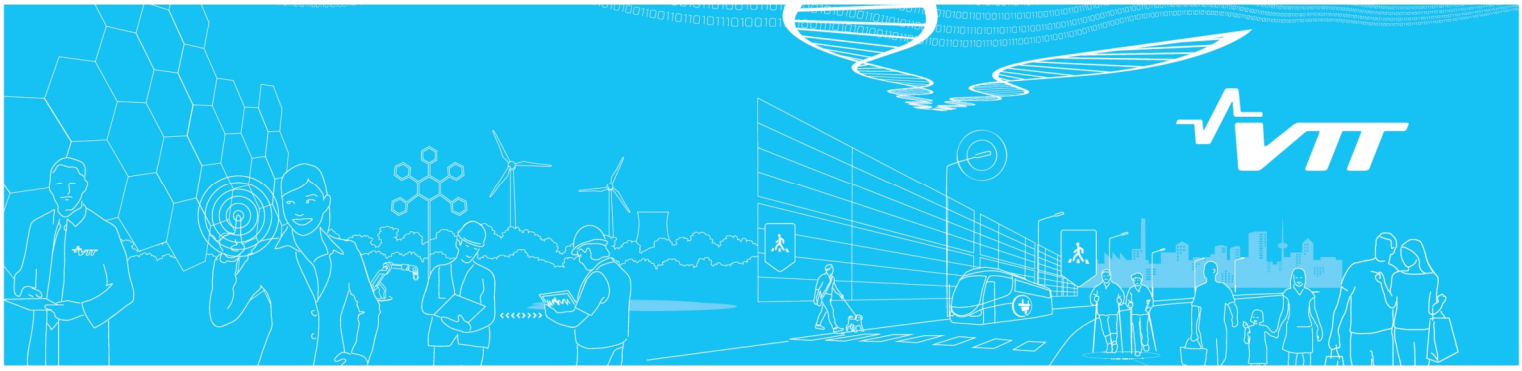

RESEARCH REPORT

VTT-R-00371-15

Review of concepts and technologies for capturing CO_2 by algae

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Summary

The objective of this work was to identify possible technical solutions for algal uptake of CO_2 from industrial gases, such as flue gases and vent gases, with focus on processes that can maximize CO_2 uptake and conversion to organic carbon. An overview of algal cultivation from a CO_2 capture perspective is given, from how algae assimilate CO_2 to reviewing various large-scale algal cultivation methods with CO_2 supply techniques. Possible restrictions imposed on a CO_2 capture system using algae are reviewed, including CO_2 gas quality as well as impurities, temperature, pH, light and nutrient requirements. Finally, an overview of important pilot facilities from a CO_2 capture perspective is given.

Using algal cultivation for CO_2 capture is not a straightforward process. Both overfeeding and underfeeding of CO_2 can be harmful to the algae and typically the CO_2 gas loss to the atmosphere from the algal cultivation is relatively high. As algae can thrive using CO_2 from desulphurized flue gases injected into the cultivation water, there is no need for costly CO_2 separation processes, as long as the algal cultivation is built next to a suitable industrial CO_2 source. The most promising systems for CO_2 capture seem to be those using separate bubbling carbonation columns, both for open ponds and closed photobioreactors. This makes the design of the photobioreactors simpler, as CO_2 is fed readily dissolved by recycling the cultivation water through the bubbling columns. Using separate bubbling columns for open ponds enables a higher CO_2 concentration in the ponds than what can be achieved by direct injection, and reduces the risk for release of gaseous harmful flue gas components into the area surrounding the ponds. The addition of alkaline salts and nutrients can significantly improve the CO_2 uptake of water as well, without turning the water too acidic for the algae.

Confidentiality	Restricted

Espoo, 24.11.2014

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Preface

This work was carried out in the Carbon Capture and Storage Program (CCSP) research program coordinated by CLEEN Ltd. with funding from Finnish Funding Agency for Technology and Innovation, Tekes, and VTT Technical Research Centre of Finland. The report was reviewed by Marilyn Wiebe, Mona Arnold and Kristian Spilling.

Espoo, 27.1.2015

Sebastian Teir

Contents

1 Introduction

Microalgal biotechnologies have been developed since the last century (Burlew, 1953; Borowitzka & Borowitzka, 1988). Micro-algae can be used as a source for e.g. fine chemicals, oils, polysaccharides, and as a food ingredient. About 10,000 t/a microalgae biomass is produced commercially at facilities around the world, mainly for nutritional supplements (van Harmelen & Oonk, 2006). Micro-algae are also used for waste water treatment. The oil crises in the 1970's led to significant efforts into developing liquid biofuels from algal production in the 1980's and 1990's in the U.S. In the 1990's the need to mitigate the ongoing climate change motivated research in capture of CO_2 from flue gases using algae, especially in Japan, where RITE's (Research Innovative Technologies of the Earth) ten-year program for microalgal biofixation of CO_2 had a total funding of 250 MUSD and included participation of over twenty private companies and several government research institutions (Benemann et al. 2003). However, these research efforts were not continued, partially due to the very unfavourable economic projections of CO_2 capture by algae. Technical advances and the increased urgency to reduce greenhouse gas emissions has lately revived the research into biofuels from micro-algae (DOE, 2010).

The most common procedure for cultivation of microalgae is autotrophic growth (Perez-Garcia et al. 2011). Autotrophic organisms produce complex organic compounds, such as fats, proteins and carbohydrates, from simple substances, such as carbon dioxide. Many microalgae are also phototrophic, i.e. organisms that use energy from light to carry out various cellular metabolic processes. In order to grow photoautotrophic algae efficiently sufficient illumination, natural or artificial, and an enriched source of CO_2 are required.

Research has shown that microalgae can be cultivated using flue gases (for instance Stepan et al. 2002; Doucha et al. 2005). Integrating algal cultivation with CO_2-containing flue gases or vent gases from industrial sources provides an opportunity for capturing CO_2. However, CO_2 is not permanently sequestered in the algae, as it is reused in the form of fuels and other products derived from the algal biomass. The greenhouse gas mitigation comes from the substitution of fossil fuels by the algal biofuel. Also, algae production is very energy demanding and could in some cases require more energy input than what energy output can be had from the biofuel (DOE, 2010).

According to Benemann et al. (2003) the use of flue gas CO_2 has not been considered a major R&D issue, since CO_2 transfer into ponds and utilization by the algae is sufficiently well understood and represents a small fraction of the costs. Nonetheless, sufficient CO_2 supply to the cultivation is an important engineering issue, as the transfer of CO_2 through a neutral gas-liquid interface is so slow that special methods must be devised to provide the lengthy time and wide surface area required to maximize transfer (Borowitzka & Borowitzka, 1988). Pumping of excessive amounts of flue gas requires energy and increases cost. Pure CO_2, as used in current commercial algae production, is also valuable. CO_2 supply systems are therefore designed and operated so that the pH can be kept at levels suitable for maintaining the cultures while minimizing loss of CO_2 to the atmosphere.

The objective of this report was to identify possible technical solutions for supplying CO_2 to algae using industrial gases such as flue gases and vent gases as sources for CO_2, with the focus set on maximizing the CO_2 uptake from a carbon capture perspective. The work included a review on applicable gas absorption techniques (scrubbers, dispergers, etc.) taking into account the quality of the CO_2 containing gas source, including potentially inhibiting compounds, temperature, water recycling systems and pH. In addition, cultivation systems for carbon capture by microalgae was assessed including studies on cultivation unit

type, shape, CO_2 retention time, etc., also taking into consideration the algal cell-level characteristics and development that are relevant in maximizing carbon uptake.

