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How to optimise photosynthetic biogas upgrading: a perspective on system design and microalgae selection

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Abstract

Photosynthetic biogas upgrading using microalgae provides a promising alternative to commercial upgrading processes as it allows for carbon capture and re-use, improving the sustainability of the process in a circular economy system. A two-step absorption column-photobioreactor system employing alkaline carbonate solution and flat plate photobioreactors is proposed. Together with process optimisation, the choice of microalgae species is vital to ensure continuous performance with optimal efficiency. In this paper, in addition to critically assessing the system design and operation conditions for optimisation, five criteria are selected for choosing optimal microalgae species for biogas upgrading. These include: ability for mixotrophic growth; high pH tolerance; external carbonic anhydrase activity; high CO_2 tolerance; and ease of harvesting. Based on such criteria, five common microalgae species were identified as potential candidates. Of these, *Spirulina platensis* is deemed the most favourable species. An industrial perspective of the technology further reveals the significant challenges for successful commercial application of microalgal upgrading of biogas, including: a significant land footprint; need for decreasing microalgae solution recirculation rate; and selecting preferable microalgae utilisation pathway.

Keywords: Biogas Upgrading; Biomethane; Microalgae; CO_2 capture and reuse; Photobioreactors.

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1 Introduction

1.1 Biogas and Biomethane

Biogas derived from anaerobic digestion of wet organic materials is a renewable source of energy, with significant importance in future energy systems to reduce greenhouse gas (GHG) emissions from industry, transportation and domestic sectors amongst others (Scarlat et al., 2018; Wall et al., 2017). Biogas typically comprises of 45-70% CH_4, 20-55% CO_2, and other gases, namely, N_2 (0-3%), O_2 (0-1%), water vapour (1-10%), hydrogen sulphide (0-10,000 ppm), ammonia (0-100 ppm), and traces of hydrocarbons, siloxanes and chlorine (Angelidaki et al., 2018; Awe et al., 2017; Muñoz et al., 2015; Ullah Khan et al., 2017). All gases except methane either lower the calorific value of biogas and/or are considered environmental pollutants, leading to unwanted emissions from their use. Subsequent to a primary cleaning of biogas for the removal of H_2S and other trace compounds, its calorific value can be enhanced by removal of CO_2, a process termed "biogas upgrading" (Angelidaki et al., 2018). The resulting cleaned and upgraded gas is known as biomethane (Angelidaki et al., 2018; Ullah Khan et al., 2017).

1.2 Innovative Biogas Upgrading Technologies including carbon capture and reuse

Strategies for biogas upgrading traditionally entail physicochemical removal of CO_2 (Angelidaki et al., 2018). While chemical methods include absorption of CO_2 with solvents or mineral carbonation, CO_2 can be physically separated from biogas by membrane separation, pressure swing adsorption, cryogenic separation among others (Zhou et al., 2017). Most of these technologies, even though commercialized, continue to suffer from a significant energy penalty (3-6% of the energy content of biogas) and a high cost (up to 30% of the total cost of upgraded biogas) (Angelidaki et al., 2018; Xia et al., 2015). Negative emission technologies are seen as an essential requirement *to allow humanity to meet the Paris Agreement's targets of avoiding dangerous climate change* (European Academies Science Advisory Council (EASAC), 2018). Bioenergy with carbon capture and reuse can reduce the CO_2 footprint of biogas systems. Biological biogas upgrading systems integrating microalgae cultivation (with associated revenue) and production of value-added products is a potential future solution for cost-efficient upgrading in an optimised system providing direct CO_2 sequestration on or near site (Farrelly et al., 2013; Zhou et al., 2017); it can also improve the energy balance in generating more energy in the form of algal biofuels.

1.3 Photosynthetic Biogas Upgrading

A commercial photosynthetic biogas upgrading system must be able to operate continuously while maintaining a CO_2 concentration in the range 2-6% and an O_2 concentration of lower than 0.5% in the upgraded biomethane (Technical Committee CEN/TC 234 "Gas Supply," 2011). Low oxygen content is essential to prevent a potentially explosive environment. Nonetheless, oxygen generated during photosynthesis, causing a rise in the O_2 levels in the upgraded biomethane continues to be a major challenge for this biological biogas upgrading process. In addition, other challenges including: *1)* low CO_2 mass transfer; *2)* lack of effective control of process parameters including gas and liquid flow

rates and pH; *3)* diurnal variability in operations due to photo-autotrophy (absorption of carbon by microalgae, assisted by chlorophyll only in the presence of light); and *4)* intermittent operations from seasonal temperature fluctuations affecting microalgae growth, are significant.

A two-step photosynthetic biogas upgrading process with a separate microalgae harvesting step (Figure 1) allows each step: *i) Biogas Upgrading* for CO_2 removal to grid injection standards, *ii) CO_2 Sequestration* by fixing the captured CO_2 by microalgae and *iii) CO_2 utilization* by harvesting microalgae for use in biofuels or chemicals for their own optimisation strategies. In addition, through the selection of microalgae species with specific properties, there can be opportunity for further optimisation of the system. However, to the best of the knowledge of the authors, simultaneous considerations of both microalgae strain selection and system parameter optimisation for photosynthetic biogas upgrading is rare in the literature.

1.4 Novelty and Objectives

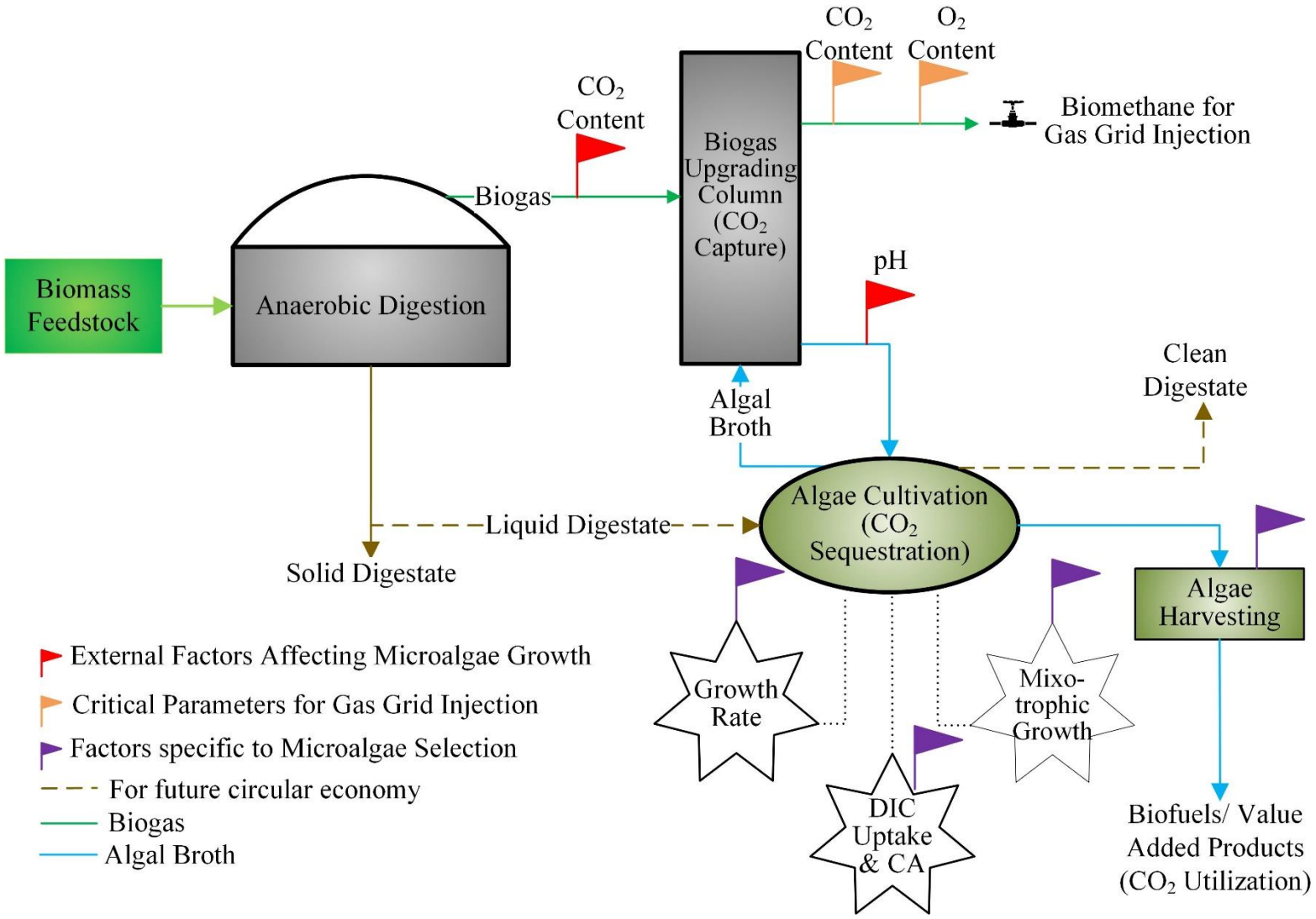
This paper aims to fill a significant knowledge gap within the photosynthetic biogas upgrading technology. In a novel approach, a perspective on overcoming the identified challenges by optimising different process parameters and selecting the optimal microalgae species considering the intrinsic interlinks with system parameters have been provided. In this regard, the technology of biogas upgrading with microalgae cultivation has been systematically reviewed with an emphasis on the following knowledge, currently limited in literature:

- The crucial factors affecting system performance.
- The essential criteria for selecting the microalgae species.
- Identification of a few common microalgae species suitable for biogas upgrading.
- A broad scale-up perspective of such systems.

2 Biological Carbon Uptake and Influence of Microalgae Choice

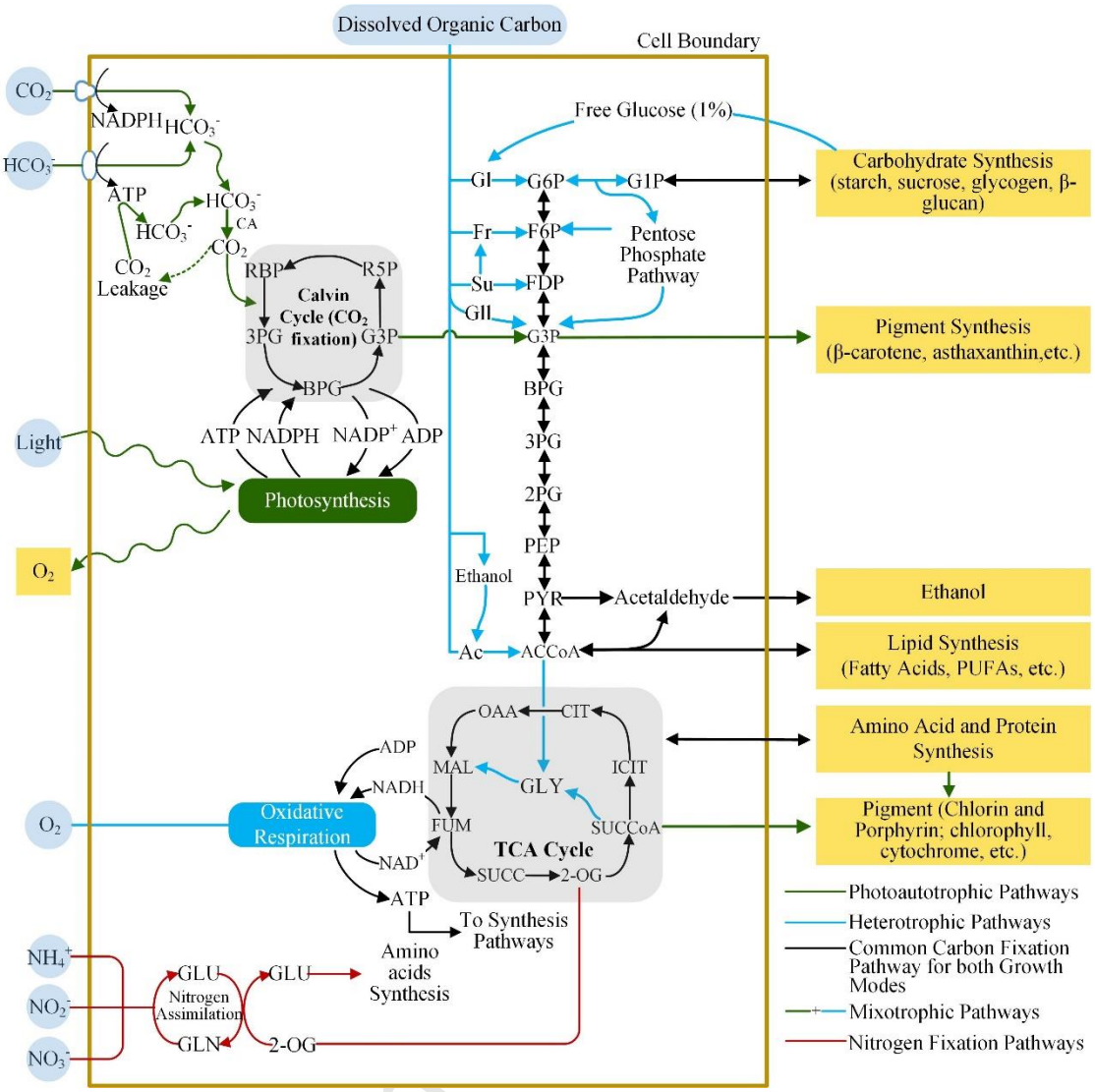
2.1 Carbon Assimilation Pathways in Microalgae

Microalgal species favouring rapid carbon uptake provide effective carbon fixation via either photo-autotrophic (accept inorganic carbon in the presence of light), heterotrophic (accept organic carbon in presence or absence of light) or mixotrophic (accept inorganic and organic carbon) pathways. Three primary photosynthetic carbon uptake strategies by microalgae can be synthesised as follows: *i)* direct uptake of CO_2 through plasmatic membrane; *ii)* assimilation of bicarbonates through active transporters on the plasma membrane; and *iii)* using extracellular carbonic anhydrase or CA (a zinc metalloproteinase enzyme associated with the external cell surface of some microalgae) for enhanced conversion of bicarbonates into intracellular CO_2 (Vuppaladadiyam et al., 2018). The form of dissolved inorganic carbon (DIC) is governed by the pH of the aqueous medium, viz., CO_2 (pH<5); Carbonic Acid (5<pH<7); Bicarbonate ions (7<pH<9); and Carbonate ions (pH>9) (Fan et al., 2008; Klanchui et al., 2017). Therefore, based on the CO_2 uptake strategy, native environment of microalgae (freshwater (pH 7), marine (pH 8 to 8.2) and soda lakes (with a high content of sodium salts and a pH of 9.5 and above)), as well as the presence/ absence of external CA, the respective tolerable and desired pH ranges of individual microalgae species can be identified.



DIC: dissolved inorganic content; CA Carbonic anhydrase

Figure 1 Process Flow Diagram and System Configuration for Biogas Upgrading with Microalgae.



