CO_2-e /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 CO_2-e /t diesel (Table S3). Eliminating the need for gas compression would reduce

this by between 0.09 and 0.76 ton CO_2-e /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 0.0226m^2 hollow fibre membrane achieving 0.38 $g \cdot L^{-1} \cdot d^{-1}$ maximum biomass productivity), a microalgae pond of 0.3m depth and 25 g m^{-2} d^{-1} areal productivity, would require approximately 4 $m^2_{membrane}$ m^{-2}_{area} 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 $m^{-2}_{membrane}$ [40, 41], leading to capital costs of US$ 8 to $32 m^{-2}_{area}.

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.

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