2 Concept

Photosynthetic processes convert CO_2 into biomass, which is used as biofuel as such for power & heat production or converted into biofuels for use in transportation. As microalgae have the potential to accumulate significant amounts of lipids (in some cases more than 50% of their ash-free cell dry weight) they are seen as having a great potential for producing high-energy dense fuels (DOE, 2014). Other benefits for making biofuel from algae include:

- High productivity per area
- Non-food based feedstock resources
- Use for non-productive, non-arable land
- Use of a wide variety of water sources (brackish, fresh, marine, saline, produced, and wastewater)
- Co-production of other valuable products
- Potential for recycling of CO_2 and other nutrient waste streams

Development and scale-up of algal cultivation for CO_2 capture and biofuel production need to consider site location, resource availability and end-use perspectives (Figure 1).

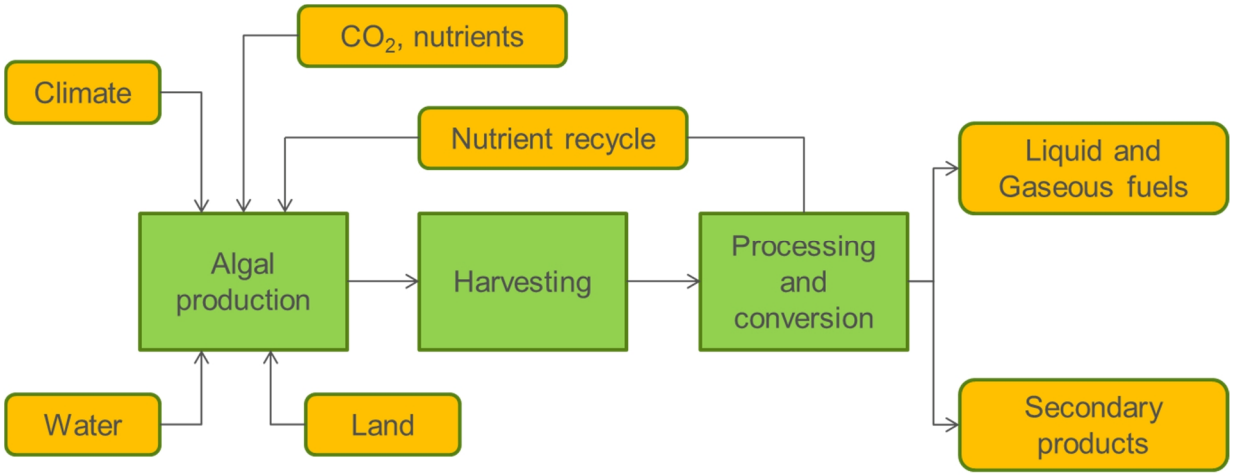

Figure 1. Key siting and resource elements for algae biofuel production (after Maxwell et al., 1985).

2.1 How is CO_2 taken up and used by algae?

In order to assess various technologies for capture of CO_2 by algae, we must first analyse how CO_2 is taken up by microalgae. Many algae consume CO_2 and convert it into carbon molecules using photosynthetic processes similar to plants. Photosynthesis uses the energy from light to reduce carbon from CO_2 to complex carbon. Photosynthesis occurs in two stages in a cell (Figure 2). In the first stage, light-dependent reactions absorb light and convert it into high energy molecules (nicotinamide–adenine dinucleotide phosphate reduced form; NADPH, and adenosine triphosphate; ATP). The light-dependent reactions take place

on the thylakoid membranes. In the second stage, the light-independent Calvin cycle utilizes these high energy molecules to convert carbon dioxide and water into organic compounds that can be used by the organism, so the Calvin cycle represents the actual carbon fixation (Moroney & Ynalvez, 2009). The sum of the reactions is the following:

$3CO_2 + 6NADPH + 5H_2O + 9ATP \rightarrow$ glyceraldehyde-3-phosphate (G3P) + $2H^+ + 6NADP^+ +$ 9ADP (adenosine diphosphate) + $8P_i$ (inorganic phosphate) (1)

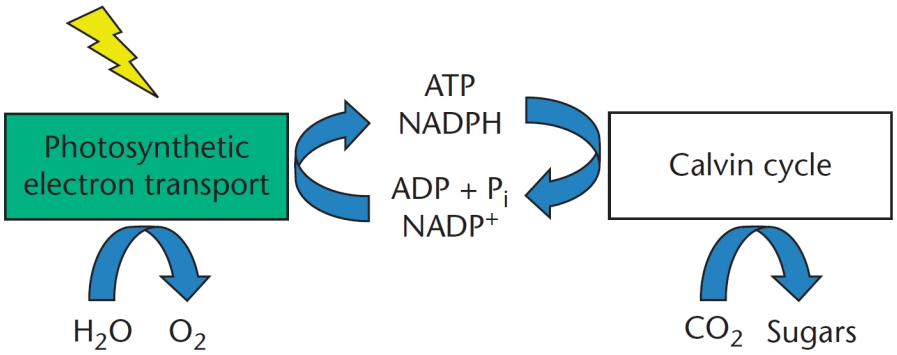

Figure 2. Principle of algal photosynthesis (Moroney & Ynalvez, 2009)

The CO_2 conversion step in the Calvin cycle is catalysed by the enzyme ribulose bisphosphate carboxylase/oxygenase (RuBisCO):

RuBP (ribulose-1,5-biphosphate) + Carbon dioxide $\rightarrow$ 2 (3-PGA) (2)

where 3-PGA is 3-phosphoglyceric acid. RuBisCO is found in all algae and higher plants that fix carbon dioxide. RuBisCO can also catalyse the addition of oxygen with RuBP, resulting in one molecule of 3-PGA and one of phosphoglycollate (Moroney & Ynalvez, 2009):

Oxygen + RuBP $\rightarrow$ 3-PGA + Phosphoglycollate (3)

Therefore, oxygen and carbon dioxide are competitive substrates, since both can react with RuBP in plants and algae. If phosphoglycollate is formed, the algae must recycle it by photorespiration, which converts them into 3-PGA and carbon dioxide. This pathway uses a considerable amount of energy and is considered non-productive. Photorespiration can be reduced by increasing the concentration of concentration of CO_2. Heterotrophic (dark) CO_2 fixation is also important in both autotrophic and heterotrophic growth of algae (Stewart, 1974).

Carbon dioxide exists in water in different forms depending on pH (Figure 3). At pH below 6, the main form is dissolved CO_2, of which a small fraction exists as carbonic acid (H_2CO_3):

$CO_2(aq) + H_2O \leftrightarrow H_2CO_3(aq)$ (4)

At pH 6.5-10, the dominant form is bicarbonate (HCO_3^-).