Compound abbreviations are summarized as follows: ***2-OG****: 2-oxoglutarate;* ***2PG****: 2-phosphoglycerate;* ***3PG****: 3-phosphoglycerate;* ***R5P****: ribulose-5 phosphate;* ***ACCoA****: acetyl-Coenzyme A;* ***ADP****: adenosine-diphosphate;,* ***ATP****: adenosine-triphosphate;* ***BPG****: 1,3-biphosphoglycerate;* ***CIT****: citrate;* ***F6P****: fructose-6 phosphate;* ***FDP****: Fructose 1,6-biphosphate;* ***FUM****: fumarate;* ***G1P****: glucose-1 phosphate;* ***G3P****: glyceraldehyde-3 phosphate:* ***G6P****: glucose-6 phosphate;* ***GLN****: glutamine;* ***GLU****: glutamate;* ***ICIT****: isocitrate;* ***MAL****: malate;* ***NAD$^+$****: nicotinamide adenine dinucleotide (oxidized);* ***NADH****: nicotinamide adenine dinucleotide (reduced);* ***NADP$^+$****: nicotinamide adenine dinucleotide phosphate (oxidized);* ***NADPH****: nicotinamide adenine dinucleotide phosphate (reduced);* ***OAA****: oxaloacetate;* ***OXA****: oxalosuccinate;* ***PEP****: phosphoenolpyruvate;* ***PYR****: pyruvate;,* ***RBP:*** *ribulose-1,5 biphosphate;* ***SUCC****: succinate;* ***SUCCCoA****: succinyl-Coenzyme;* ***Gl****: Glucose;* ***Fr****: Fructose;* ***Su****: Sucrose;* ***Gll****: Glycerol;* ***Ac****: Acetate*

Figure 2 Simplistic Schematic representation for inorganic and organic carbon transport for CO_2 accumulation and partitioning pathways in a microalgal cell along with nitrogen fixation pathways (Perez-Garcia et al., 2011; Zhou et al., 2017)

In a typical photo-autotrophic mechanism, for species favouring direct CO_2 uptake, carbon fixation occurs via a three-step regenerative cycle, (the Calvin-Benson Cycle) using Adenosine Triphosphate (ATP) (Figure 2) (Calvin, 1989; Venkata Mohan et al., 2015). For such species, like *Chlorella vulgaris*, a highly alkaline environment would require bicarbonate uptake using ATP. This in turn would lower its availability for carbon assimilation, and hence decrease both the carbon uptake capacity and growth rate (Y. Huang et al., 2017). Extreme alkaliphilic microalgae, on the other hand are well adapted to grow at a

pH >10 with HCO_3^- as the primary inorganic carbon source. Converting bicarbonate to CO_2 by carbon concentrating mechanisms (CCMs) within the cell (Vadlamani et al., 2017), these species can subsequently fix carbon via the Calvin-Benson cycle. High alkalinity also provides an increased carbon supply, through the rapid scavenging of CO_2 from the atmosphere enabling high growth and carbon fixation rates for most naturally occurring alkaliphilic microalgae (Canon-Rubio et al., 2016; Vadlamani et al., 2017).

Alternate to photosynthesis, some microalgae can assimilate organic carbon, viz., glucose, acetate, etc. both in the presence and in absence of sunlight via the heterotrophic mechanism. However, the uptake of only organic carbon along with the release of CO_2 during dissimilation of organic carbon (Smetana et al., 2017) would limit the application of heterotrophic growth when aiming for CO_2 removal. Mixotrophic organisms can alternate between photo-autotrophic and heterotrophic pathways (Figure 2) (Venkata Mohan et al., 2015; Vuppaladadiyam et al., 2018). This not only allows for greater flexibility of carbon assimilation but potentially results in greater carbon uptake and microalgae yield, along with lower photo-inhibition and photo-limitation (Venkata Mohan et al., 2015; Wang et al., 2014). However, only the genera of *Anabaena*, *Spirulina* and *Synechococcus* (cyanobacteria) along with specific species of other genera have been reported to show mixotrophic growth, as listed in Table 1.

2.1.1 Microalgae Selection Criteria 1: Mixotrophic Growth

Genera/species able to grow in mixotrophic condition can provide a significant advantage over other species, especially when wastewater or digestate treatment is combined with biogas upgrading, facilitating the development of circular economy systems. This can be argued from a range of perspectives including; high microalgae growth rate, economic viability of microalgae biofuel, ability to work well with wastewater or liquid anaerobic digestates (in circular economy system), and the ability to maintain productivity and cell density in the algal culture even during the dark phase. Although CO_2 release during heterotrophic growth would seem non-ideal while removing CO_2 from biogas, operating in a highly alkaline solution would provide considerable buffer capacity by dissolving CO_2 to counteract this effect. This is discussed in detail in the following sections. Indeed, if no waste water or digestate treatment is intended, adherence to the criteria would not be essential for microalgae selection.

2.2 Carbon Partitioning

Based on the carbon assimilation pathway and favourable growth conditions, most microalgae exhibit default distribution mechanism of the photosynthetic and metabolic products such as starch, lipids, proteins, and pigments. This results in distinct and predictive cellular composition, as shown in Figure 2 (Perez-Garcia and Bashan, 2015; Sialve et al., 2009; Xia et al., 2015). However, under variable environments, or so-called stressed conditions, individual species show either dramatically different behaviour (acclimation response) or continue to maintain balanced cell composition (homeostatic response) (Montechiaro et al., 2006; Vuppaladadiyam et al., 2018). During biogas upgrading the effect of specific stress-conditions on the microalgae species including exposure to a high CO_2 and/or HCO_3^- concentration need to be studied in detail after a suitable strain selection.

Table 1 CO_2 Metabolism pathways for microalgae species/genera

Autotrophic Microalgae Genera	Heterotrophic Microalgae Genera* (Behrens, 2005; Geider and Osborne, 1989)	Mixotrophic Microalgae Genera/ Species# (Abu Hajar et al., 2017; Cecchin et al., 2018; Kadkhodaei et al., 2015; Kang et al., 2004)
Almost all species can grow autotrophically.	*Amphora* *Anabaena* *Ankistrodesmus* *Chlamydomonas* *Chlorella* *Chlorococcum* *Crypthecodinium* *Cyclotella* *Dunaliella* *Euglena* *Nannochloropsis* *Nitzschia* *Ochromonas* *Spirulina* *Synechococcus* *Tetraselmis*	*Anabaena* *Brachiomonas submarina* *Chlorella* spp. *Chlorococcum* sp. *Cyclotella cryptica* *Dunaliella salina* *Euglena gracilis* *Haematococcus pluvialis* *Nannochloropsis* spp. *Neochloris oleubundans* *Navicula saprophila* *Nitzschia* sp. *Ochromonas minima* *Phaeodactylum tricornutum* *Rhodomonas reticulate* *Scenedesmus obliquus* *Spirulina* *Synechococcus*

**Genera refers to the family of organisms below which specific species or sub-species are grouped, usually comprising at least 2 species*

 # Species is one particular organism within the family or organisms or genera

3 Biogas Upgrading and Influence on Microalgae Choice

Decrease in contact time between the algal solution and the unprocessed biogas is essential to lower methane loss and oxygen contamination of biomethane during biogas upgrading. Direct bubbling of the unprocessed biogas into algal cultures requires significant contact time with the algae solution to ensure sufficient removal of CO_2. Consequently, the oxygen concentration in the biomethane ensuing from such systems was between 10-24% (Converti et al., 2009; Prandini et al., 2016). Alternatively, in a bubble column-photobioreactor configuration (indirect biogas upgrading), as shown in Figure 1, the biogas upgrading and microalgae growth can be optimised as two separate processes. This can significantly decrease the contact time between the recirculated algal solution and the biogas. Indirect biogas upgrading can result in a CO_2 and O_2 content in the upgraded biomethane of 6% and 5% respectively as compared to 13% and 32% respectively for direct bubbling of biogas in algae cultivation under similar conditions (Meier et al., 2015). Henceforth, only indirect photosynthetic biogas upgrading process was considered in this paper.

3.1 CA Promoted CO_2 Removal in a CA Alkaline Environment

The use of carbonate solutions at pH>9 in a bubble column allows CO_2 to be transferred into the aqueous medium in the form of bicarbonate as shown in Eq. 1. Notwithstanding the benefit of the higher dissolution of CO_2 in an alkaline solution, the reaction continues to be relatively slow, with the reaction rate constant (k_{CA}) varying between $2x10^3$ and $3x10^5$ m^3/kmol-s at temperatures between 293-373 K (Borhani et al., 2015; Ye and Lu, 2014). In addition, there are other disadvantages to using a highly alkaline solution for CO_2 absorption, especially when applied to a photosynthetic biogas upgrading

system. The overall mass transfer coefficient for oxygen and nitrogen increases with pH (Toledo-Cervantes et al., 2016), leading to increased O_2 content in the resulting biomethane. Furthermore, a high pH also results in phosphorus deposition as phosphates, causing nutrient deficiency in microalgae cultivation (Delgadillo-mirquez et al., 2016; Larsdotter et al., 2010). Low nutrients leading to lower growth rates of microalgae would then imply lower carbon fixation, diminishing the sustainability of a photosynthetic biogas upgrading system.

Enhancing the rate of absorption of CO_2 in an alkaline medium by the application of promoters (Dutcher et al., 2015; Imle et al., 2013) could provide distinct benefits. Not only would this lower the contact time between the biogas and algal solution to reduce the O_2 stripping, but also potentially allow lower pH levels to be employed with similar benefits. Carbonic anhydrase (CA) has recently gained much research interest as an organic promoter due to its *i)* ability to catalyse the reversible CO_2 hydration reaction (Eq. 1) in an environmentally friendly way; *ii)* limited influence on the CO_2 vapour-liquid equilibrium and heat of absorption; *iii)* compatibility with conventional CO_2 absorbing substrates including carbonates, amines, as well as with membrane separation processes (Hu et al., 2016).

$$CO_2 + H_2O + CO_3^{2-} \rightarrow 2HCO_3^- \quad \Delta G \simeq -50\text{kJ/mol}(300K) \qquad (1)$$

Of the different isoforms of the CA enzyme, viz., $\alpha, \beta, \gamma, \delta$ and ζ (Ores et al., 2016), the most widely reported α -CA has a typical k_{CA} value between $1.1x10^8$ and $3.5x10^8$ m^3/kmol-s (Luca et al., 2013; Ye and Lu, 2014). CO_2 absorption rates would therefore be significantly increased with the addition of CA. An alkaline algal solution containing microalgae species with external CA actvity in lieu of a stand-alone alkaline carbonate solution can thus be hypothesized to enhance CO_2 absorption rates. Indeed, absence of external CA would require cell rupturing to release internal CA, decreasing the effectiveness of the overall process.

Unfortunately, most of the enzymes are reported to suffer drastic degradation at high temperatures and sustained operation at high pH (Hu et al., 2016; Thee et al., 2015). Moreover, limited literature is available on β and γ - CA, mostly present in microalgae (Klanchui et al., 2017). Most of the experiments have been performed considering pure CA enzymes, with a considerable lack of studies under actual conditions (Ye and Lu, 2014). Therefore, significant research is needed to develop and further the understanding of the catalytic influence and performance of microalgal CA on CO_2 absorption in alkaline carbonate solutions.

3.2 Carbonate/Bicarbonate Cycle for CO_2 capture

CO_2 absorption in the alkaline (carbonate rich) solution, followed by the transfer of the bicarbonate rich solution for microalgae cultivation is graphically represented in Figure 3. For microalgae uptaking bicarbonate (HCO_3^-) and showing external CA activity, the bicarbonate is incorporated within the cell as CO_2 through dehydration, thus releasing hydroxide represented in Eq. 2. The released hydroxide, subsequently increases the pH, allowing carbonate (CO_3^{2-}) regeneration as per Eq. 3. The formation of bicarbonate by CO_2 absorption and subsequent regeneration of carbonate from algal activity thus leads to both a natural maintenance of the carbonate/bicarbonate cycle and pH regulation. This saves the need for costly equipment and large energy expense for carbonate regeneration.

$$HCO_3^- \xrightarrow{CA} CO_2 + OH^- \qquad (2)$$

$$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O \qquad (3)$$

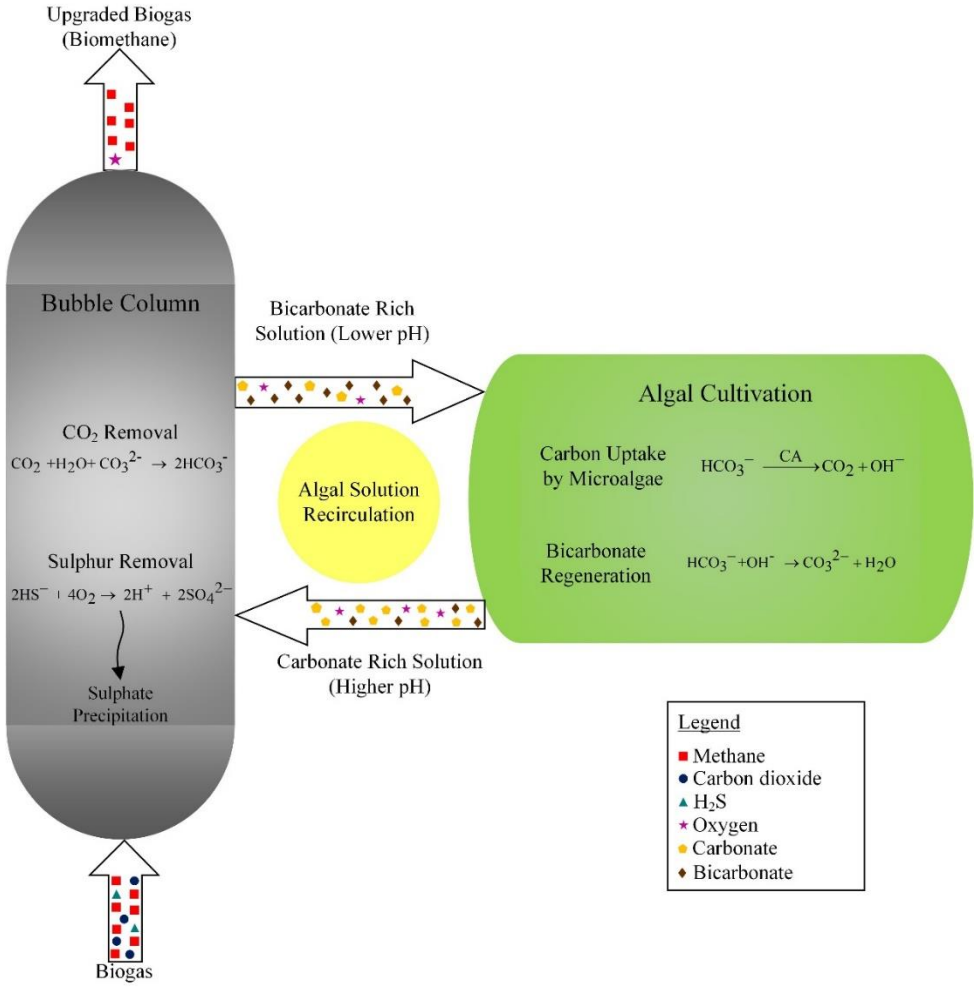


Figure 3 Biogas Upgrading by microalgae in an alkaline (Carbonate) algal solution via Carbonate/Bicarbonate cycle (The number of markings of each chemical species are indicative only to their relative quantity and not in absolute terms)

Dosing with alkanolamines can further enhance the effectiveness of CO_2 removal through additional bicarbonate formation and maintenance of the carbonate/bicarbonate cycle (Behr et al., 2011). Nevertheless, the addition of too high concentrations of alkanolamines can inhibit the growth of microalgae. Therefore optimization between CO_2 capture efficiency and microalgae growth is necessary to employ alkanolamine dosing effectively in photosynthetic biogas upgrading.

3.3 H_2S Removal and Impact on Oxygen in Biomethane

Another important contaminant in biogas, H_2S, being acidic in nature, is removed similar to CO_2 by the carbonate rich solution. At the working pH between 9 and 11, aided by a high dissolved oxygen concentration due to photosynthetic activity, a fast sulphate precipitation occurs even in the absence of sulphur oxidising bacteria (Meier et al., 2018; Esther Posadas et al., 2015) as per the following Eq. 4. This additionally prevents the inhibition of algal growth from excess H_2S (Meier et al., 2018; Prandini et al., 2016).

$$2HS^- + 4O_2 \rightarrow 2H^+ + 2SO_4^{2-} \quad (4)$$

Depending on the volume of H_2S in the unprocessed biogas, a fraction of the oxygen would thus be also removed by sulphate precipitation. Indeed, as reported by Bahr et al., (2014), presence of 1000 ppm of H_2S in simulated biogas yielded biomethane with 0.5 ± 0.3% O_2, in comparison to 0.7 ± 0.3% O_2 with 500 ppm H_2S. Therefore, the fraction of H_2S in the unprocessed biogas plays a crucial role in determining the quality of biogas in terms of the oxygen content.