$H_2CO_3(aq) \leftrightarrow HCO_3^-(aq) + H^+(aq)$ (5)

At higher pH, the main form is carbonate (CO_3^{2+}):

$HCO_3^-(aq) \leftrightarrow CO_3^{2-} + H^+(aq)$ (6)

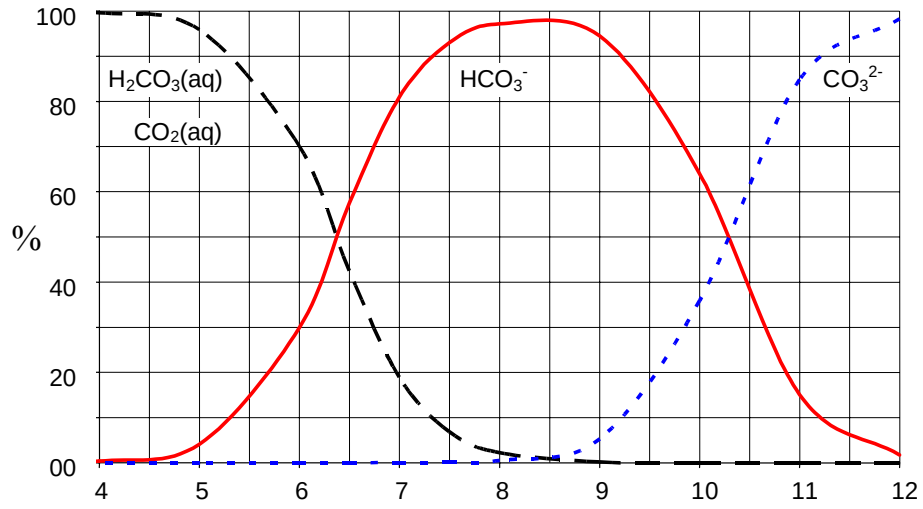

Figure 3. Distribution of carbonate species at equilibrium as functions of pH (calculated using Henry's law).

The major carbon source for photosynthesis is unhydrated CO_2 (i.e. dissolved CO_2, not carbonic acid). At high pH values, some algae are able to actively transport HCO_3^- into their cells, where it is converted to CO_2 in order to be used by photosynthesis (Stewart, 1974). Bicarbonate-using algae are able to raise the pH in their environment to values in excess of those attained by species only able to use CO_2 (Giordano et al. 2005). According to Mukherjee & Moroney (2011), algae must acquire their carbon dioxide from the carbon dioxide and bicarbonate dissolved in their aqueous environment. The dissolved CO_2 enters the cell by passive diffusion.

According to Borowitzka & Moheimani (2013) no species can take up carbonate ions as a carbon source for photosynthesis. Some authors mention that a few algal species can use carbonate, although carbonate can be toxic to other species (Borowitzka & Borowitzka, 1988; Round, 1981).

Although RuBisCO has a relatively low affinity for CO_2 and also has an affinity for O_2, all cyanobacteria examined, most algae and many aquatic plants have additional mechanisms that overcome the deficiencies of RuBisCO (Giordano et al. 2005). Because of these so called carbon dioxide-concentrating mechanisms, algae are very efficient at absorbing inorganic carbon in comparison to higher plants. This is a vital mechanism for algae, because the rate of diffusion of CO_2 in water is thousands of times slower than that of CO_2 in air (Mukherjee & Moroney, 2011). However, the efficiency of these mechanisms decreases when algae are grown in high carbon dioxide concentrations (5-10 times that of air; Moroney & Ynalvez, 2009). Most carbon dioxide-concentrating mechanisms in cyanobacteria and algae are based on active transport of HCO_3^- and/or CO_2 across one or more of the membranes separating the bulk medium from RuBisCO.

2.2 Potential and maturity of using algae for CO_2 capture and biofuel production

During the last decades algae have become of interest from the perspective of producing biofuel. The oil productivity of algae currently ranges between 12 000 and 30 000 litres of oil/ha/year, which is far higher than that of palm oil and rapeseed oil (BIOREF-INTEG, 2009).

In photobioreactors (PBRs), productivities of 59 000 – 137 000 litre of oil per ha have been reported (Christi, 2007). At this stage of development use of algae for CO_2 capture and biofuel production is not ready for commercial implementation and significant research, development, demonstration, and investments are required for the technology to become mature. The current net energy requirement for algae production in raceway ponds is 3-4 times higher than that for most agricultural crops due to the energy requirements for mixing, harvesting, concentrating and drying of the algal biomass.

The CO_2 fixation capacity per tonne of algal biomass is slightly below 2 t CO_2 – about 0.5 t carbon, depending on the algal species. The productivity per land usage area is about 8000 t dry biomass/km^2/year (open pond system), which is slightly lower than that for agricultural crops (Styring et al., 2011). The fixation of 1 Mt CO_2 per year would then require an algae cultivation surface of about 70 km^2. In contrast, PBRs require much less area, raising the productivity to 23000 t dry biomass/km^2/year (semi closed PBR, calculated using numbers from Table 1), lowering the area need to one third of that of open ponds. However, the construction cost for open pond systems are ca. 10 USD/m^2 while that of PBRs are >100 USD/m^2. This means that the construction costs for a system capturing 1 Mt CO_2 per year would be 700 MUSD for an open pond system and 2400 MUSD for a PBR system, producing 1-2 million barrels of oil per year.

Growing algae on non-cultivatable land and even in the sea, would limit competition for land use with food production or the cultivation of other energy crops. However, in order to use microalgae for biofuels anticipated production costs need to be substantially reduced and the scale of production needs to be increased significantly. Co-production of commercial biochemicals with higher value than bio-energy, such as lipids, proteins, and polysaccharides, might result in microalgal plants becoming economically viable in the long run. Also, the combination of CO_2 capture with waste water treatment and fertiliser recycle and production is seen as a possibility, particularly in warmer and sunnier regions (Van Harmelen & Oonk, 2007).

3 Cultivation systems

The cultivation system puts the main restrictions on the type of CO_2 supply system that can be used. There are four major types of cultivation conditions that can be used for microalgae (Chen et al., 2011):

- *Photoautotrophic cultivation*. This occurs when microalgae use light as the energy source and inorganic carbon (e.g. CO_2) as the carbon source to form chemical energy through photosynthesis and is the most commonly used cultivation method for microalgae. A common engineering problem with photoautotrophic cultivation is to enable access to light in cultivations with high cell density.

- *Heterotrophic cultivation*. Heterotrophic cultivation occurs when microalgae grow by consuming organic carbon (e.g. glucose, acetate, glycerol, sucrose, lactose, galactose and mannose) under dark conditions, like bacteria. Considering biofuel production heterotrophic cultivation can yield higher productivity rates than photoautotrophic cultivation. But heterotrophic culture can get contaminated very easily, especially in open cultivation systems. However, as this work focus on the use of CO_2 as a raw material for feeding algae, heterotrophic cultivation is outside the scope of this study.

- *Mixotrophic cultivation.* This occurs when microalgae undergo photosynthesis and use both organic compounds and inorganic carbon (CO_2) as a carbon source for growth.

- *Photoheterotrophic cultivation*. Photoheterotrophic cultivation is when the microalgae require light as an energy source although using mainly organic compounds as the carbon source. According to Chen et al. (2011) photoheterotrophic and mixotrophic cultivation are rarely used in microalgal oil production.

Macroalgae (or seaweed) has different cultivation needs that require open off-shore or coastal facilities. In addition, transfer of nutrients (particularly CO_2) from the water to macroalgae requires considerable mixing and, thus, energy input, making macroalgae less suitable for biofuel/CO_2 capture concepts than microalgae (Benemann, 1993).

The systems used for large-scale photoautrophic cultivation of microalgae are either “open” systems, where the culture is directly exposed to the environment, or (semi-) “closed” systems, where the culture is enclosed within a vessel or photobioreactor (PBR). To these systems water, nutrients and CO_2 are supplied. Except for providing space to grow the mixing of the culture is an important task for the cultivation system. The relative movement between water and algae is important for algae, as it exposes the algae to fresh media and continuously removes extra-cellular products (Round, 1981). Also, mixing enables access to light for all algal cells.

This section gives a brief summary of the main photoautotrophic cultivation systems. Commercial systems today use lagoons, raceway and circular ponds, as well as tubular photobioreactors. In addition, fermenter tanks are used, where algae grow in heterotrophic conditions (in the dark feeding on organic substances, but these are excluded from this overview as they don’t consume CO_2). See Borowitzka & Moheimani (2013) for a more thorough review of cultivation systems.

3.1 Open pond cultivation systems

Open cultivation systems are the main systems used to produce microalgae commercially as well as in wastewater treatment systems, mainly because they are the most economical systems for large-scale cultivation (Borowitzka & Moheimani, 2013). Open pond culture systems can be divided into:

- Shallow lagoons and ponds
- Inclided systems
- Circular central-pivot ponds
- Mixed ponds
- Raceway ponds

3.1.1 Shallow lagoons and ponds

The most simple cultivation systems are shallow lagoons and ponds. These have been used as simple wastewater treatment systems for thousands of years. The largest commercial microalgae production plants in the world are the two *Dunaliella salina* β-carotene plants located in Australia by BASF, where algae are grown in ver large (up to about 200 ha each) unlined shallow ponds. Mixing is only by wind and convection currents, as well as by a carefully managed waterflow through the system.

Figure 4. The large open ponds used for cultivating Dunaliella salina *at Hutt Lagoon, Western Australia.*[1]

3.1.2 Inclined systems

These ponds are built on inclined surfaces, so that the algae culture flows downwards, is collected at the bottom and pumped back to the top. In the prototypes constructed in Czech Republic (see also the section on pilots) the culture is circulated on the inclined surfaces during daytime, whereas at nigh the culture is kept in a large tank where it is aerated and mixed. This reduces the overall pumping costs and also reduces the degree of cooling of the culture at night. A few large-scale inclined systems are available. For instance, in Rupite, Bulgaria, a 3000 m^2 plant with sloping ponds has been constructed, with reported daily productivities of *Arthrospira* and *Scenedesmus* of 18-25 g/m^2 (Borowitzka & Moheimani, 2013).

3.1.3 Circular central-pivot ponds

Circular ponds used in Taiwan, Japan, and Indonesia for cultivation of Chlorella are some of the oldest pond types used for commercial cultivation of algae. These concrete ponds may be up to 0.5 ha in area and 50 m diameter. Mixing is achieved with a rotating arm mounted at the center of the pond. Therefore, the further from the center of the pond, the more intensive the mixing.

3.1.4 Mixed ponds

Mixed ponds are mainly used for production of algae for aquaculture feed. The simplest type is a pond or tank about 50-80 cm deep, where ariation from the base of the pond provides some mixing of the culture. Due to uneven mixing and the depth of the ponds the

[1] http://www.bsb.murdoch.edu.au/groups/beam/BEAM-Appl4a.html

productivities are low. An alternative mixing method suitable for rectangular ponds as a “drag board”, which is a board covering the cross-section of the pond (except for a few centimeters at the bottom) and which is dragged from one end to the other by a motor. Although some reports show a lower power use than for paddlewheels, the mechanical system is more complex and prone to failures.

3.1.5 Raceway ponds

The most common cultivation systems for commercial production of algae today are High Rate Algal Ponds (HRAP), also called “raceway ponds”. The culture in the ponds must be circulated at about 20–30 cm/s, keeping the algae suspended as well as providing relatively even illumination to the algae and preventing thermal stratification (Borowitzka & Moheimani, 2013). In HRAPs, the cultures are typically mixed with paddle wheels that have moderate energy costs. Also other methods for mixing have been tested, such as air-lifts, propellers, Archimedes screws and water jets. These methods all have higher energy requirements than that of paddle wheels except for propellers, which have similar energy requirements to that of paddle wheels (Borowitzka & Moheimani, 2013). HRAPs can be built at relatively low investment costs (ca. 10 USD/m^2) and can be easily scaled up (Styring et al., 2011). A major drawback of the open systems is that the options for process control is limited, which also limits the productivity. In addition, open ponds are easily contaminated, which pose a limit on the species which can be successfully cultivated in open systems. The ponds can be covered, typically using clear plastic, but this can cause very high temperatures in high light locations. From a CO_2 capture perspective, open ponds are far from ideal systems. Care must be taken to minimize the amount of CO_2 outgassing to the air by the design of the CO_2 supply system and careful dosing of the CO_2.

Figure 5. Earthrise Farms Arthrospira production plant (Calipatria, CA, USA)[2]

[2] http://www.intechopen.com/books/plant-science/microalgal-biotechnology-prospects-and-applications

3.2 Closed or semiclosed cultivation systems

Closed or semiclosed PBRs are controlled environments, which allow algal species to be cultivated that cannot be grown in open systems. Most of the start-up companies in the algal biofuel sector focus on PBRs. PBRs have a number of advantages of open pond systems, including minimal CO_2 and water losses, much better process control and flexibility, and minimal dependence on weather (Table 2). Also, PBRs may attain higher productivities than ponds and require less space (Table 1). However, the investment costs are typically more than 10 times higher (>USD 100/m^2) compared to open systems and scale-up is more difficult because of engineering issues related to gas/liquid mass transfer, prevention of wall growth, as well as energy efficient mixing and cooling of the culture (Styring, 2011).

Table 1. Basic values of various cultivation plants (Pulz, 2001).

	Unit	Raceway	Incl. Surface type Open pond, high layer thickness	Tubular Open pond, low layer thickness	Plate	
					Semi-closed tubular system	Semi-closed plate system
Illuminated surface	m^2	500	200	600	500	
Total volume	m^3	75	5	7	6	
Space required	m^2	550	250	110	100	
Layer thickness	cm	10–30	0.5–1	4	3	
Flow rate	cm s^{-1}	30–55	30–45	50–60	120	
Biomass conc.(DW)	mg l^{-1}	300–500	3,000–6,500	5,000–8,000	5,000–8,000	
Productivity (DW)	g l^{-1} d^{-1}	0.05–0.1	0.8–1.0	0.8–1.2	0.8–1.3	

Table 2. Advantages and disadvantages of open and closed algal cultivation plants (Pulz, 2001).

Parameter	Open ponds (raceway ponds)	Closed systems (PBR systems)
Contamination risk	Extremely high	Low
Space required	High	Low
Water losses	Extremely high	Almost none
CO_2-losses	High	Almost none
Biomass quality	Not susceptible	Susceptible
Variability as to cultivatable species	Not given, cultivation possibilities are restricted to a few algal varieties	High, nearly all microalgal varieties may be cultivated
Flexibility of production	Change of production between the possible varieties nearly impossible	Change of production without any problems
Reproducibility of production parameters	Not given, dependent on exterior conditions	Possible within certain tolerances
Process control	Not given	Given
Standardization	Not possible	Possible
Weather dependence	Absolute, production impossible during rain	Insignificant, because closed configurations allow production also during bad weather
Period until net production is reached after start or interruptions	Long, approx. 6–8 weeks	Relatively short, approx. 2–4 weeks
Biomass concentration during production	Low, approx. 0.1–0.2 g/l	High, approx. 2–8 g/l
Efficiency of treatment processes	Low, time-consuming, large volume flows due to low concentrations	High, short-time, relatively small volume flows

The following principles lead to maximum productivities of algal cultivation systems (Borowitzka & Moheimani, 2013):

1. Adequate mixing to provide a suitable light-dark cycle to the cells and avoid biofouling
2. High mass transfer capacity to efficiently supply CO_2 and prevent O_2 build-up
3. High surface-to-volume ratio to increase cell concentration and volumetric productivity
4. Control of temperature at or near the optimum for the cultivated organism

5. Accurate control of pH, CO_2 and nutrient concentrations
6. Adequate harvesting regime to maintain the optimal population density.