3.4 Impacts of Other Trace Gases on Microalgae Growth

No inhibitory impact of methane on microalgae growth has been reported in literature (Kao et al., 2012; Toledo-Cervantes et al., 2017b). Nitrogen and hydrogen have limited solubility in water (Schmidt, 1979), and therefore do not impose a significant stress factor on the overall microalgae growth conditions. Other trace gases (such as siloxanes, ammonia, and chlorine) in biogas are of significantly low quantity to be assumed to have minimal influence on the growth of microalgae. Indeed, to the best of the authors' knowledge, no study has reported the influence of the trace gases on this system of biogas upgrading and microalgae growth.

3.5 Microalgae Selection to Enhance Biogas Upgrading

3.5.1 Microalgae Selection Criteria 2: High pH Tolerance

To withstand a carbonate solution with pH above 9 alkaliphilic microalgae strains uptaking bicarbonates as the primary DIC would be ideal. Alkalihalophilic cyanobacteria, such as *Spriulina* and *Euhalothece* (strongly alkaliphilic), *Synechococcus* and *Anabaena*, (moderately alkaliphilic) are preferable (Kishi and Toda, 2018; Klanchui et al., 2017). Within the chlorophyte genera species several strains have recently been identified, which grow well even at pH 10. Most of these strains are native to soda lakes such as *Chlorella sorokiniana* SLA-04 (Vadlamani et al., 2017), a mutant strain of *Chlorella sp.* AT1 (Kuo et al., 2017) and Dunaliella salina NIES-2257 (Kishi and Toda, 2018). Alternatively, some freshwater species like *Scenedesmus obliquus* can also tolerate a high pH of 10.6 (Goldman et al., 1982), allowing it to be the dominant species in a mixed culture system for biogas upgrading at a pH of 9.37 (Granada-Moreno et al., 2017). However, interaction of each species with other cultivation conditions besides pH must be studied in detail to establish the dominant species in a shifting microalgae community (Granada-Moreno et al., 2017; Marín et al., 2018).

3.5.2 Microalgae Selection Criteria 3: External Carbonic Anhydrase Activity

The hypothesised catalytic effect of microalgae species exhibiting external CA activity towards CO_2 absorption in a carbonate solution, could significantly improve the overall CO_2 capture efficiency. Thus, either or both the operational pH and the contact time between the biogas and the alkaline solution in the bubble column can be reduced to decrease the oxygen content in the resulting biomethane, while ensuring sufficient CO_2 removal. All cyanobacterium species possess external CA activity, though of different variant of CA strains. Of the chlorophyte genera, *Chlamydomonas reinhardtii*, *Chlorella vulgaris*, *Chlorella sorokiniana* and *Scenedesmus obliquus* among others, display external CA activity.

4 Bio-Fixation of Absorbed CO_2 by Microalgae Cultivation

4.1 Impact of CO_2 Concentration in Biogas on Microalgae Growth

To utilise the bio-catalytic effect of microalgae with external CA activity, the species would come in direct contact with biogas near the inlet of the upgrading column as shown in Figure 3. Due to the limited contact time, the ability of the species to survive under high CO_2 concentration forms the limiting factor, as opposed to the relative drop in growth in a high CO_2 environment, seen in Table 2. *Spirulina*, *Anabaena* and *Synechococcus* can tolerate a 100% CO_2 environment with or without pH control (Kumari et al., 2014; Thomas et al., 2005). Of the chlorophyte species, *Scenedesmus obliquus* is able to tolerate up to 80% CO_2, while *Chlorella vulgaris* is completely inhibited at a CO_2 concertation beyond 60% (Hanagata et al., 1992). *Chlorella* genera is one of the most versatile in tolerating a high range of CO_2 concentrations with a typical limit of around 40% CO_2 (Maeda et al., 1995; Sung et al., 1998). CO_2 acclimatization can further improve the CO_2 tolerance of microalgae (Miyachi et al., 2003; Yun et al., 1997).

Table 2 High-CO_2-tolerant species of microalgae reported in the literature

Species	Maximum CO_2 Tolerance	Culture Concentration at Maximum CO_2	Optimum CO_2 Level	Culture Concentration at Optimum CO_2	Reference
Anabaena sp.	100%	NR*	12%	3 g/L after 8 days	(Thomas et al., 2005; Yoon et al., 2008)
Chlorella sp (ZY-1)	70%	0.776 g/L after 6 days	10%	5.772 g/L after 6 days	(Yue and Chen, 2005)
Chlorella vulgaris	60%	0.05 g/L after 8 days	5-20%	0.8 g/L after 8 days	(Hanagata et al., 1992; Lam and Lee, 2013)
Chlorococcum littorale	50%	0.5 g/L after 12 days	5%	~ 84 g/L after 25 days	(Hu et al., 1998)(Ota et al., 2009)
Euglena graciliis	40%	~ $5x10^6$ cells/ml after 7 days	5%	~ $15x10^6$ cells/ml after 7 days	(Nakano et al., 1996)
Scenedesmus obliquus	80%	~0.04 g/L after 8 days	12-15%	0.85 g/L after 14 days; 2 g/L after 20 days	(de Morais and Vieira, 2007; Hanagata et al., 1992; Patil and Kaliwal, 2017)
Spirulina platensis	100% (with 8.4g/L NaOH)	1.83 g/L after 4 days	12%	~ 4g/L after 20 days	(de Morais and Vieira, 2007; Kumari et al., 2014)
Synechococcus sp	100%	NR	5%	NR	(Miyari, 1995; Thomas et al., 2005)

**NR: Not reported*

4.1.1 Microalgae Selection Criteria 4: High CO_2 Tolerance

The CO_2 concentration in biogas ranges from about 20% to 55%. As such, a high CO_2 tolerating microalgae strain is desirable. Although most CO_2 tolerant species continue to maintain respectable growth under high CO_2 concentration, external CA activity is inhibited. This leads to a preference for direct uptake of CO_2. Even though this might increase the overall carbon uptake efficiency for strains favouring CO_2, it would be undesirable according to *Criteria 3* (external CA activity).

4.2 Impact of Bicarbonate Concentration on Microalgae Growth

A pH of 10 could lead to a high bicarbonate ion concentration of up to 1.0 M (Xia et al., 2015), suitable for alkalihalophilic microalgae. de Farias Silva et al., (2016) reported a high productivity of the moderately alkaliphilic cyanobacterium, *Synechococcus* sp. (PCC 7002) of 1.12 g/L/day in a batch process with a bicarbonate concentration of 88 g/L (1.05M), and a pH of 8.5 controlled by HCl addition. Sodium bicarbonate in the range 2-4 g/L (0.02-0.05 M) was found to be optimal for the growth of *Spirulina platensis*, even though, no significant differences were noticed at a concentration of 13.5 g/L (El-kassas et al., 2015). In another study, Kishi and Toda,(2018) reported optimal bicarbonate concentration of 0.23M for *Spirulina platensis*, a result similar to that reported by Zhu et al., (2018a). *Dunaliella salina* on the other hand exhibited optimal growth at a bicarbonate concentration of 0.5M, while *Euhalothece* sp. preferred 1.1M $NaHCO_3$. For the alkali tolerant mutant strain, *Chlorella sp.* STI, a high specific biomass productivity of 0.726 g/L/day was recorded at pH 10. For neutrophilic microalgae (species favouring pH between 7.0-8.0), the presence of bicarbonate has been shown to significantly improve the growth rate, and affect the chemical composition, however, at a controlled pH (Mokashi et al., 2016; White et al., 2013). Therefore, impact of growth and carbon partitioning mechanisms of each species under high bicarbonate and pH conditions would provide essential knowledge on the effective bio-fixation of the captured CO_2 from biogas upgrading.

4.3 Carbon Balance during Bio-fixation of CO_2

$$M_{C_{BG,in}} = M_{C_{BG,out}} + M_{C_{Biom}} + M_{C_{Resp}} + M_{C_{effl}} + M_{C_{stripping}} + M_{C_{L,acc}} \quad (5)$$

Eq. 5 is a mass balance of carbon across the closed system starting from biogas upgrading without digestate treatment). The primary source of inorganic carbon entering the system is the CO2 in biogas ($M_{C_{BG,in}}$). The right side of the equation includes inorganic carbon in treated biogas ($M_{C_{BG,out}}$), carbon leaving the system through the liquid effluent ($M_{C_{effl}}$), and carbon lost via stripping or desorption ($M_{C_{stripping}}$). Microalgae sequester a significant portion of the inorganic carbon during light phase through photosynthesis ($M_{C_{Biom}}$), while a fraction is lost through respiration during the dark phase ($M_{C_{Resp}}$). In addition, carbon can also be accumulated in the liquid phase as DIC, included as $M_{C_{L,acc}}$. Accordingly, an elemental inorganic carbon balance can be developed as shown in Figure 4.

Each of the components can be further represented as a percentage of the total source of CO_2, a review of the values of which is summarized in the Table 3. On reviewing Table 3, for open pond cultivation, desorption or stripping can be concluded to be a prominent contributor to carbon loss. Both the dissolved carbon content and the pH of the medium are important factors in this context. Therefore, except for CO_2 concentrations below 2-5% in the feed gas, a high CO_2 uptake by microalgae is seldom reached. However, the use of closed photobioreactors (PBRs) decreases the CO_2 stripping rate considerably. Unlike other researchers, Marín et al., (2018) reported a complete CO_2 fixation in an open pond environment at an average temperature of 23-24 $^{\circ}$C and a high pH of 9.3-9.7 using a mixed cyanobacteria-chlorophyta culture. However, the results from a similar set-up continued to show low CO_2 fixation rates (Franco-Morgado et al., 2017).

A high pH can significantly lower the carbon loss by desorption due to the presence of bicarbonates and also inhibit the bacterial and parasitic growth, improving carbon uptake of the microalgae culture (Chi et al., 2011; Xia et al., 2015). However, for open systems with pH higher than the saturation pH corresponding to the dissolved bicarbonate, scavenging of atmospheric CO_2 occurs. Especially at lower bicarbonate concentrations, this leads to additional supply of inorganic carbon to boost the carbon uptake, although the overall biomass productivity would be lower. This phenomenon was reported by Zhu et al., (2018b), where, increasing the bicarbonate concentration from 0.1M to 0.7M caused the carbon uptake efficiency to drop from almost 90% to 40% for the microalgae *Neochloris oleoabundans*. Nonetheless, in absence of desorption, DIC loss through effluent can also be significant. Up to 60-70% of the DIC was found to be lost through the effluent by Meier et al., (2017).

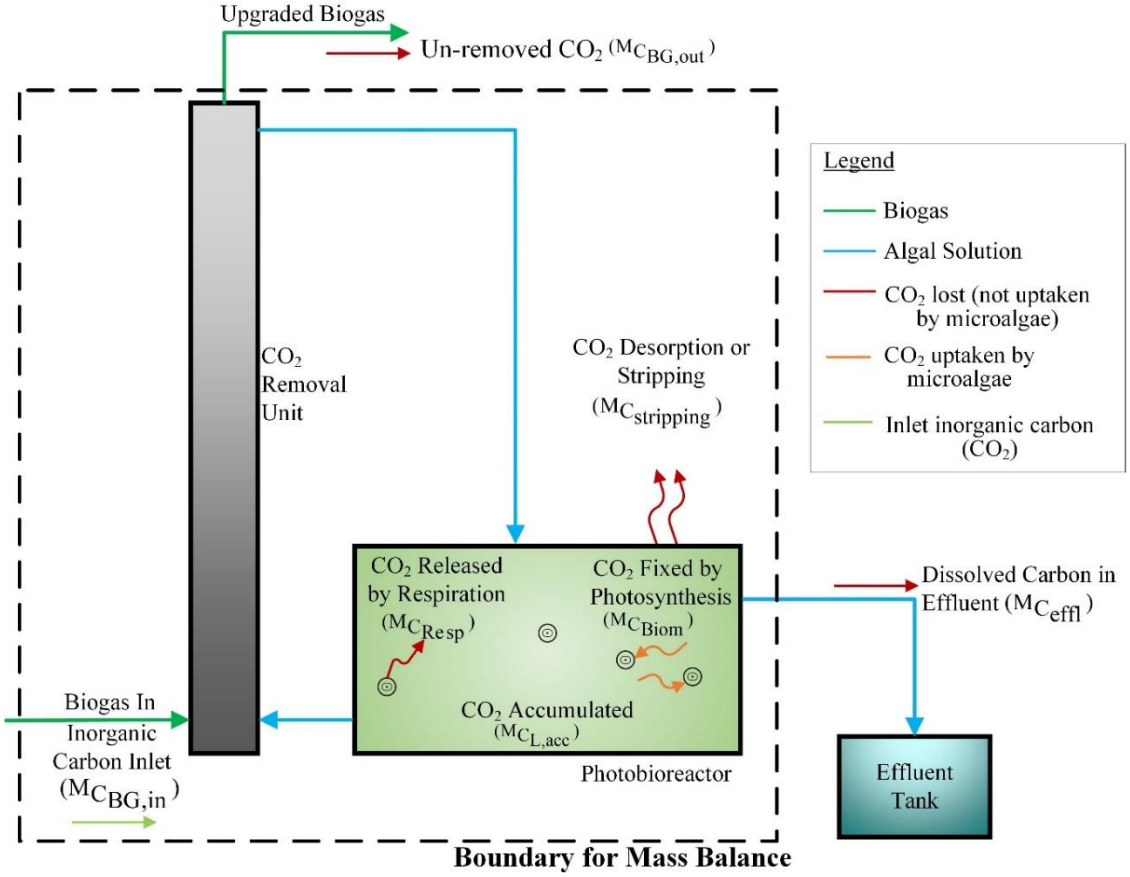


Figure 4 Schematic Representation of Overall Biogas Upgrading process with Microalgae Indicating flow of Inorganic Carbon for Mass Balance within the System

Multiple pathways have been proposed to increase the carbon uptake efficiency of microalgae. By adding 5 mM Triethylamine (TEA), the CO_2 fixation rate improved by 39.3% (Kim et al., 2013). However, the growth of *Scenedesmus* sp. was hindered at higher TEA concentrations. Cheng et al., (2013) proposed sequential bioreactors in addition to adjusting illumination intensity and nutrient content. The use of such sequence of reactors increased the CO_2 residence time, also referred to as the empty bed residence time, within the bioreactor. Consequently, a CO_2 fixation efficiency of up to 70.5% was attained while supplying the algal solution with air containing 15% CO_2. Through intermittent lighting at a 10s/10s cycle, a 95% carbon uptake efficiency was obtained as opposed to 56% under continuously illuminated condition (Li et al., 2013). Nevertheless, such measures are often discrete, requiring further research for industrial applications.