Photobioreactors can be of horizontal, vertical or inclined in design. Vertical photobioreactors are more convenient than horizontal reactors, because it is more easier to strip the inhibitive oxygen from the algal suspension in vertical reactors (Kastanek et al. 2010). Most of the PBR concepts presented here are designed to meet the criteria listed above.

3.2.1 Tubular photobioreactors

Tubular photobioreactors are the most common design available and the preferred PBR for commercial algae production. These reactors are normally glass or plastic tubes in which the culture is circulated with pumps or airlift systems. These can be either serpentines or manifolds and have horizontal, inclined, vertical, or conical arrangements.

In vertical tubular PBRs CO_2 containing gas is provided by spargers. The incoming gas stream also provides the overall mixing. There are two main types of vertical tubular reactors that can be differentiated, based on their mode of liquid flow. *Bubble column reactors* are cylindrical vessels with a height larger than twice the diameter. Mixing and CO_2 mass transfer is accomplished through the bubbling gas mixture from the gas sparger in the bottom of the reactor. In contrast to bubble columns, where the gas moves randomly, *airlift photobioreactors* are vessels that have two interconnecting zones – a riser, where the incoming gas mixes with the cultivation media and a downcomer, where the cultivation media is returned, after the gas has disengaged from the media. The riser and downcomer can be two separate tubes or the zones can exist in the same vessel, separated only by flow patterns due to reactor design.

Horizontal tubular photobioreactors are placed horizontally to maximize sunlight uptake. However, oxygen is more difficult to remove from these systems, causing oxygen buildup that reduces the photosynthetic efficiency. Another major drawback is high energy consumption – about 2000 W/m^3 in comparison to 50 W/m^3 for bubble columns and flat plate PBRs (Kumar et al. 2011). This is required to reach high liquid velocities of about 20-50 m/s to achieve turbulent conditions.

A design combining the different features of the basic types presented above is the inclined airlifted reactors constructed and tested at MIT using flue gas as the CO_2 source (Figure 6). As gas is supplied from the bottom of the tube the gas bubbles travel along the inner upper surface of the tube and make it difficult for algae to stick to the surface, thereby preventing fouling. This self-cleaning behaviour of the light penetrating surface reduces maintenance requirements. According to Vunjak-Novakovic et al. (2005) The measured CO_2 removal efficiency was up to 80 % on sunny days. This system was later developed into a larger system by GreenFuel Technologies (see “Pilots” section).

The helical type photobioreactor consists of a coiled transparent and flexible tube of small diameter with separate or attached degassing unit (Figure 7). A centrifugal pump is used for driving the culture through the long tube to the degassing unit. It’s advantage includes better CO_2 transfer from gas phase to liquid due to its long CO_2 absorbing pathway. However, the energy requirements due to the pump are relatively high and the associated shear stress limits its commercial use. Also, fouling is a problem.

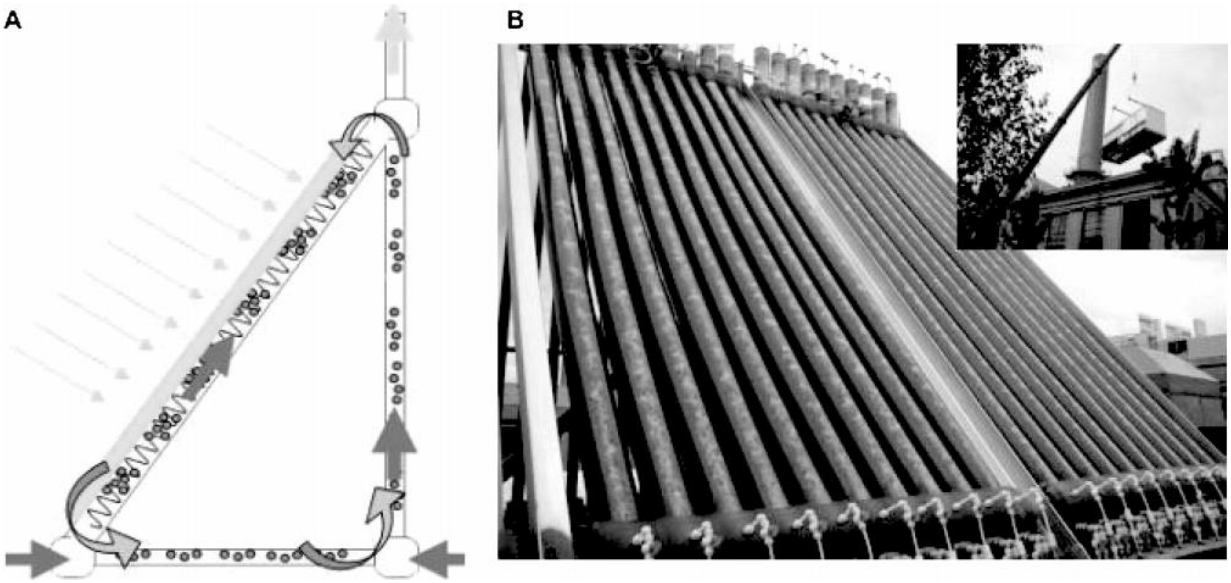

Figure 6. Inclined airlifted reactors. (A) schematic side-view. Gas enters from the bottom of the inclined tube, while the water flows counter current to the gas (downward along the inclined tube). (B) An array of 30 PBRs, each with a volume of 30 L containing a culture grown on flue gas (Vunjak-Novakovic et al., 2005).

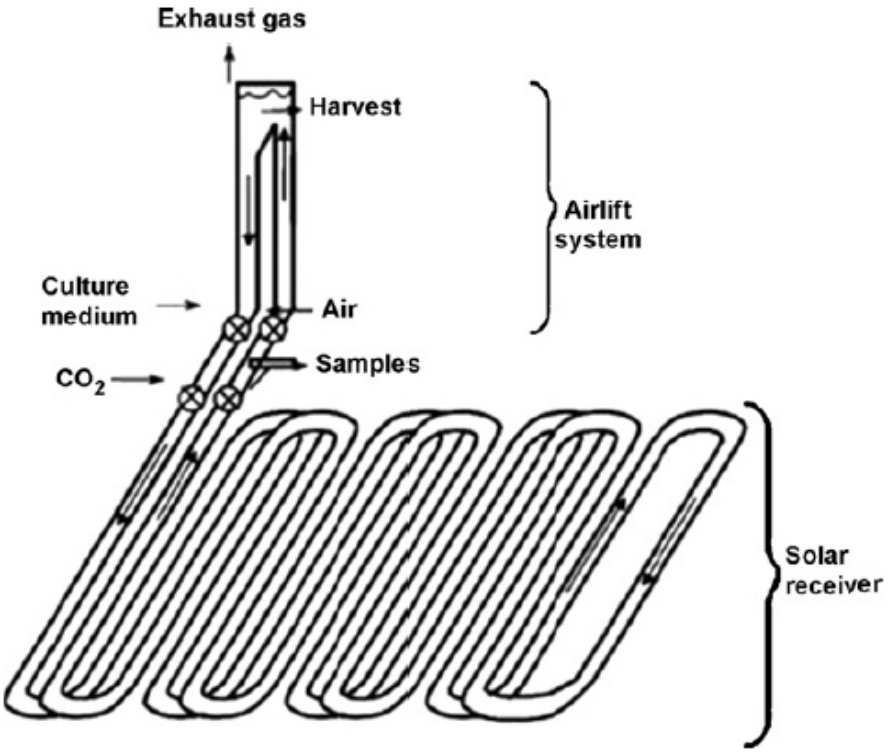

Figure 7. Helical type photobioreactor (Singh & Sharma, 2012).

3.2.2 Flat photobioreactors

Flat panel PBRs have a cuboidal shape, designed to minimize the light path. They are characterized by high surface area to volume ratio and open gas disengagement systems. CO_2 containing gas is also provided by various spargers in flat panel PBRs, and mixing can be either purely by incoming gas or aided by mechanical motors.

Inclined or verctical flat PBRs represent very promising culture systems (Borowitzka & Moheimani, 2013). These can be oriented and tilted at different angles in order to adjust the intensity of incoming light and make use of diffuse and reflected light. Flat panels can also be closely packed together in order to achieve high areal productivities. Air-bubbling can be used for mixing, ensuring adequate turbulence, a good mass transfer capacity, and scouring of the reactor walls. However, relatively high bubbling rates must be used to be efficient, which require typically much more energy than raceway pond mixing. Temperature control can be achieved by evaporative cooling (water spraying) or by heat exchangers. Some of the designs show good scalability.

As an example of flat photobioreactor designs, a Flat Panel Airlift (FPA) photobioreactor, developed and patented in the early 2000's, has recently been scaled-up and tested by Subitec GmbH for CO_2 removal (see "Pilots" section). The basic design of the reactor is a plastic plate divided into large riser zones, into which compressed air is injected, and smaller down-comer zones. The rising air bubbles induce vortices that move the cells in and out of the illuminated layers. Productivities of 1.5 g L^{-1} day^{-1} have been achieved with various microalgal species. Power requirements are 200 W/m^3. The reactor cost is about €1 L^{-1}, equivalent to about 40 €/m^2. The main advantages of this system are industrial relatively low reactor production costs, good mixing and short light-path. Using the numbers from the pilot installation a biomass production cost of 4.2 €/kg was estimated (Borowitzka & Moheimani, 2013).

Another recent development is the use of vertical flat-panel reactors made from thin polyethylene film, or vertical thin film reactors, which are expected to reduce the investment costs substantially. These designs allow for longer material lifetime and reduced energy requirements for cooling and mixing (Wijffels et al. 2010). The algal growth rate with GreenFuel Technologies vertical thin film configuration was estimated at 98 g/m^2/day[3].

3.3 Innovative concepts

3.3.1 Combined system – flat panel with open pond

A new approach is a coupled photobioreactor-open pond cultivation system, where PBRs are combined with a large open pond area. Raceway ponds are less expensive than PBR, although easily contaminated. PBRs, being closed, minimize air-borne contaminations, but have higher installation and operation costs. A combination of both systems seems a promising strategy for cost-effective cultivation and can also be well adapted to two-stage cultivation processes: in the first stage, cultivation is carried out in a PBR to produce the inocula; in the second stage, the algae are cultivated in the open pond until fully grown. Since the cultivation in the pond lasts only few days, there should not be time for contaminants to develop and prevail (Borowitzka & Moheimani, 2013). The results from pilot-scale activities show that selective cultivation is possible in this system, giving a high yield

[3] http://www.nrel.gov/biomass/pdfs/sun.pdf

and reduced costs. Algal oil production cost in a full scale system was estimated at US$84/barrel (Huntley & Redalje, 2007).

3.3.2 Algal turf scrubber

Another alternative cultivation technology is the algal turf scrubber, which has been used for cleaning waste waters (Manninen & Spilling, 2013). An algae turf scrubber typically creates a thin film of water flowing continuously over a suitable, flat substrate. A biofilm, consisting of algae and associated bacteria, quickly forms and can be very effective in re-moving both nutrients and contaminants. The biomass can be harvested by simply scraping it off at regular intervals. The biofilm that is formed is very effective in absorbing the light in the top layer, creating problems with high light intensities at the surface and self-shading for the cells further down.

3.3.3 McConchie-Stroud system

Fibre-optic-based systems, in which visible solar light is collected by mirrors, concentrated through lenses and delivered into the bioreactor via an array of flexible, optical fibres or transparent bars or plates, are also under development. As an example, Algae.Tec has developed a novel modular photo-reactor system called the McConchie-Stroud system[4]. Algae are cultivated in a synthetic material shaped in a honeycomb pattern for providing a high surface area within modified 40-foot steel shipping containers (Figure 8). The system allows growth of algae deep within the containers, and according to the company, requires only one tenth of the land that open ponds require. Light for growing the microalgae is supplied primarily through a parabolic solar collection system located close to the modules

Figure 8. Algae.Tec's photobioreactors (source: Algae.Tec).

[4] http://tenbagsfull.com.au/aeb/post/2013/7/10/aeb-the-mcconchie-stroud-system-details/4948

and secondarily through an artificial light system during night. According to the company, R&D work has shown that high yields of algae can be produced by the McConchie-Stroud system[5].

4 Restrictions

As living organisms algae require certain conditions to thrive. Water, carbon dioxide, minerals and light are all important factors in algal cultivation, and different algae have different requirements. These requirements need to be taken into consideration when assessing suitable systems for supplying CO_2 to algae.

4.1 Algal species

Algae for CO_2 uptake and as feedstock for bioenergy are a wide and diverse group of organisms that include microalgae, macroalgae (seaweed) and cyanobacteria.

Cyanobacteria (such as *Spirulina*) are often called blue-green algae, but some considered this misleading as cyanobacteria are prokaryotic (i.e. their cells lack a membrane-bound nucleus) and algae are eukaryotic (i.e. their cells contain a nucleus and other structures enclosed within membranes). Genetic manipulation of cyanobacteria is more advanced than that of eukaryotic algae, because many of the tools that have been developed for bacterial genetics can be used (DOE, 2014), making them potential organisms for biofuels production.

Table 3. Comparison of the growth characteristics and CO_2 fixation performance of microalgal strains under different CO_2 concentrations, temperatures, and NOx/SOx contents (Ho et al., 2011).