Table 3 Summary of CO_2 Bio-fixation and Losses Reported in Recent Experiments

Microalgae Species	CO_2 % in Feed Gas, $M_{C_{BG,in}}$	Type of Reactor and pH	Light/ dark period (h)	% C Uptake by Microalgae, $M_{C_{Biom}}$	% C in Biomethane, $M_{C_{BG,out}}$	% Inorganic C lost				Reference
						In effluent $M_{C_{effl}}$	Desorption $M_{C_{Stripping}}$	Respiration $M_{C_{resp}}$	Accumulated $M_{C_{L,acc}}$	
Phaeodactylum tricornutum	100 to 40	Airlift Photobioreactor and pH of 7.6-8.2	10:14	60	NA	NR				(Sobczuk et al., 2000)
Synechococcus sp.	5	NR	NR	<5%	NA	NR			~4%	(Fukuzawa et al., 1992)
Spirulina Platensis	0.04 to 18	Erlenmeyer Flask with pH of 8.26 ± 0.45 to 9.88 ± 0.35	12:12	74 for 0.04% CO_2, 5.52 for 6% CO_2, 1.13 for 18% CO_2	NA	NR				(de Morais and Vieira, 2007)
		Vertical Tubular Photobioreactor, 2L at pH of 6.83 ± 0.53 to 9.04 ± 0.72		96.8 for 0.04% CO_2, 9.30 for 6% CO_2, 2.48 for 18% CO_2		NR				
		Vertical Tubular Photobioreactor, 4L and pH of 6.83 ± 0.53 to 9.04 ± 0.72		99.9 for 0.04% CO_2, 9.15 for 6% CO_2, 3.48 to 18% CO_2		NR				
Scenedesmus accuminatus	5%	1L Erlenmeyer Flasks with pH of 7.4-7.6	24:0	5.71% without TEA	NA	NR				(Kim et al., 2013)
				7.18% at 5mM TEA addition		NR				
	4%			10.57% at 5mM TEA addition		NR				
Scenedesmus obliquus	30-50%	5.3L Translucent cylindrical plastic tank, at pH of 6.5-8	16:8 average	7.1%	NA	NR				(Thiansathit et al., 2015)

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Microalgae Species	CO_2 % in Feed Gas, $M_{C_{BG,in}}$	Type of Reactor and pH	Light/ dark period (h)	% C Uptake by Microalgae, $M_{C_{Biom}}$	% C in Biomethane, $M_{C_{BG,out}}$	% Inorganic C lost				Reference
						In effluent $M_{C_{effl}}$	Desorption $M_{C_{Stripping}}$	Respiration $M_{C_{resp}}$	Accumulated $M_{C_{L,acc}}$	
Nannochloropsis Oculata	15%	Open Cylindrical Glass Tube Photobioreactor	14:10	10.23% at 12 hours CO_2 supply 2.57% at 24 hours CO_2 supply	NA	NR				(Basu et al., 2015)
	12±2	High Rate Algal Pond with pH between 6 and 7.8	12:00	71.4 to 35.6%	NA	NR				(Cheng et al., 2018)
	Air	Bubble Column Photobioreactor at pH of 7-8	12:12	30-55%	NA	NR				(Valdés et al., 2012)
Neochloris oleoabundans	HCO_3^- Medium, 0.1-0.7M	Erlenmeyer flask and variable pH	24:0	~88% at 0.1 M of HCO_3 (pH 9.5); ~40% at 0.1 M (pH 10.1);	NA	NR				(Zhu et al., 2018b)
Chlorella vulgaris	15%	Closed raceway pond with paddle wheel and pH between 6.18 ± 0.14 and 7.22 ± 0.05	24:0	56% with Continuous gas sparging	NA	NR				(Li et al., 2013)
				95% with intermittent gas sparging of 10s at an interval of 10s	NA	NR				

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Microalgae Species	CO_2 % in Feed Gas, $M_{C_{BG,in}}$	Type of Reactor and pH	Light/ dark period (h)	% C Uptake by Microalgae, $M_{C_{Biom}}$	% C in Biomethane, $M_{C_{BG,out}}$	% Inorganic C lost				Reference
						In effluent $M_{C_{effl}}$	Desorption $M_{C_{Stripping}}$	Respiration $M_{C_{resp}}$	Accumulated $M_{C_{L,acc}}$	
Chlorella sp.	4%	Airlift Photobioreactor at pH of 7.0	12:12	13.8- 4% as per gas inlet velocity	NA	NR				(Hulatt and Thomas, 2011)
	15%	Perforated inverted arc trough (PIAT) inserted into flat plate Photobioreactor	NR	Fixation rate of 36.6 $mgCO_2\ L^{-1}\ h^{-1}$, an increase of 26.2% over conventional flat plate Photobioreactor	NA	NA				(Xia et al., 2018)
	2%	Cylindrical glass Photobioreactor at pH of 6.4		58%	NA	NR				(Chiu et al., 2008)
	15%			16%	NA	NR				
	5%	Bubble Column Photobioreactor and pH of 5.6	24:0	28 ± 1.2%	NA	NR				(Vo et al., 2018)
Chlorella PY-ZU1	15%	Sequential Bubble Column Photobioreactor and pH between 5.5 and 7	24:0	50.31% at 10 min empty bed residence time	NA	NR				(J. Cheng et al., 2013)
				70.48% at 140 min empty bed residence time	NA	NR				
Chlorella sorokiniana	32.0 ± 1.9%	Photobioreactor connected to bubble	Light phase	19%	11%	13%	57%	NA	NA	(Meier et al., 2017)

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Microalgae Species	CO_2 % in Feed Gas, $M_{C_{BG,in}}$	Type of Reactor and pH	Light/ dark period (h)	% C Uptake by Microalgae, $M_{C_{Biom}}$	% C in Biomethane, $M_{C_{BG,out}}$	% Inorganic C lost				Reference
						In effluent $M_{C_{effl}}$	Desorption $M_{C_{Stripping}}$	Respiration $M_{C_{resp}}$	Accumulated $M_{C_{L,acc}}$	
		column at average pH between 7.3-7.4	Dark Phase	0%	7%	-	60%	3%	30%	
Picochlorum sp. and *Halospirulina* sp. mixed culture	29.50%	High Rate Algal Pond connected to absorption column (AC) at pH between 9.3-9.7	12:12	7%	6%	71%	5%	NR	11%	(Franco-Morgado et al., 2017)
			24:0	27%	11%	52%	4%	NA	6%	
Phormidium sp. (71%), *Oocystis* (20%) and *Microspora* sp. (9%) Mixed Culture	30%	Indoor HRAP connected to absorption column (AC) at pH between 8.1 ± 0.1	24:0	9 ± 2%	40%	1%	49 ± 5%	NR	NR	(Alcántara et al., 2015)
Nannochloropsis gaditana.	28 ± 2%	Indoor HRAP connected to absorption column (AC) and pH between 7.5 and 8	24:0	81%	6%	14%	NA			(Meier et al., 2015)
Mixed Cyanobacteira-Chlorophyta culture including *Leptolyngbya lagerheimii* (54%) and *Chlorella vulgaris* (28%)	29.5%	Outdoor HRAP connected to absorption column and pH between 9.4-.6	14:10	47 ± 2% at average temperature of 15.3 ± 7.3ºC	NR	NR	53%	NR	NR	(Marín et al., 2018)
			12:12	100% at average temperature of 23.4 ± 3.8ºC	NA					

NA: Not Applicable; NR: Not Reported

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5 System Design for Biogas Upgrading by Microalgae

The complete photosynthetic biogas upgrading system (as illustrated in Figure 1 with detail in Figure 3) can be divided into four fundamental components, namely (1) the *Absorption Column* for biogas upgrading, (2) the *Bioreactor* for microalgae cultivation followed by (3) the *Microalgae Harvesting System* and (4) *Accessories dedicated to the above three systems including pumps and automation systems*

5.1 Absorption Column

5.1.1 Gas-Sparged Bubble Column

Conventional removal of CO_2 in alkaline or amine solution commonly employs packed columns in a counter-current mode. However, while utilizing algal solutions directly for biogas upgrading, the packed bed column may suffer from clogging (Toledo-Cervantes et al., 2016), resulting in high operation and maintenance cost. A similar performance is achieved by the gas-sparged multi-phase bubble column without any packing (Bahr et al., 2014). Typically, the alkaline algal liquid acts as the dispersed medium, with biogas sparged from the bottom of the column. This results in a high mass transfer rate through efficient mixing removing the requirement for moving parts (Leonard et al., 2015; Toledo-Cervantes et al., 2017b).

The homogeneous flow regime provides preferential operating conditions for CO_2 absorption. More uniform flow and smaller bubbles developed in this regime allows for a larger surface area and an improved performance (L. Cheng et al., 2013; Leonard et al., 2015). For a homogeneous flow regime, assuming similarity with air-water systems, the superficial gas velocity should always be below 4 cm/s at ambient temperature and pressure (Kantarci et al., 2005; Rollbusch et al., 2015). This minimizes the influence of the sparger design, (Götz et al., 2017) and reduces; bubble coalescence, breakage and collision (Pourtousi et al., 2015). The presence of microalgae as the solid phase inside the bubble column improves the CO_2 absorption rates further by increasing the gas hold-up and mass transfer rates (Manjrekar et al., 2017). This is due to the increased specific contact area of bubbles through the modification in surface tension and bubble breakage from collision between the gas and the dispersed phase (Kantarci et al., 2005; Manjrekar et al., 2017).

5.1.2 Comments on Absorber Column Design and Research Gaps

Reported studies for indirect CO_2 removal by microalgae in an external column are summarized in Table 4. As can be seen, most columns have been operated at a superficial gas velocity well below 4 cm/s together with a liquid velocity much below 4 cm/s. As for the flow configuration, despite favouring higher gas hold-up, the counter-current configuration was reported to suffer significant drawbacks. A drop in pH from 10.2 to 9.5 led to lower microalgae growth and associated CO_2 removal. In combination with clogging of gas spargers from sulphur deposition, biomass accumulation was observed at the top of the column. In addition, growth of invasive non-photosynthetic cyanobacteria at the bottom of the column and greater stripping of the dissolved oxygen due to increased gas hold-up has been observed for the counter-current mode operation (Toledo-Cervantes et al., 2017b). Thus, the co-current configuration has generally been preferred.

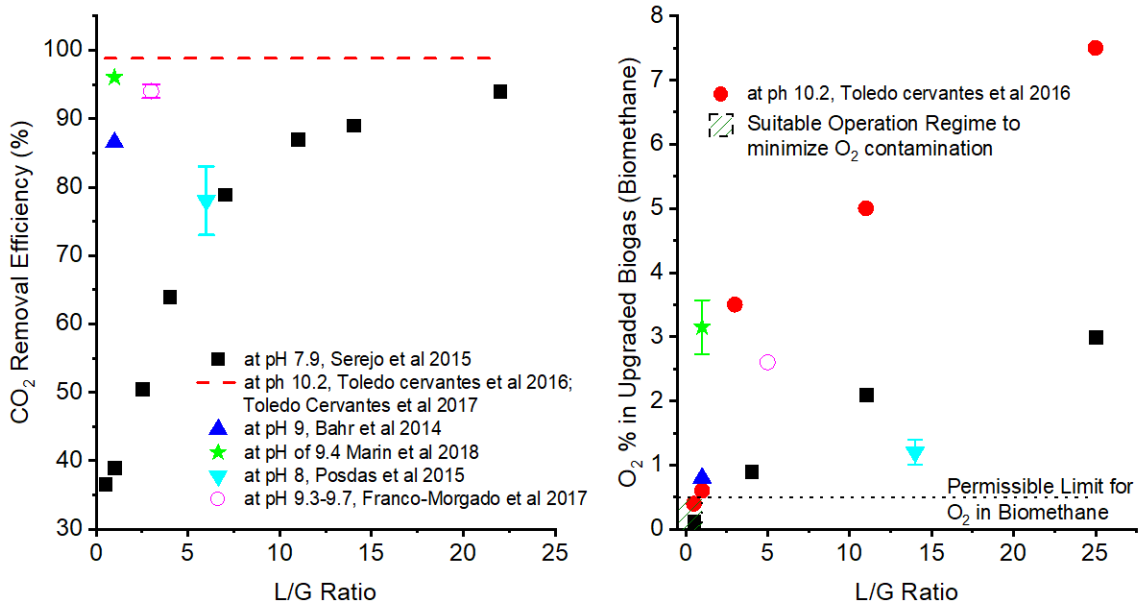


Figure 5 Influence of pH and L/G ratio on the mass transfer performance of the Absorber Column

Significant increase in CO_2 removal alongside ensuring a lower O_2 content in the upgraded biomethane can be achieved by optimising the pH of the recirculating liquid (algal solution) and the liquid to gas flow (L/G) ratio. As can be observed from the results of previous studies, compiled in Figure 5, CO_2 removal is significantly improved above pH 9, irrespective of the L/G ratio. As high as 98% CO_2 removal efficiency was obtained at a constant pH of 10.2. However, this fell to 96% at a pH of 9.5 (Toledo-Cervantes et al., 2017b). Similar CO_2 removal rates of 95-96% were reported between pH 9.3-9.7 (Franco-Morgado et al., 2017; Marín et al., 2018). In contrast, for lower pH ranges, a L/G ratio of greater than 15 was required to ensure a CO_2 removal efficiency of over 90% (Serejo et al., 2015). H_2S removal in most cases has been reported to be almost 100% at a pH over 9 irrespective of the L/G ratio (Franco-Morgado et al., 2017; Posadas et al., 2016; Toledo-Cervantes et al., 2017b).

A higher L/G ratio causes a greater oxygen stripping to the upgraded biomethane, with this effect amplified at higher pH. Therefore, for the same L/G ratio, oxygen content in the biomethane can be observed to be much higher at a pH of 10.2 than at a pH of 7.9 (Figure 5). Toledo-Cervantes et al., (2017b) advised the use of an L/G ratio lower than 1 to ensure oxygen content in biomethane meets grid injection standards at a high pH of 10.2 (Figure 5). However, using the same L/G ratio of 1, Marín et al., (2018) reported an O_2 concentration of 3.15 ± 0.42% in the upgraded biomethane during year-round operations with an open algal pond. Interestingly, unlike the L/G ratio, which was the same for both the studies, a higher liquid flow rate, as well as different microalgae species were used. In a similar study, at a much lower pH (c. 6.5) and an at an L/G ratio of 5, Meier et al., (2017) reported the oxygen content of lower than 1% in the upgraded biogas while the corresponding CO_2 varied between 2 and 4% respectively during light and dark cycles.

Research gaps for absorption column design can be identified as follows:

- **Impact of pH at a constant L/G ratio, but variable liquid and gas flow rates** have not been reported in any literature for the biogas upgrading purposes by algal liquid.

Table 4 Details of Absorption Columns used in Experiments for Biogas Upgrading with Microalgae

Column Type	Column dimensions				Liquid Flow		Gas Flow		L/G	Mode	Sparger		pH	CO_2 in supplied biogas	CO_2 in upgraded biomethane	Reference
	H_c (cm)	D_c (cm)	H_c/D_c	V_c (L)	Flow rate, L (ml/s)	u_L (cm/s)	Flow rate, G (ml/s)	u_G (cm/s)			Type	d_0 (mm)				
Bubble Column	165	4.4	37.5	2.5	0.867	0.057	0.867	0.057	1	C			9.4	29.5%	0.7% to 11.9%	(Marín et al., 2018)
	165	4.4	37.5	2.5	1.734	0.114	0.867	0.057	2	C	MD	0.002	8.8-9.8	29.5%	1.5% to 14.25% from high to low pH	(Posadas et al., 2017)
	165	4.4	37.5	2.5	Varies	Varies	0.667	0.044	0.3-1	C			10.2 ± 0.5	29.5%	0.35%	(Toledo-Cervantes et al., 2017b)
	3000	1.2	2500	NR	0.347	0.307	0.579	0.512	0.6	CC	NR	NR	7.3	32.0 ± 1.9%	2-4% between light and dark cycles respectively	(Meier et al., 2017)
	80	1.9	42.1	NR	1.274	0.449	0.2545	0.089	5	C	PS	NR	9.5	30%	1.5% to 4.5%	(Franco-Morgado et al., 2017)
	NR	1.9	NR	0.35	0.031	0.011	0.181	0.064	8.43	CC	NR	NR	9.37	30%	NR	(Granada-Moreno et al., 2017)
	165	4.4	37.5	2.5	Varies	Varies	Varies	Varies	0.05-60	C			10 ± 0.3	29.5%	0.3% to 0.4%	(Toledo-Cervantes et al., 2016)
	165	4.4	37.5	2.5	5.499	0.362	0.514	0.034	10.7	C	MD	0.002	8	29.5%	5% to 7.4%	(E. Posadas et al., 2015)
	165	4.4	37.5	2.5	Varies	Varies	Varies	Varies	0.5-67	C			7.9	29.5-30%	Varies between 3% and 18%	(Serejo et al., 2015)

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Column Type	Column dimensions				Liquid Flow		Gas Flow		L/G	Mode	Sparger		pH	CO_2 in supplied biogas	CO_2 in upgraded biomethane	Reference
	H_c (cm)	D_c (cm)	H_c/D_c	V_c (L)	Flow rate, L (ml/s)	u_L (cm/s)	Flow rate, G (ml/s)	u_G (cm/s)			Type	d_0 (mm)				
	220	2	110	0.7	0.055	0.014	0.024	0.006	2.33	CC	NR	NR	7.7 ± 0.2	30%	13% CO2	(Meier et al., 2015)
	50	4.5	11.1	0.8		0.027 - 0.106	0.833	0.052	0.4-1.6	CC	NR	NR	7-10	30%	24% to lower than 0.5% at pH 10	(Bahr et al., 2014)
Packed Column	50	4.5	11.1	0.8		0.027 - 0.106	0.833	0.052	0.4-1.6	CC	NR	NR	7-10	30%	No removal at pH 7 to lower than 0.5% at pH 10	

H_c: *Bubble Column Height*; D_c: *Bubble Column Diameter;* V_c*: Bubble Column Volume;* u_L *: Liquid Superficial Velocity;* u_G *: Gas Superficial Velocity;* d_0*: sparger diameter;* C: *Co-current flow;* CC: *Counter-current flow;* MD: *Metallic Diffuser;* PS: *Porous Stone*

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- **Impact of gas/liquid velocity at a constant L/G ratio:** Even for a constant L/G ratio, a higher gas velocity would be required for industrial scale-up of the present technology. This is essential to maintain sufficient residence time at a considerable column height. Based on recent experiments, a low gas flow rate of c. 0.05 cm/s would require an extremely high volume of bubble columns and be a severe limitation, unless optimized. There is a need to decrease the empty bed residence time (time required by gas to rise through the column in case of no liquid) to around 3-6 minutes, typical values similar to those for aerobic or anoxic biotrickling filters (Bahr et al., 2014), thereby allowing the possibility for industrial scale-up.
- **Impact of photosynthetic activity and algae concentration** on the overall biogas upgrading remains to be studied as a potential optimization strategy. A higher photosynthetic activity results in a higher dissolved oxygen, which, in turn, has shown to increase the oxygen content in the upgraded biogas (Meier et al., 2017). It should also be noted that in most of the studies, algae solution after harvesting is recirculated into the bubble column, and hence the effect of the presence of microalgae on CO_2 removal could seldom be established.
- **Influence of CO_2 content in the biogas** on determining the overall system operations has also been scarcely reported.

5.2 Photobioreactor Design

To optimise the sequestration of the captured carbon, an ideal photobioreactor should be able to provide a sufficient residence time of the dissolved carbon through the matching of microalgae growth parameters with the CO_2 absorption rate (Vasumathi et al., 2012). This can be achieved by controlling multiple factors, widely reviewed in literature (Q. Huang et al., 2017; Vasumathi et al., 2012; Vo et al., 2019). Simultaneous optimisation of both light intensity and frequency of light and dark cycles for each microalgae species is crucial to improve its growth rate (Huang et al., 2017; Sforza et al., 2012). Minimisation of the light path by a superior surface to volume ratio, preventing significant drop in light intensity, would further aid algal growth (Shang et al., 2010). Adequate light intensity can be further controlled by maintaining culture concentration of microalgae, thus preventing increased light scattering and creation of dead zones (Vasumathi et al., 2012). This, in turn, would enable optimal uptake of carbon and nutrients from the medium (Vasumathi et al., 2012). In addition, each species has a preferable temperature and pH domain (Vasumathi et al., 2012), as well as the requirement of essential nutrients including macro-elements (such as C, N, P, S and Cl), mineral elements (K, Ca, Mg, Na) , micro-elements (Fe, Mn, Zn, Cu, B, Mo, Si, Se, V, Co, Ni and I) and/or other additives to ensure effective growth rates (Radzun et al., 2015; Zhou et al., 2017).

For photosynthetic biogas upgrading, a highly alkaline solution with high bicarbonate concentration would result. This would therefore lead to significant loss of ammonia by stripping (Delgadillo-mirquez et al., 2016; Idelovitch and Michail, 1987) and phosphorus through deposition of salts of calcium and magnesium (Delgadillo-mirquez et al., 2016; Larsdotter et al., 2010). Indeed, as high as 17% of nitrogen was reported to be lost through stripping at a pH of 10 from a high rate algal pond (Delgadillo-mirquez et al., 2016). On the other hand, Franco-Morgado et al., (2017) reported fixation of c. 50% of nitrogen and only c. 15% of phosphorus by biomass while operating a continuously lit photobioreactor. However, this fell to 13% and 4% respectively while operating the bioreactor over a 12-hour light/dark cycle. Such optimisation is possible by effective mixing, often performed via mechanical agitation by impeller or static mixer in a predominantly bicarbonate medium (Q. Huang et al., 2017). Efficient mixing would also ensure uniform pH, nutrient distribution, temperature

gradient, necessary DIC and DO concentration and adequate mass transfer rates throughout the medium. In addition, cell clumping and sedimentation, the formation of dead zones, and attachment of microalgae to the photobioreactor walls could also be avoided (Carvalho et al., 2006; Q. Huang et al., 2017). Nonetheless, care must be taken to prevent cell damage from excessive mechanical stress on the fragile microalgae from excessive mixing (Q. Huang et al., 2017; Posten, 2009).

5.2.1 Raceway Ponds

Artificial open ponds, often referred to as High Rate Algal Ponds (HRAP) are a low-cost, easy to operate and highly effective technology for large scale cultivation of microalgae (Goli et al., 2016; Q. Huang et al., 2017). CO_2 from biogas captured as bicarbonate in the highly alkaline solution means that a separate CO_2 sparging system into the open pond may not be necessary. This can further ease the design and operation of open ponds for microalgae cultivation along with biogas upgrading. However, there are significant disadvantages. These include: a high land footprint; difficulty to maintain optimum operation conditions; contamination from invasive species, bacteria and viruses (Goli et al., 2016; Zhou et al., 2017). Even though a higher pH can lower the CO_2 desorption rate, as well as contamination by invasive species, the increased loss of nitrogen would continue to be considerable limitations four coupling HRAP with biogas upgrading.

5.2.2 Photobioreactors

As a substitute to raceway ponds, PBRs allow for significant improvement in culture conditions and microalgal biomass density; up to 5-6 times higher than that of open raceway ponds (Vo et al., 2019). Yearlong operation at optimised conditions could thus be achieved. Traditionally, four PBR configurations have been recommended for scalability and suitability for mass cultivation (Q. Huang et al., 2017; Ugwu et al., 2008), simplistic sketches of which is provided in the Figure 6. Recently, the Bicarbonate-based Integrated Carbon Capture and Algae Production System on Ocean (BICCAPSO) using horizontal floating PBRs has been proposed as a low cost alternative for large scale microalgae cultivation (Zhu et al., 2018a). The waves and the surrounding water would provide necessary mixing and cooling, while aqueous bicarbonate solution could be economically supplied via ships or water pipelines (Zhu et al., 2018c, 2018a). Indeed, the use of bicarbonate and alkaliphilic microalgae would benefit the integration of the BICCAPSO technology with photosynthetic biogas upgrading. However, mixing and temperature control due to variable wave characteristics, as well as fouling inside and outside the PBR are major challenges (Zhu et al., 2018c). Further drawbacks include lower ocean temperatures in colder climates inhibiting microalgae growth and need for significant logistics for continuous transport of aqueous bicarbonates over long distances; these must be overcome to allow successful application of the BICCAPSO technology with photosynthetic biogas upgrading.

Among the four traditional PBRs shown in Figure 6, and compared in Table 5, plastic bag PBRs are the least favoured for large-scale cultivation. Both the tubular and the bubble column PBRs are major candidates for wide-scale industrial application, however, subject to significant challenges, as summarized in Table 5. Flat plate photobioreactors show several advantages including a high surface to volume ratio, superior efficiency, easy operation, and robustness. . This, added with a low reactor thickness results in 5 to 20 times more yield than other closed PBR systems (Vo et al., 2019). Novel configurations like the Thin-film Flat Plate PBR are being developed to further lower the cost and improve the scalability of the Flat Plate PBRs further (Yan et al., 2016). However, the need for use of costly materials, together with the requirement of optimally spacing the flat plates to minimize shading

between the reactors increases the cost and land footprint, thus limiting the cost-benefit and scale-up of such reactors.

Table 5 Comparative Summary of Closed Photobioreactors for Mass Cultivation (Endres et al., 2018; Guo et al., 2017; Q. Huang et al., 2017; Nag Dasgupta et al., 2010; Sierra et al., 2008; Vasumathi et al., 2012)

Points of Comparison	Types of photobioreactors			
	Tubular PBR	Plastic Bag PBR	Column Airlift PBR	Flat Plate PBR
Temperature Control	Low-temperature control; difficulty in cooling during summer.	Depending on the size of the bag, effective control of temperature may or may not be obtained.	Effective temperature control can be achieved with proper design.	Ease of temperature control by water spraying in summer or immersion in a water bath and through internal heat exchangers in winter
Light Control	Photo-limitation is a common phenomenon, especially for larger diameter tubes.	Photo-limitation is a major problem due to distortion of bags.	Optimization of column diameter is needed to ensure adequate light control across the cross-section of the reactor and prevention shading	High to volume ratios, leading to high light intensity control. However, needs to be optimally placed to avoid shading.
Effective Mixing and Mass Transfer	Reactors with long tubes encounter mass transfer and mixing problems.	Inadequate mixing, requiring an aerator.	Efficient mixing and mass transfer at a low shear stress on the cells.	Efficient mass transfer and mixing at a low shear stress on the cells.
pH control	difficult due to poor mixing	difficult due to poor mixing	Good pH control	Effective control of pH is achieved.
Surface to Volume Ratio (Illuminated)	High	Low	Moderate	High
Robustness	A robust system that can be operated both indoors and outdoors.	Frail, prone to leakage and a short lifespan.	Robust design, however within material limits.	Extremely robust in design
Materials of Construction	Glass or plastic tubes are the most common materials.	Plastic bags, usually polyethene.	Mostly glass.	Both glass and plastic can be used.
Capital Costs	High	Low	High	High (with glass).
Operational Costs and primary issues	Cleaning is the major challenge, especially the inner walls of the tube, raising operating cost.	Frail systems and poor mixing results in high recurring costs. Disposal of plastic bags is also a major issue.	Difficulty in cleaning leads to a higher operating cost.	Low operational cost. Cost of cleaning can be significantly reduced based on effective design
Power Requirements	Power requirement is high	Low power requirements.	Low Power Requirement	Low power requirement, however, based on the type of cooling.
Present industrial applications	Industrial application for high-value products, but with limited application for CO_2 capture and fuel production	Widely used and limited to small-scale cultivation and pilot scale projects.	Presently confined in lab scale, up to 300L due to difficulty in scalability.	Both academic and industrial scale applications have been widely performed

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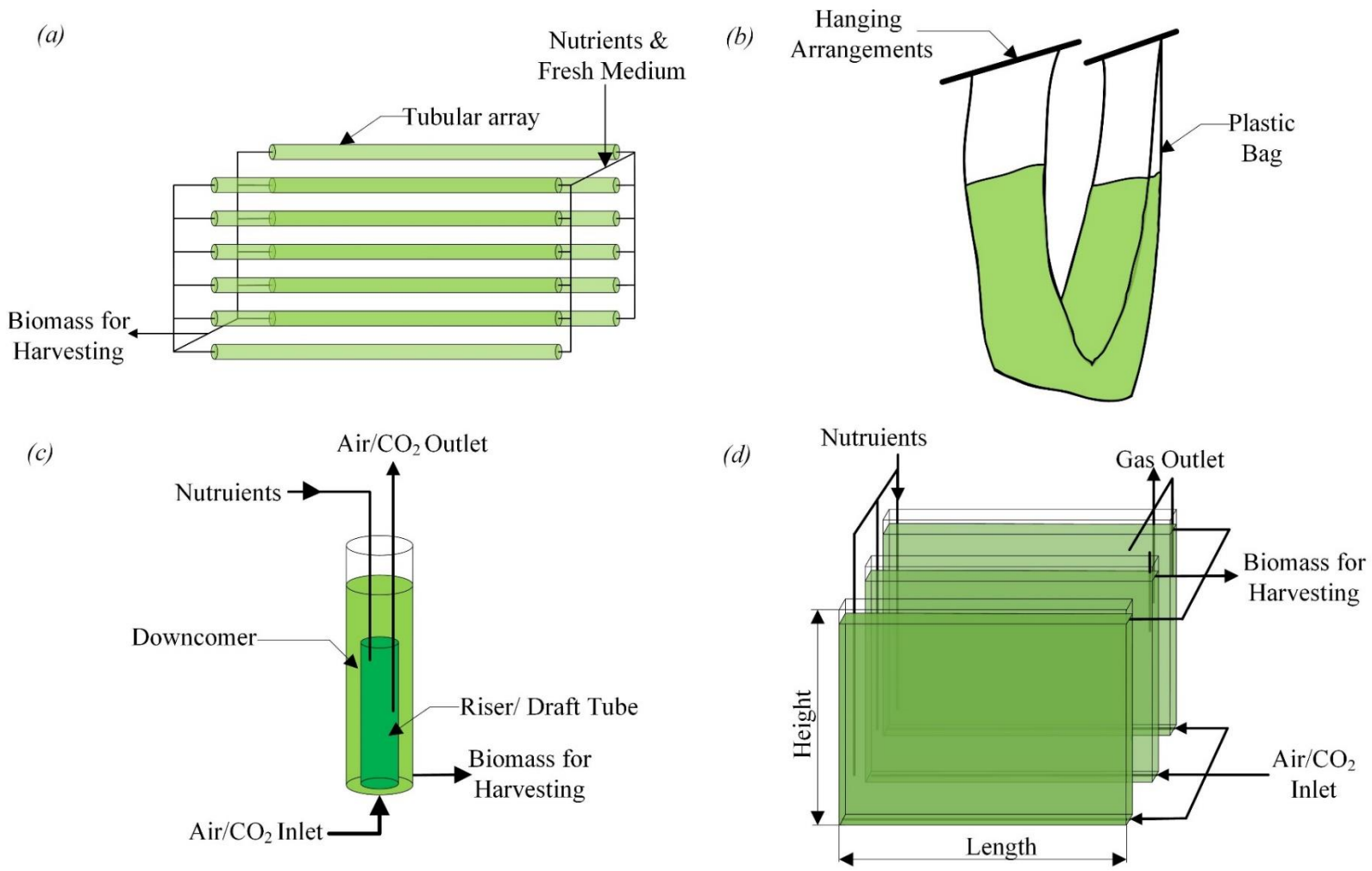


Figure 6 Simplistic schematic representation of closed photobioreactors, (a) Horizontal Tubular Photobioreactor; (b) Plastic bag Photobioreactor; (c) Air-lift Bubble Column Photobioreactor; (d) Flat Plate photobioreactor

5.2.3 Hybrid Configurations

To incorporate the relative advantages of both closed photobioreactors and open ponds, and hence improve the PBR performance, several hybrid photobioreactor configurations have been proposed. A multi-layered stacked hybrid bioreactor (Zhou et al., 2014)has been studied to provide a large cultivation area within a small footprint while maintaining most other beneficial operation parameters for photobioreactors. However, no large-scale system of such configuration has yet been reported. Jesus and Filho, (2017) proposed a concentric draft tube stirred airlift photobioreactor. The stirring speed was suggested as a major factor to influence the growth and composition of the microalgae. García-Galán et al., (2018) developed a full-scale hybrid HRAP– tubular photobioreactor system in Tarragona, Spain, where horizontal arrays of tubular PBRs were connected between two HRAPs on either end. Even though batch tests showed a culture productivity of 272.5-331.8 mg/L for a retention time of 4 days, the continuous experiments in a full scale resulted in only 13.8 mg/L/d in winter and 74.4 mg/L/d in summer for a retention time of 16 days. Hence both the design and operation optimization of such reactors are necessary to ensure the full potential of such hybrid systems.