Microalgal species	CO_2 (%)	Temperature (°C)	NOx/SOx (mg L^{-1})	Specific growth rate (d^{-1})	Biomass productivity (mg L^{-1} d^{-1})	CO_2 consumption rate (mg L^{-1} d^{-1})	Reference
Nannochloris sp.	15	25	0/50	N.D	350	658	Negoro et al. (1991)
Nannochloropsis sp.	15	25	0/50	N.D	300	564	Negoro et al. (1991)
Chlorella sp.	50	35	60/20	N.D	950	1790	Maeda et al. (1995)
Chlorella sp.	20	40	N.D	5.76	700	1316[a]	Sakai et al. (1995)
Chlorella sp.	50	25	N.D	N.D	386	725[a]	Sung et al. (1999)
Chlorella sp.	15	25	0/60	N.D	1000	1880[a]	Lee et al. (2002)
Chlorella sp.	50	25	N.D	N.D	500	940[a]	Yue and Chen (2005)
Chlorogleopsis sp.	5	50	N.D	0.65	40	20.45	Ono and Cuello (2007)
Hot spring algae	15	50	N.D	3	266.7	501.3[a]	Hsueh et al. (2007)
Chlorococcum littorale	50	22	N.D	0.95	44	82[a]	Ota et al. (2009)

[a] Calculated from the biomass productivity according to the following equation: CO_2 fixation rate (Pco_2) = 1.88 × biomass productivity (mg L^{-1} d^{-1}), which is derived from the typical molecular formula of microalgal biomass, $CO_{0.48}H_{1.83}N_{0.11}P_{0.01}$ (Chisti, 2007).

The biodiversity of microalgae is enormous and they represent an almost untapped resource on the planet. About 200,000-800,000 species have been estimated to exist, of which about 50,000 are known. Several universities have collections amounting to 2,000-3,000 strains of algae have been cultivated for decades (DOE, 2014). The type of algae used depends on the desired product(s). *Chlamydomonas reinhardtii* is the most studied eukaryotic algae. It is not an abundant lipid producer, but can function as a model for understandning the fundamentals of lipid production. *Chlorella* is another well-studied genus of green algae, and some species are abundant lipid producers. *Dunaliella salina* has an outstanding salt tolerance and can be grown under extreme conditions (DOE, 2014). Diatoms are a major group of algae that are responsible for 20% of the total global carbon fixation. Open pond mass culture of microalgal strains has been demonstrated in only a few cases (*Dunaliella*), while other algae (e.g.

[5] http://algaetec.com.au/wp-content/uploads/2011/01/AlgaeTec_Prospectus.pdf

Chlorella, Haematococcus) have been mass cultured with considerable difficulty (Benemann, 2003). Most algal species cannot yet be mass cultured in outdoor ponds.

Macroalgae, or seaweed, represent a broad group of eukaryotic photosynthetic marine organisms. They have a low lipid content but are high in carbohydrates that can be converted to various fuels. As macroalgae typically require more energy for cultivation these are considered less suitable for biofuel production/CO_2 capture concepts than microalgae and cyanobacteria (Benemann, 1993).

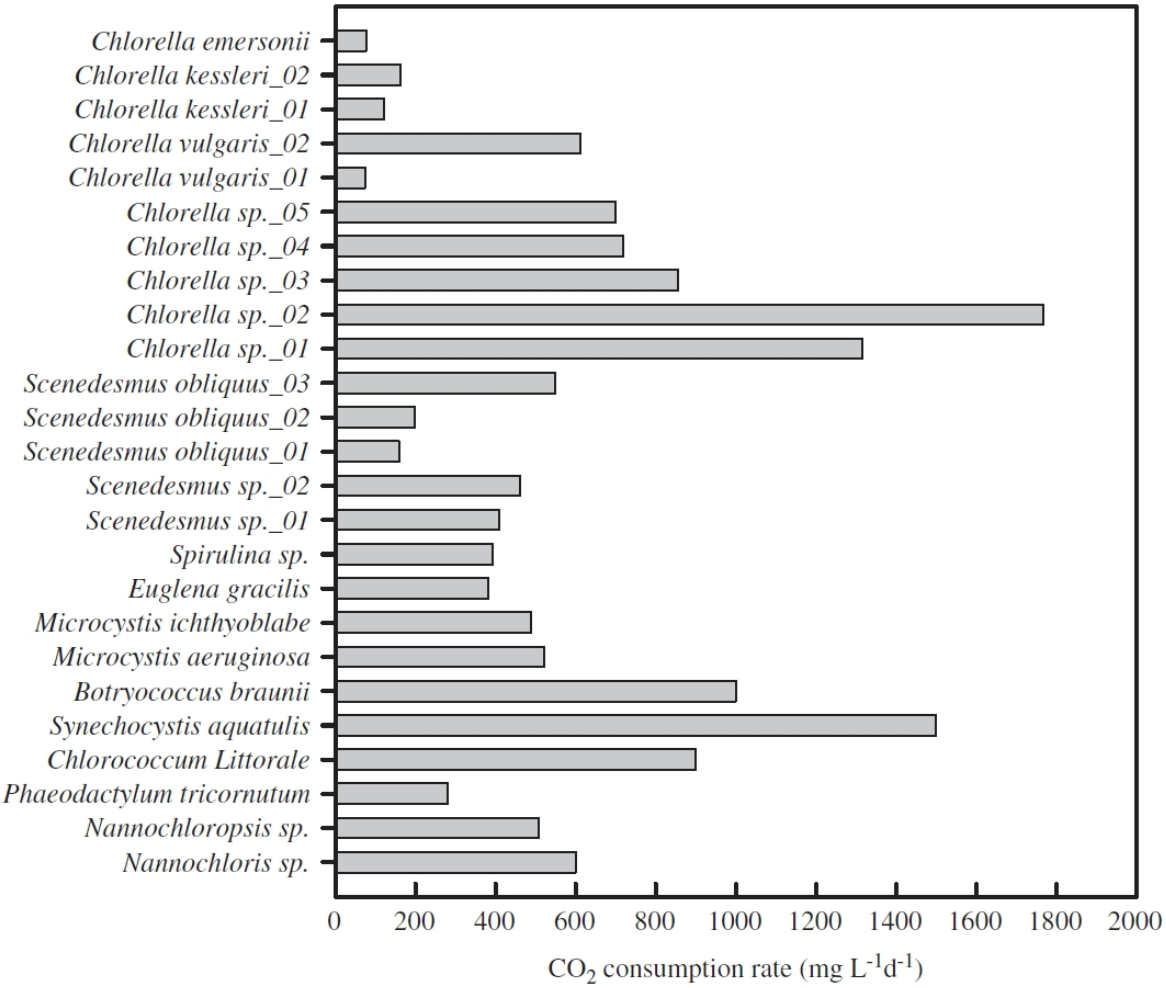

Figure 9. Example of the CO_2-fixation abilities (under batch operation) of 25 microalgal species reported in recent literature (Ho et al., 2011).

Microalgae and cyanobacteria can grow fast (particularly in waste waters) and contain valuable compounds. Favourable algal species for CO_2 capture should have a CO_2 fixation capability that positively correlates with the cell growth rate and light utilization efficiency (Ho et al. 2011). Species that grow well under natural day-night cycle are suitable for outdoor cultivation systems and strains that can directly use the CO_2 in power plant flue gases are preferred. High concentrations of CO_2 (>5%) is generally toxic to microalgae, presumably because the water becomes acidic from carbonic acid (Westerhoff et al 2010). However, some strains thrive in higher concentrations of CO_2. Table 3 lists microalgal strains that are tolerant to high-temperatures, high CO_2 concentrations and toxic compounds such as NOx and SOx. A few *Chlorella* and cyanobacteria species could grow well and achieve a high

CO_2 fixation capacity (0.5-1.8 kg/m^3/day) with a relatively high tolerance for temperature or CO_2 concentration (Figure 9). Some *Chlorella sp.* have both high CO_2 removal uptake and an affinity for removing sulphur dioxides, nitrogen oxides and volatile organic compounds.