5.2.4 Comments on Bioreactor Design and Research Gaps

Of the different photobioreactor designs employed in cultivating microalgae after carbon capture from biogas, HRAPs are the most preferred (Table 6). All the studies reported so far have been on a lab scale, highlighting the low technology readiness (TRL) of the present technology. In fact, Marín et al., (2018) conducting experiments in Valladolid, Spain, reported no biomass growth during the winter period at an average temperature of 9 ºC. This caused a much lower concentration of biomass (around 55 mg Total Suspended Solids/L) a clear decrease from the inoculated concentration of 210 mg TSS/L. The CO_2 removal efficiency correspondingly dropped from around 96% in summer (average temperature 24 ºC) to only 63% in the months of December and January (average temperature 9 ºC). The mean daily productivity in open ponds did not significantly vary between experiments. Nevertheless, based on the type of microalgae, a significant variation in culture density was obtained (Table 7), with the highest 2.6 g/L from *Mychonastes homosphaera* (Toledo-Cervantes et al., 2017a). A lower average cell density obtained from *Spirulina* cultivation was reported at 1.2 g/L by Bahr et al (Bahr et al., 2014), while using a light intensity of 80 µmol/m^2-s. Indeed, this indicates scope for optimization of culture conditions. As an example, Kebede and Ahlgren, (1996) reported photo-inhibition of *Spirulina* at a light intensity of around 300 µmol/m^2-s while it was found to be 432 µmol/m^2-s by Toor et al., (2013). Based on the above considerations, the following can be identified as the significant research gaps concerning photobioreactor design for the present technology:

- **Selecting microalgae and optimizing culture conditions:** Only a few studies (Bahr et al., 2014; Marín et al., 2018; Toledo-Cervantes et al., 2017b) have used cyanobacteria species favouring high pH for assessment of their optimal growth. In contrast most other studies have either utilized freshwater chlorophyte species (*Chlorella* sp.) or a consortium of microalgae and cyanobacteria favouring a neutral pH (Franco-Morgado et al., 2017; Meier et al., 2017; Esther Posadas et al., 2015; Serejo et al., 2015). However, even for those, the optimization of culture conditions has not been critically considered, leading to a considerable research scope in future.
- **Choice of Photobioreactor:** With the exception of Meier et al., (2017), open HRAP were selected as the bioreactor, either indoors or outdoors. Indeed, a comparison of results in Table 6 reveals cell density decreases significantly in outdoor culture, even

with similar mean daily productivity and similar inoculation. None of the potential closed PBRs discussed above or a hybrid system have so far been applied to microalgal biogas upgrading. Indeed, the evaluation of the closed PBRs under a controlled environment for yearlong operation, especially in colder climates is urgently needed to expand the applicability of microalgal biogas upgrading worldwide.

5.3 Microalgae Harvesting

Algae harvesting is usually referred to the technique to increase the total solid content up to 10-25% TSS from a dilute algal broth (Barros et al., 2015; Singh and Patidar, 2018). Screening is the first step for microalgae harvesting. Even though mesh sizes in micro-strainers of as low as 1 μm are available, the harvesting efficiency continues to be low by screening (Show and Lee, 2014). Only filamentous species, for example, *Spirulina* sp., with a filament length varying between 50 and 500 μm (Habib et al., 2008) can be relatively easily screened with a higher screen size and at a higher flow rate, significantly decreasing the process economics. Vibrating screens have been shown to be more efficient, which in fact, is the current commercial process for harvesting *Spirulina*, resulting in a recovery of 8-10% TSS with a flow rate of 20 m^3/h (Habib et al., 2008).

5.3.1 Algae Harvesting Techniques

For most microalgae the initial thickening of algal broth via gravity sedimentation is accelerated by the addition of flocculants as the most common harvesting technology (Christenson and Sims, 2011; Rawat et al., 2011). However, the requirement for a low working pH (5-6), together with the necessity of large quantities of corrosive inorganic chemical flocculants such as metallic salts (which contaminates the growth medium) are severe limitations (Barros et al., 2015; Singh and Patidar, 2018). Increasing the pH to enhance flocculation, or auto-flocculation has received considerable success at lab scale. This reduces the cost and energy needs of the harvesting process and is non-toxic. Up to 95% recovery of the total biomass content within 30 mins for *Chlorella vulgaris* at a pH of 10.5 was reported by García-pérez et al., (2014); reports of more than 90% recovery of the total biomass content for freshwater species (*Chlorella vulgaris, Scenedesmus sp. and Chlorococcum sp.*), as well as marine algae (*Nannochloropsis Oculata, Phaeodactylum tricornutum*) at a pH of around 10.6 (Wu et al., 2012) are encouraging. However, the exact mechanism behind auto-flocculation is uncertain; and the significant unreliability of this technique is still a major bottleneck to its large-scale commercial application (Singh and Patidar, 2018).

Further to thickening, filtration is one of the most promising dewatering techniques. By this technique, the microalgae is strained off from the liquid by being forced through a membrane at a pressure gradient (Barros et al., 2015). However, clogging is a major drawback, especially for harvesting high-density cultures (Singh and Patidar, 2018). For a scale handling more than 20 m^3/d of liquid flow, centrifugation provides the fastest alternative but is hindered by high cost and energy demand (Molina Grima et al., 2003). Hence, its applicability is justified only when high value products are extracted from microalgae, such as unsaturated fatty acids, pharmaceuticals, or cosmetic products (Christenson and Sims, 2011; Rawat et al., 2011).

Table 6 Summary of Photobioreactors types and operational details for microalgae cultivation with simultaneous biogas upgrading

PBR Type	PBR Details		Operation Details								Biomass Productivity		Reference
	V_R (L); A_{ill} (m^2)	Dim. (cm)	Mode	T_R (ºC)	L.I. (µmol/ m^2-s)	L:D	W_{comp} (L/d)	[DO] (mg/L)	pH	Inocculation (mg TSS/L)	r_{evap} (L/m^2/d)	B_{mean} (g/m^2/d)	X_{avg} (mg/L)	
Outdoor HRAP	180 and 1.2	Depth 15cm	C	9.1 ± 4.1	679 ± 420	10:14	NA	6.0-10.9	9.2-9.4	210 [*Leptolyngbya lagerheimii* (54%), *Chlorella vulgaris* (28%), *Parachlorella kessleri* (9%), *Tetradesmus obliquus* (5%) & *Mychonastes homosphaera* (2%)]	-1.2	0	55-314	(Marín et al., 2018)
				15.3 ± 7.3	1587 ± 150	14:10	3.9±3.2 (TW)	7.5-10.6	9.3-9.6		2.0-6.2	7.5	447.5	
				24.4 ± 5.8	1626 ± 60	15:9	7.7±2.0 (TW)	6.8-7.9	9.4		6.7 ± 4.9	15	519-571	
				23.4 ± 3.8	1326 ± 71	12:12	5.9±2.4 (TW)	5.3-6.4	9.6-9.8		5.9 ± 3.4	22.5	625-514	
				18.4 ± 7.0	820 ± 0	10:14	2.0±1.8 (TW)	6	9.6		3.2 ± 2.1	15	424	
Outdoor HRAP	180 and 1.2	Depth 15cm	C	23.8 ± 6.7	1427 ± 65	12:12	0.6±0.4 (TW)	1.4 - 15.6	8.3 ± 0.33	210 [*Chlorella sp*]	7 ± 2	15	660 ± 17	(Posadas et al., 2017)
				23.5 ± 6.4	1258 ± 140	11:13	0.8±0.4 (TW)	1.3 - 16.7	9.9 ±0.09		9 ± 1	15	1078 ± 84	
				20.0 ± 6.7	946 ± 174	9:15	NA	0.9 - 13.2	10.06 ±0.13		3 ± 2	15	665 ± 79	
Indoor HRAP	180 and 1.2	Depth 15cm	C	NR	1500 ± 600	14:10	NR (TW)	15.9 ± 1.6	10.2	NR [*Mychonastes homosphaera*]	NR	15	2600 ± 300	(Toledo-Cervantes et al., 2017b)
Indoor PBR (Glass Vessel)	50 and 0.871	15x50 x67	C	20-28	4 steps up to 100	12:12	NR	8.5	7.1-7.4	NR [*Chlorella srooknina*]	NR	0.06 g/L/d	600	(Meier et al., 2017)
Indoor HRAP	25 and 0.28	125x 25x14	C (HRT: 9.5 d)	NR	500	12:12	DW	11.4 ± 0.5 /2.8 ± 0.1 (Light/dark)	9.71 / 9.39 (Light/dark)	120 [*Picochlorum sp.* & *Halospirulina sp*]	NR	0.023 ± 0.001 (g/L/d)	230 ± 50	(Franco-Morgado et al., 2017)

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PBR Type	PBR Details		Operation Details								Biomass Productivity		Reference
	V_R (L); A_{ill} (m^2)	Dim. (cm)	Mode	T_R (ºC)	L.I. (µmol/ m^2-s)	L:D	W_{comp} (L/d)	[DO] (mg/L)	pH	Inocculation (mg TSS/L)	r_{evap} (L/m^2/d)	B_{mean} (g/m^2/d)	X_{avg} (mg/L)	
Indoor HRAP	25 and 0.28	125x 25x14	C (HRT: 9.5 d)	20-25	500	24:0	NR	NR	>9	4.8*10^8 cells/ml [dominated by *Picochlorum sp.* & *Scenedesmus sp*.]	NR	120.2*	1230	(Granada-Moreno et al., 2017)
	180 and 1.2	Depth 15cm	C	22 ± 3 25 ± 2 28 ± 1	420±105	16:8	NR (TW)	5.4 ± 0.8 7.5 ± 1.4 9.6 ± 0.4	9.1 ± 0.1 9.6 ± 0.3 10.6 ± 0.1	NR [*Geitlerinema sp.* (61.5%), *Staurosira sp.* (1.5%) & *Stigeoclonium tenue* (37%)]	NR	2.2 ± 1.4 4.4 ± 1.5 7.5 ± 0.1	1600 ± 100 1200 ± 400 900 ± 100	(Toledo-Cervantes et al., 2016)
	180 and 1.2	Depth 15cm	C (HRT: 7.4 ± 0.2 d)	24 ± 1	104 ± 25	16:8	NR	7 ± 1 (max)	≈8	910 [*Planktolynga brevicellularis* (81%), *Stigeoclonium tenue* (14%) & *Limnothrix planktonica* (5%)]	4.4 ± 1.4 - 7.3 ± 0.2	11.4±1.8 to 13.5±2.2	933 ± 49 to 1228 ± 36	(E. Posadas et al., 2015)
	180 and 1.2	Depth 15cm	C (HRT: 7.4 ± 0.3 d)	26 ± 2	104 ± 25	16:8	NR	4.2 ± 0.5 -8.2 ± 0.9)	≈7.9	600 [*Chlorella vulgaris*]	NR	12 ± 1	130 ± 70	(Serejo et al., 2015)
Indoor PBR (Glass Vessel)	75 and 0.525	15x50 x100	C	25 ± 1	100 ± 20	24:0	NR	Around 7	≈8	NR [*Nannochloropsis gaditana*]	NR	0.03 g/L/d	450 ± 30	(Meier et al., 2015)
Indoor HRAP	180 and 1.2	Depth 15cm	C (HRT: 2 d)	26 ± 1	80	NR	NR	≈ 10	9.4 7	NR [*Spirulina Platensis*]	6	NR	1200 ± 100 600 ± 20	(Bahr et al., 2014)

V_R: Bioreactor Volume; A_{ill} : Illuminated Area; Dim: Dimensions; C:Continuous; T_R: Reactor Temperature; L.I.: Light Intensity; L:D: Light to Dark Ratio; W_{comp} : Water Consumption; [DO] : Concentration of dissolved oxygen; r_{evap} :Rate of Evaporation; B_{mean}: Mean Biomass Yield; X_{avg}: Average biomass concentration.; HRT: Hydraulic Retention Time; d: days

* *Considering each gram of algal biomass is produced by sequestering 1.8 grams of CO_2* (Chisti, 2007)

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Decoupling harvesting from cultivation by the use of a separate settling tank has been mostly applied while upgrading biogas with microalgae. This suggests the use of gravity separation as the preferred harvesting technology. Toledo-Cervantes et al., (2017b) used an organic flocculant or polyelectrolyte, polyacrylamide-based flocculant solution, (due to its low cost for a higher sludge volume) in an external stirred tank to harvest *Mychonastes homosphaera.* Such limited reports available in the literature, therefore, leave significant research gaps to understand the coupling of commercial harvesting techniques with biogas upgrading by microalgae including further understanding of auto-flocculation technology.

5.3.2 Microalgae Selection Criteria 5: Ease of Harvesting

Ease of harvesting can provide a significant advantage by improving the overall energetic and economic balance of the biogas upgrading system. Harvesting filamentous species like *Anabaena* and *Spirulina* (Komárek and Johansen, 2015) through screening provides the easiest of all harvesting techniques. On the other hand, unicellular microalgae like *Chlorella* sp. or *Chlorella vulgaris* or *Scenedesmus obliquus* are extremely hard to harvest. In such cases, flocculation, followed by gravity separation or centrifugation, based on the downstream application would be the most techno-economic option.

6 Discussion and Perspectives

6.1 Selection of Microalgae Species

Microalgae selection for effective biogas upgrading and system operation is intrinsically interlinked with system parameters. This work suggests five criteria for microalgae selection and assesses these for 15 common microalgae species in Table 7. Green tabs represent a beneficial response of the species; red a detrimental response. The cyanobacteria species of genera *Anabaena* and *Spirulina* are suggested as the most suitable for biogas upgrading. Of the Chlorella genera, specific strains of *Chlorella sorokiniana* and *Scenedesmus obliquus* are the most preferable, while the preference of *Chlorella vulgaris* for uptake of CO_2 at high pH might decrease its effectiveness. Any species, showing two or more red tabs would hence be difficult to be considered suitable for biogas upgrading.

6.2 Industrial Scale Application

Based on the above design conditions an overall system sizing for an industrial scale microalgal biogas upgrading system can be estimated. Assuming the culture liquid drawn for harvesting to be half of the liquid recirculated in the bubble column, 0.75 m^3 of algae would be necessary for each cubic metre of biogas upgraded for an L/G ratio of 0.5. This implies a requirement of 1.5 m^3 of algae cultivation for a flat plate PBR system, while 11.25 m^2 of open pond system would be required for a 0.2 m deep pond with HRT of 2 and 3 days respectively (Ruiz et al., 2013; Takabe et al., 2016). A detailed calculation is summarized in BOX 1. This result is comparable to the assumption of Toledo-Cervantes et al., (2017a), whereby 4.84 m^2 of open pond was proposed for each m^3 of biogas upgraded for an L/G ratio of 0.5 without separate withdrawal of culture for harvesting and a lower hydraulic retention time.

Therefore, for continuous operation of a 1 MWel biogas power plant with 35% efficiency and generating biogas at 60% methane content, 5,746.2 m^3 of algal solution would be necessary to be circulated through the bubble column(s) per day. This is after assuming the lower heating value of methane is 35.8 MJ/m^3 (Sialve et al., 2009). For a flat plate PBR

system, measuring 0.07 m in width, 1.5 m in height and 2.5 m in length (Sierra et al., 2008), the overall PBR land footprint would be 4.93 hectares *(BOX 1)*. On the other hand, approximately 12.93 hectares of open pond algae cultivation would be required per MW_e of biogas plant capacity. This can be reduced if less algae solution is drawn for harvesting. Indeed, thus, lowering the L/G ratio would be one of the key strategies to ensure the scale-up of this biogas upgrading technology.

Table 7 Evaluation of 15 common microalgae species with regards to defined Microalgae Selection Criteria for Biogas Upgrading compiled based on the following references

Species	Genera	Criteria				
		Mixotrophy	High pH Tolerance (above 9)	External CA Activity	CO_2 Tolerance	Ease of Harvesting
Chlamydomonas reinhardtii	*Chlamydomonas*	No	No	Yes	17%	No, Unicellular
Chlorella vulgaris	*Chlorella*	Yes	Up to10 (Free CO_2 Preferable)	Yes	60%	No, Unicellular
Chlorella sorokiniana	*Chlorella*	Yes	Yes	Yes	40%	No, Unicellular
Chlorococcum littorale	*Chlorococcum*	Yes	Up to 10	No	60%	No, Unicellular
Desmodesmus sp.	*Desmodesmus*	No	Up to 11	Yes	Reported up to 20%	No, Unicellular
Dunaliella salina	*Dunaliella*	Yes	9-11	Yes	12%	No, Unicellular
Neochloris oleobundans	*Neochloris*	Yes	Up to 10.2	Yes	Reported up to 6%	No, Unicellular
Scenedesmus obliquus	*Scenedesmus*	Yes	Maximum 10.6	Yes	80%	No, Unicellular
Tetraselmis suecica	*Tetraselmis*	No	Not Reported	Yes	14%	No, Unicellular
Phaeodactylum tricornutum	*Phaeodactylum*	No	Maximum 10.3	Yes/No	100%	No, Diatom
Emiliania huxleyi	*Emiliania*	No	No	Yes/No	Very Low	No, Unicellular
Nannochloropsis gaditana	*Nannochloropsis*	No	No	No	15%	No, Unicellular
Euglena gracilis	*Euglena*	Yes	No	No	40%	No, Unicellular Flagellate
Anabaena cylindrica	*Anabaena*	Yes	Moderately Alkaliphilic	Yes	50%	Yes, Filamentous
Spirulina platensis	*Arthrospira*	Yes	Strongly Alkaliphilic	Yes	100%	Yes, Filamentous
Synechococcus sp	*Synechococcus*	Yes	Moderately Alkaliphilic	Yes	100%	No, Unicellular

The number and dimensions of bubble columns would depend on multiple factors. Superficial gas velocity, column diameter, temperature and pressure of operation are of considerable significance in this regard. Indeed, Toledo-Cervantes et al., (2017a), estimates 1.2 m^3 of effective column volume per m^3 of biogas upgraded per hour at a gas superficial velocity of 0.05 cm/s. However, this could be significantly reduced to 60 L per m^3 of biogas upgraded per hour for a gas superficial velocity of 1 cm/s. Therefore, optimizations of biogas

flow velocity, together with other operational parameters are urgently required to avoid severe limitations to practical applications of such designs.

BOX 1: *Calculation for Industrial Scale Perspective of Photosynthetic Biogas Upgrading*

1MW electricity plant with an electrical efficiency of 35% on continuous operation. Assuming the Lower Heating Value of methane as 35.8 MJ/m^3 and biogas contains 60% methane:

➔ Energy input = $\frac{1000*24}{0.35} = 68,571.43\text{kWh/day} \approx 246.86\times10^3\text{MJ/day}$

➔ Biogas Generated (G_d) = $\frac{246.86\times10^3}{35.8\times0.6} = 11,492.4\text{m}^3\text{/day}$

Assuming L/G ratio as 0.5 as per the current technological trend observed in Table 4,

➔ Algal broth circulated in bubble column (L_d) = $11,492.4\times0.5 = 5746.2\text{m}^3\text{/day}$

Algae Cultivation System

Algal broth drawn separately for harvesting is assumed as 0.5 times that ciruclated in the bubble column. A 3 day hydraulic retention time (HRT) is recommended for open pond cultivations (Takabe et al., 2016). For flat plate PBRs, HRT of $2\mu^{-1}$ is advised, μ being the specific growth rate (day^{-1}) (Ruiz et al., 2013). For *Scenedesmus obliquus* with average growth rate of 0.94 ± 0.08 day^{-1} (Ruiz et al., 2013), an HRT of 2days would be sufficient.

➔ Open pond volume = $(L_d + 0.5L_d)\times HRT_{pond} = 1.5\times5746.2\times3 = 25,857.94\text{m}^3$

➔ Flat Plate PBR volume = $(L_d + 0.5L_d)\times HRT_{plate} = 1.5\times5746.2\times2 = 17,238.63\text{m}^3$

➔ Open pond area (with 0.2m depth) = $\frac{25,857.94}{0.2\times10000}$ =12.93 ha

➔ Flat Plate PBR (2.5mX1.5mX0.07m) = $\frac{17,238.63\times S}{10\times10000}$ =4.93 ha

When,

➔ Surface to Volume ratio of Flat Plate PBR (S) $\approx \frac{2\times(2.5\times1.5)}{2.5\times1.5\times0.07}$ =28.57m^2/m^3

and assuming the need of a tenth of the surface area of the reactors as land requirement of the flat plate PBRs (Płaczek et al., 2017).

Parasitic consumption would vary significantly depending on the type of harvesting system, whereby up to 54% of the overall energy consumption for biogas upgrading has been calculated to be expended (Toledo-Cervantes et al., 2017a). An electricity consumption of 0.14 kWh/m^3 of biogas with 30% CO2 for open pond systems was calculated for outdoor cultivation in open ponds without harvesting (Marín et al., 2018), lower than most of the

commercial physicochemical methods. A total parasitic loss of 2.5% can thus be envisaged. However, for a flat plate PBR, the electricity consumption of 53 W/m^3 (Sierra et al., 2008), can significantly improve the overall performance of the upgrading system.

Economies of scale and the flowrates of biogas are significant factors in assessing the cost of biomethane (Angelidaki et al., 2018). For a 300 Nm^3/h biogas flow, a specific capital expenditure (CAPEX) of 6034 €/(Nm^3/h) was predicted for photosynthetic biogas upgrading using open pond for algae cultivation (Toledo-Cervantes et al., 2017a). This was 1.6 times higher than a traditional activated carbon-water scrubbing based upgrading technology. The corresponding operational expenditure (OPEX) of the photosynthetic biogas upgrading system was 0.03 €/Nm^3 of biogas treated. These costs are applicable for a $1MW_e$ biogas power plant (generating around 479 Nm^3/h biogas or 10GJ/h). For a flat plate PBR system, although less land would be required than an open pond system, the high cost of the PBRs would lead to an increased CAPEX (Richardson et al., 2014). Notwithstanding the increased energy demand from pumping, the lower cost of labour and requirement of less energy intensive harvesting techniques due to a higher concentration of biomass systems would lower its corresponding OPEX (Richardson et al., 2014).

The final usage of the microalgae is crucial towards the economic vaibility of the photosynthetic upgrading system. Toledo-Cervantes et al., (2017a) calculated a payback of 5 years while selling biomethane at natural gas prices without incentives through the added revenue generated from microalgae sales. Indeed, extraction of high value products based on the microalgae composition (Borowitzka, 2013) or the production of bioproducts or biofuels could provide added economic benefits towards the commercialisation of the photosynthetic biogas upgrading system. Indeed, a higher economic benefit from a flat Plate PBR over an open pond system can be envisaged only when a high value product is aimed for from the produced microalgae (Gifuni et al., 2018)

The presence of oxygen in the upgraded biomethane could lead to a significant economic penalty to the photosynthetic biogas upgrading system. Physicochemical O_2 scavenging via adsorption with activated carbon/ molecular sieves, or catalytic reduction using hydrazine, sodium sulphite or pyragallol is commercially feasible (Peppel et al., 2017). However, this would not only raise the CAPEX, but the OPEX as well, due to the requirement for high temperature and pressure differentials to carry out the same (Peppel et al., 2017). Therefore, minimisation of the oxygen content in biomethane must be aimed for. For this, the most important strategies highlighted in the paper include: *1)* lowering the contact time between the unprocessed biogas and algae solution, *2)* reducing the pH of the working media and *3)* optimising the relative biogas and algal solution recirculation flow rate, or the L/G ratio *4)* suitably selecting microalgae species to benefit the first three strategies. However, although the parameters and strategies for lowering the oxygen content in the biomethane are well understood, a lack of agreement regarding their exact values to achieve grid quality biomethane needs to be overcome for techno-economic viability of this technology in an industrial scale.

7 Conclusions

Biogas upgrading with microalgae is a novel technology, allowing the unique opportunity for on-site CO_2 removal, sequestration and use. In this paper, the fundamental principles governing biogas upgrading with microalgae have been identified and critically analysed for possible optimisation strategies.

- Five criteria affecting the selection of microalgae have been identified; ability for mixotrophic growth, high pH tolerance, external CA activity, high CO_2 tolerance and ease of harvesting. Five common microalgae species have been identified to fit best for biogas upgrading, namely: *Anabaena cylindrica, Chlorella sorokiniana, Scenedesmus obliquus, Spirulina platensis and Synechococcus sp.*
- The gas-sparged bubble absorption column, together with the flat plate photobioreactor are the most promising for biogas upgrading and microalgae cultivation, allowing for yearlong operation. Working parameters needing optimization have also been identified.
- A 1 MW electric biogas plant would require 12.9 hectares of open pond or 4.9 hectares of flat plate PBRs with an L/G ratio of 0.5, at the present technological level.

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Journal Pre-proof

- System design and operation of photosynthetic biogas upgrading critically reviewed.
- Essential criteria for selecting the microalgae species proposed.
- *Spirulina platensis* is the most favourable microalgae for biogas upgrading.
- 12.9 ha of open pond could upgrade biogas from a 1MW-electric Biogas plant.

Journal Pre-proof

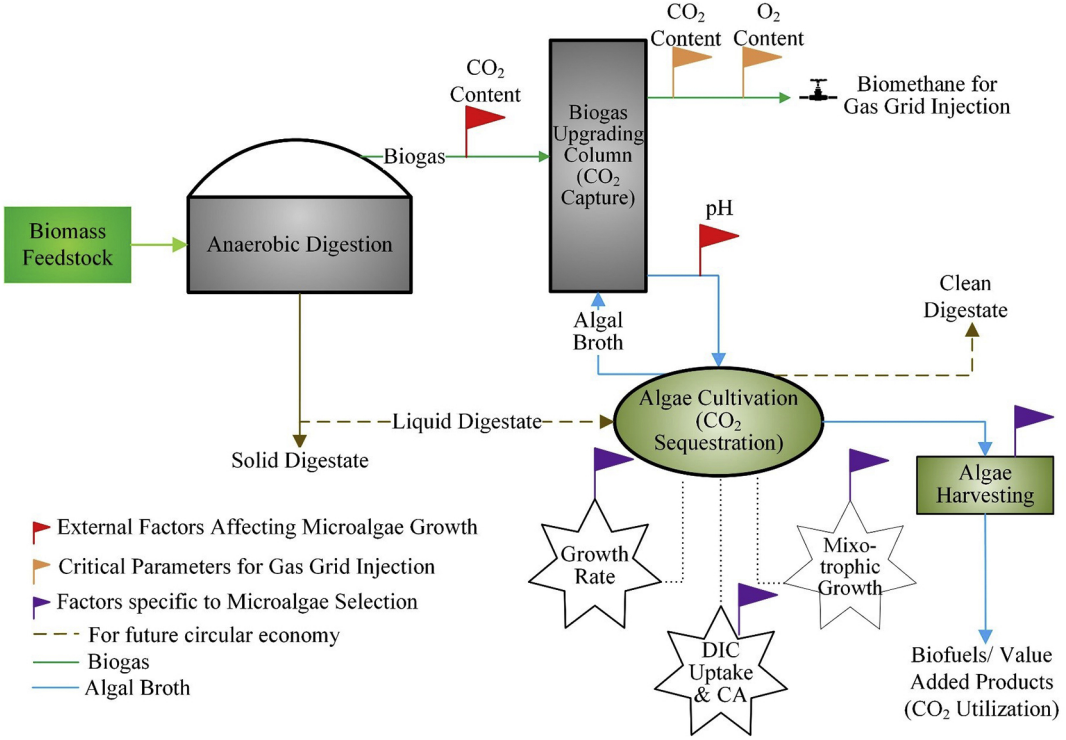

CO_2 Content
O_2 Content
CO_2 Content
Biomethane for Gas Grid Injection
Biogas Upgrading Column (CO_2 Capture)
Biogas
Biomass Feedstock
Anaerobic Digestion
pH
Clean Digestate
Algal Broth
Liquid Digestate
Solid Digestate
Algae Cultivation (CO_2 Sequestration)
Algae Harvesting
External Factors Affecting Microalgae Growth
Critical Parameters for Gas Grid Injection
Factors specific to Microalgae Selection
For future circular economy
Biogas
Algal Broth
Growth Rate
Mixo-trophic Growth
DIC Uptake & CA
Biofuels/ Value Added Products (CO_2 Utilization)

Figure 1

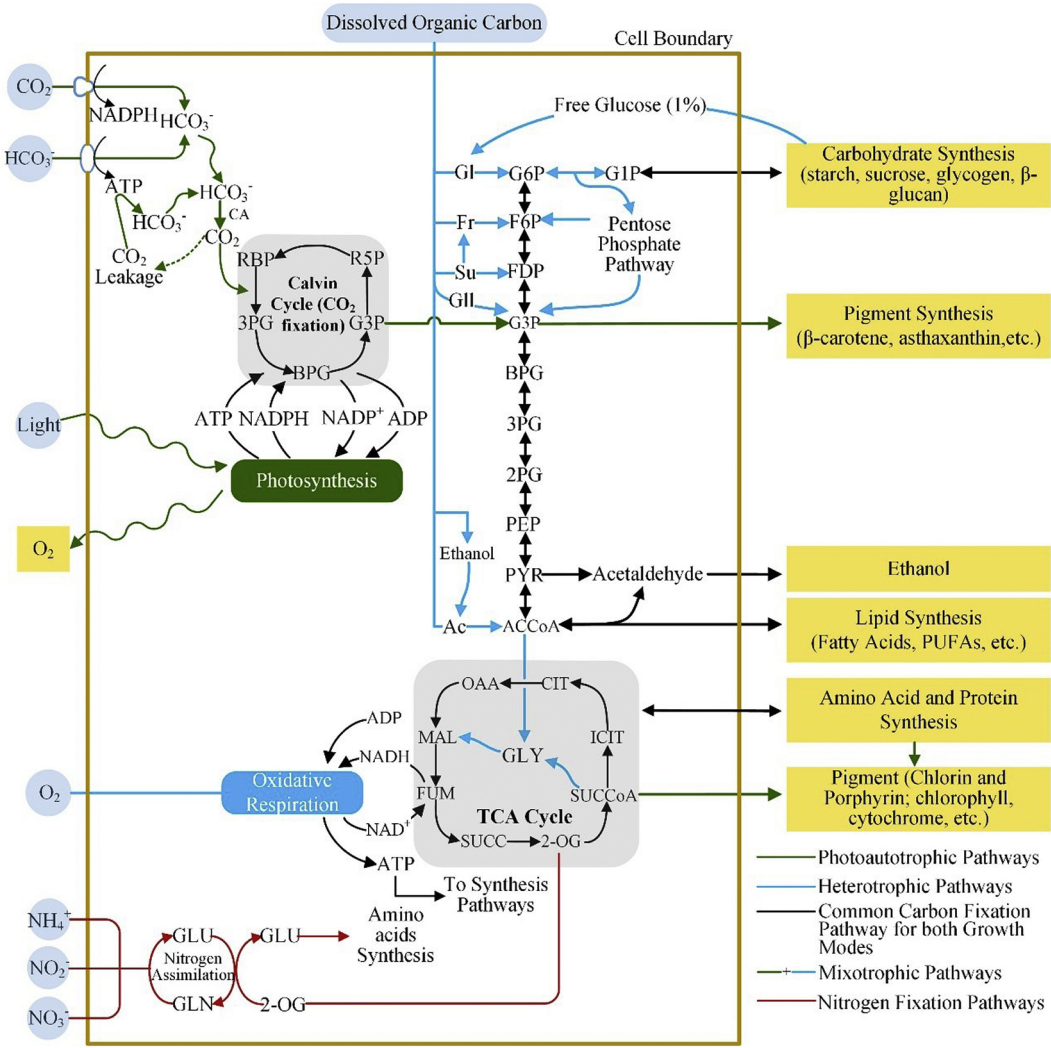

Dissolved Organic Carbon
Cell Boundary
CO_2
HCO_3^-
NADPH
ATP
CA
CO_2 Leakage
Calvin Cycle (CO_2 fixation)
RBP
R5P
3PG
G3P
BPG
Light
ATP NADPH $NADP^+$ ADP
Photosynthesis
O_2
Free Glucose (1%)
Gl
G6P
G1P
Fr
F6P
Su
FDP
Gll
Pentose Phosphate Pathway
Carbohydrate Synthesis (starch, sucrose, glycogen, β-glucan)
Pigment Synthesis (β-carotene, asthaxanthin,etc.)
2PG
PEP
Ethanol
PYR
Acetaldehyde
Ac
ACCoA
Lipid Synthesis (Fatty Acids, PUFAs, etc.)
OAA
CIT
ADP
NADH
MAL
GLY
ICIT
Amino Acid and Protein Synthesis
Oxidative Respiration
FUM
SUCCoA
TCA Cycle
NAD^+
SUCC
2-OG
Pigment (Chlorin and Porphyrin; chlorophyll, cytochrome, etc.)
To Synthesis Pathways
NH_4^+
NO_2^-
NO_3^-
GLU
GLN
Nitrogen Assimilation
Amino acids Synthesis
Photoautotrophic Pathways
Heterotrophic Pathways
Common Carbon Fixation Pathway for both Growth Modes
Mixotrophic Pathways
Nitrogen Fixation Pathways

Figure 2

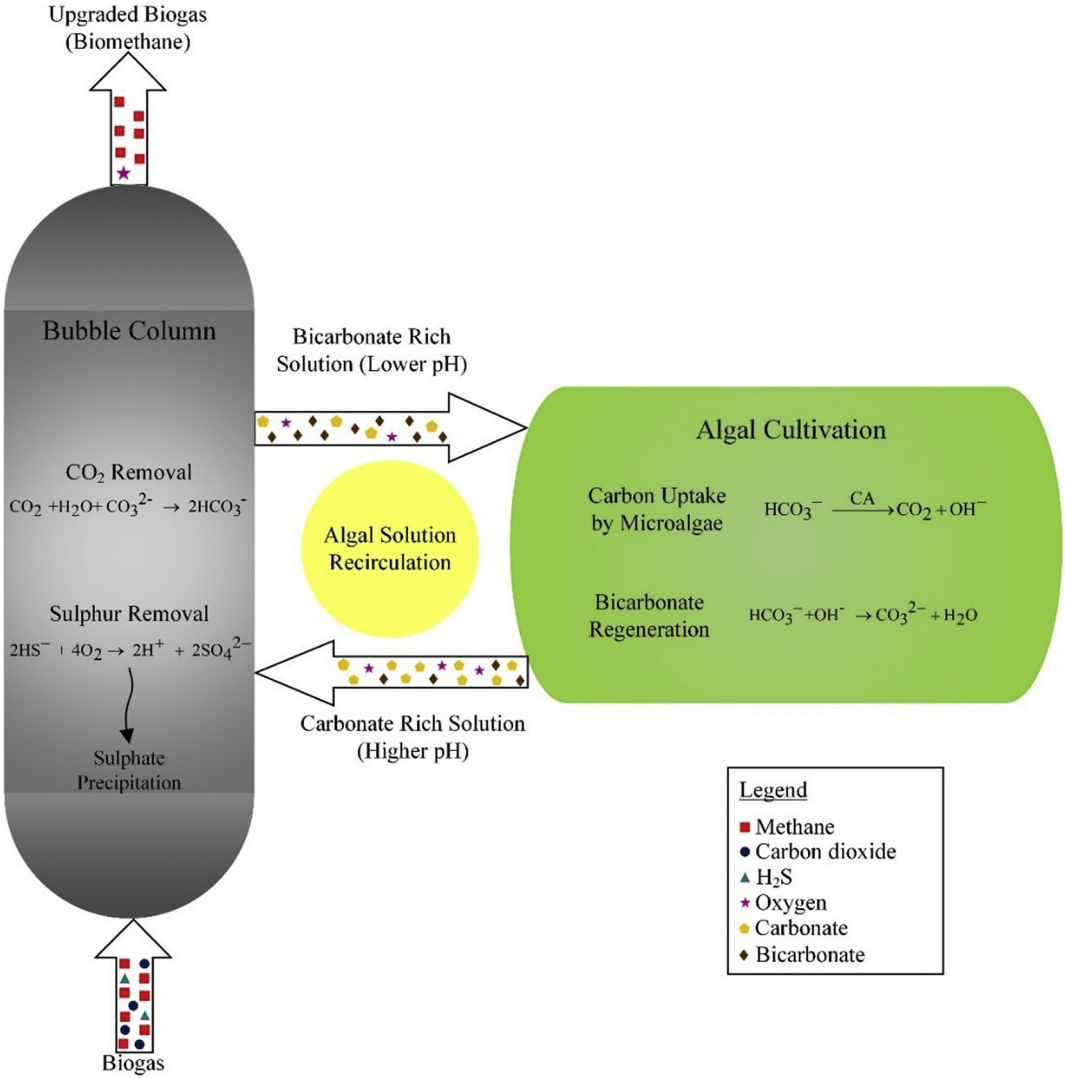

Upgraded Biogas
(Biomethane)
Bubble Column
Bicarbonate Rich
Solution (Lower pH)
Algal Cultivation
CO_2 Removal
$CO_2 + H_2O + CO_3^{2-} \rightarrow 2HCO_3^-$
Algal Solution
Recirculation
Carbon Uptake
by Microalgae
$HCO_3^- \xrightarrow{CA} CO_2 + OH^-$
Bicarbonate
Regeneration
$HCO_3^- + OH^- \rightarrow CO_3^{2-} + H_2O$
Sulphur Removal
$2HS^- + 4O_2 \rightarrow 2H^+ + 2SO_4^{2-}$
Carbonate Rich Solution
(Higher pH)
Sulphate
Precipitation
Legend
Methane
Carbon dioxide
H_2S
Oxygen
Carbonate
Bicarbonate
Biogas

Figure 3

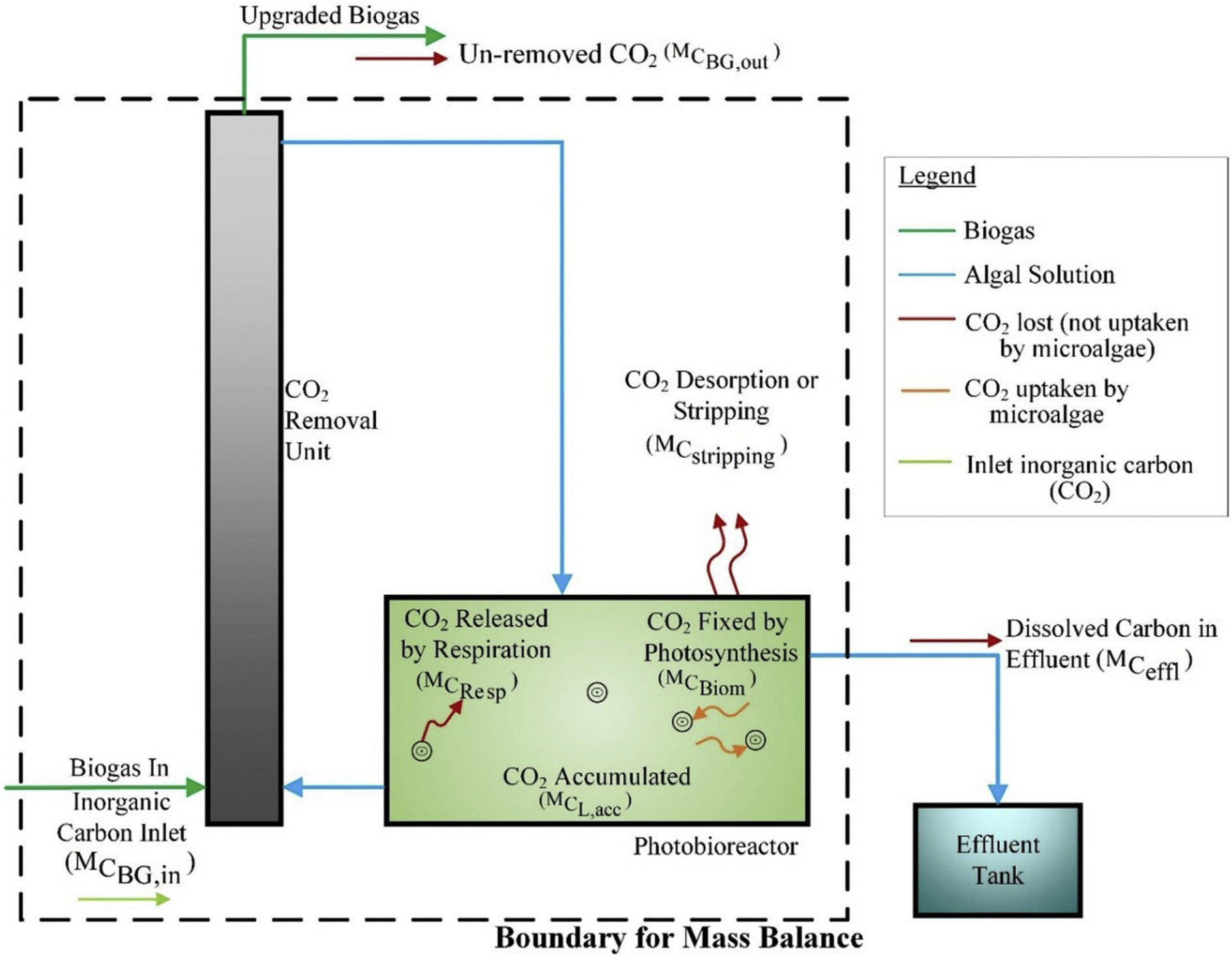

Upgraded Biogas
Un-removed CO_2 ($MC_{BG,out}$)
CO_2 Removal Unit
CO_2 Desorption or Stripping ($MC_{stripping}$)
Legend
Biogas
Algal Solution
CO_2 lost (not uptaken by microalgae)
CO_2 uptaken by microalgae
Inlet inorganic carbon (CO_2)
CO_2 Released by Respiration (MC_{Resp})
CO_2 Fixed by Photosynthesis (MC_{Biom})
Dissolved Carbon in Effluent (MC_{effl})
Biogas In
Inorganic Carbon Inlet ($MC_{BG,in}$)
CO_2 Accumulated ($MC_{L,acc}$)
Photobioreactor
Effluent Tank
Boundary for Mass Balance

Figure 4

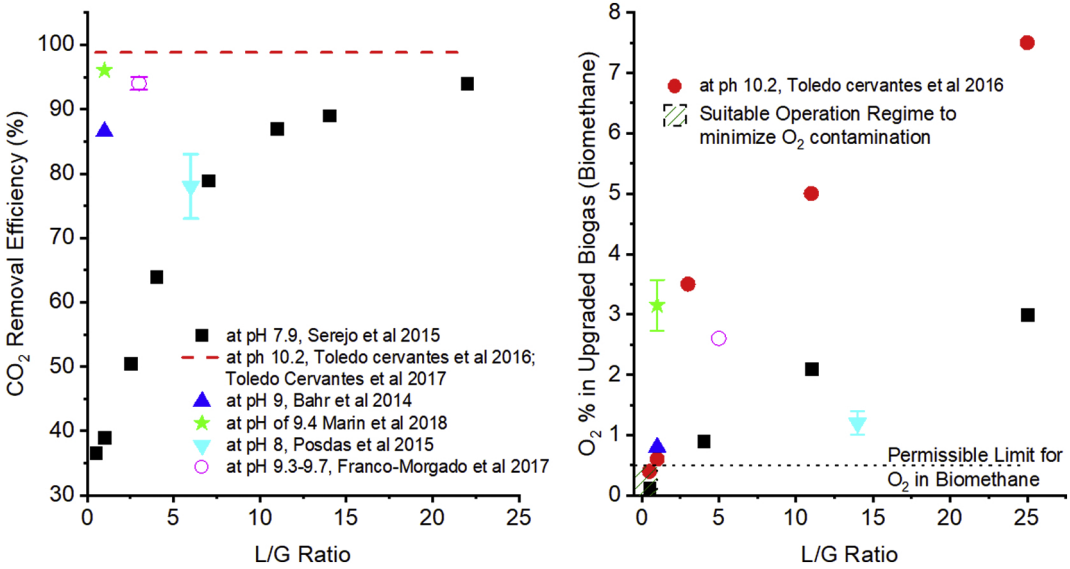

CO2 Removal Efficiency (%)
L/G Ratio
at pH 7.9, Serejo et al 2015
at ph 10.2, Toledo cervantes et al 2016; Toledo Cervantes et al 2017
at pH 9, Bahr et al 2014
at pH of 9.4 Marin et al 2018
at pH 8, Posdas et al 2015
at pH 9.3-9.7, Franco-Morgado et al 2017
O2 % in Upgraded Biogas (Biomethane)
L/G Ratio
at ph 10.2, Toledo cervantes et al 2016
Suitable Operation Regime to minimize O2 contamination
Permissible Limit for O2 in Biomethane

Figure 5

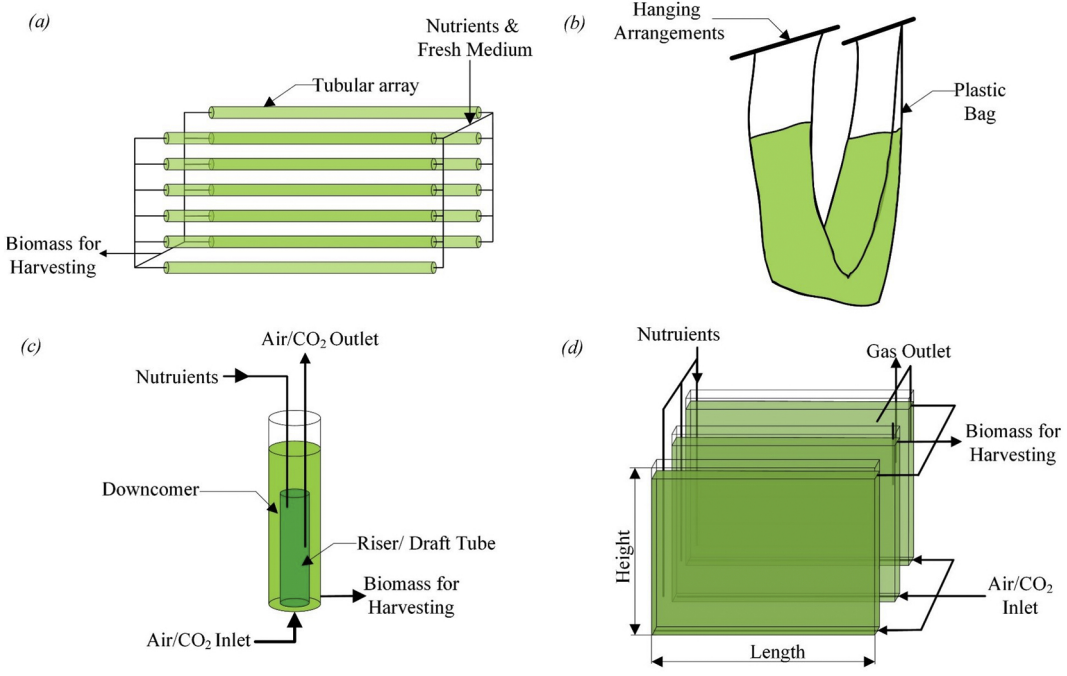

(a)
Nutrients &
Fresh Medium
Tubular array
Biomass for
Harvesting
(b)
Hanging
Arrangements
Plastic
Bag
(c)
Air/CO2 Outlet
Nutruients
Downcomer
Riser/ Draft Tube
Biomass for
Harvesting
Air/CO2 Inlet
(d)
Nutruients
Gas Outlet
Biomass for
Harvesting
Height
Air/CO2
Inlet
Length

Figure 6