4.2 Feed gas quality

Bringing a concentrated source of CO_2, such as the flue gas from a power plant, into contact with algae to increase capture efficiency and productivity has its challenges. It is important to consider the quality of the flue gas or vent gas and the possible impact it might have upon the algal cultivation.

Efficiently capturing carbon dioxide from an elevated CO_2 source depends on many factors, but one of the most limiting at present is the ability of the algae to capture and fix carbon at a sufficient rate to avoid acidification of the medium (and thus inhibition of death of the culture). Due to this, research is under way to isolate and engineer strains that are tolerant to high CO_2 levels, and are effective at taking up large quantities of CO_2 in a single stage (Milne et al., 2009).

Much work has been done on the effect of different flue gas constituents on microalgal growth rates and carbon dioxide fixation. Overall, microalgae have shown great tolerances to harsh environments. Regarding flue gases the most important concern appears to be the high level of SOx combined with the elevated temperatures of the flue gas.

4.2.1 SOx

Sulfur oxides, particularly SO_2, can have a significant effect on the growth rates and health of microalgae. The main concern comes from the effect SO_2 has on pH: when the SO_2 concentration reaches 400 ppm in the flue gas, the pH of the medium can become lower than 4 in less than a day, which significantly affects the productivity of most microalgae (Stepan et al. 2002). Although some authors claim that this can be counteracted by adding an alkaline (e.g. NaOH), it clearly imposes restrictions, as Westerhoff et al. (2010) discovered that the growth of *Scenedesmus* and *Chlorella* was reduced by 50 mM Na_2SO_3 and 0.5 M Na_2SO_3 resulted in cell death. However, many microalgal species can tolerate moderate levels of SOx (up to 150 ppm; Matsumoto et al., 1997). Therefore, control of SO_2 in the flue gas fed to the algae is needed.

4.2.2 NOx

As with sulphur oxides, nitrogen oxides can also affect the pH of the algal medium and thereby lower algal productivity, but to a lesser degree (Stepan et al. 2002). Typical NOx levels in treated flue gases (< 50-100 mg/m^3) do not seem to inhibit the growth rate of microalgae (Doucha et al., 2005; Negoro et al., 1993; Matsumoto et al., 1997). Nitrogen oxides can also serve as a nitrogen source for microalgae, because NO is oxidized to NO_2 in the presence of oxygen in the cultivation (Matsumoto et al., 1997). The greater the oxygen content of the medium, the greater the NO_2 production and microalgal productivity rates. Similarly as with SOx emissions, current European emission standards limit the emission levels to the order that seem tolerable for microalgae.

4.2.3 H_2S

Algae are sensitive to high levels of dissolved hydrogen sulphide. H_2S concentrations above 1 g S m^{-3} in pond surface waters can significantly reduce algal growth (Pearson et al. 1987).

4.2.4 O_2

Oxygen and carbon dioxide are competitive substrates,meaning that both can react with RuBP in plants and algae (Moroney & Ynalvez, 2009). Therefore, elevated concentrations of oxygen also result in growth-inhibiting algal photorespiration. In addition, algae produce oxygen while consuming CO_2. Typically, industrial flue gases contain lower oxygen concentrations than that of air (21 vol-%), meaning that these should offer more favourable conditions for algal growth in terms of oxygen content than air. However, there are exceptions. For instance, Vance & Spaldning (2005) found no effect on growth of *Chlamydomonas* when changing the oxygen concentration from 20% to 2%.

4.2.5 CO_2

Similar to SOx, NOx, and H_2S, carbon dioxide is also acidic in water. Therefore, high concentrations of CO_2 in the incoming gas lower the pH of the cultivation water unless it is buffered. For most algal species increasing the feed gas CO_2 concentration up to 5 vol% seem to have a positive effect on growth, while increasing the feed gas CO_2 concentration over 15 vol% seem to have a negative effect on growth. Many species can tolerate higher CO_2 concentrations, although the optimal concentration for growth is typically lower (Table 4). However, measuring the CO_2 concentration in the gaseous phase does not give the correct picture of the CO_2 concentration that the algae are exposed to. Many parameters affect the solubility of CO_2 in the medium, such as temperature of the cultivation media and the chemical composition of both the cultivation media (nutrients and other chemicals possibly buffering or affecting the pH of the media) and feed gas (e.g. presence other acidic gases).

Table 4. CO_2 tolerance of various species (review by Ono & Cuello, 2003)

Species	Known Maximum CO_2 Concentration
Cyanidium caldarium	100%
Scenedesmus sp.	80%
Chlorococcum littorale	60%
Synechococcus elongatus	60%
Euglena gracilis	45%
Chlorella sp.	40%
Eudorina spp.	20%
Dunaliella tertiolecta	15%
Nannochloris sp.	15%
Chlamydomonas sp.	15%
Tetraselmis sp.	14%

4.2.6 Soot dust and ash

The effect of soot dust and ash containing heavy metals has received limited attention. Soot and ash will absorb light, reducing the available light for the algae. Soot dust concentrations greater than 200,000 mg/m3 influence algal productivity negatively, but commonly the concentration in flue gas is on the order of 50 mg/m^3 (Stepan et al. 2002). Similarly, high concentrations of heavy metals can affect algal productivity, but as the typical concentration in flue gas is very low.

4.3 pH

There is a complex relationship between CO_2 concentration and pH in microalgal cultivation systems due to the chemical equilibria of the various carbonate species (Figure 3). Most microalgal species are favored by neutral pH, whereas some species are tolerant to higher pH (e.g. *Spirulina platensis* at pH 9) or lower pH (e.g. *Chlorococcum littorale* at pH 4; Kumar et al., 2010). Increasing CO_2 concentrations can lead to higher biomass productivities, but also lowers the pH, which has an adverse effect upon the microalgal physiology (Kumar et al., 2010). As microalgae consume CO_2 the pH can rise up to 10-11 in open ponds, which also can inhibit their growth. The growth of many algal species is increasingly inhibited at pH higher than 8. Also, the speciation of NH_3 and NH_4^+ is strongly dependent on pH: NH_3 competes with water molecules in oxidation reactions leading to release of O_2.

From a CO_2 capture perspective, the higher the pH of the cultivation water is, the better its CO_2 uptake capacity (i.e. more CO_2 can be dissolved). However, at higher pH more of the carbon is in the form of bicarbonate and carbon ions and less carbon is in the form of dissolved CO_2. In this sense, algal species that can thrive at high pH, i.e. feed on bicarbonate and possibly carbonate ions, are of particular interest from a CO_2 capture perspective.

4.4 Temperature

Temperature is one of the major factors that regulate cellular, morphological and physiological responses of microalgae (Kumar, 2010). Higher water temperatures increase the metabolic activity of microalgae, but also decrease the solubility of CO_2 (Beardall & Giordano, 2002). The optimal temperature varies among microalgal species. Many microalgae species are capable of carrying out photosynthesis and cellular division at 15-30 °C, with optimal conditions at 20-25 °C (Ras et al., 2013).

Temperature control is a major engineering challenge, especially in closed photobioreactors and in regions of high irradiation. According to Borowitzka & Moheimani (2013), 95% of areal specific light energy gets converted to heat. Mechanical equipment and mixing of the cultivation also add heat to the system. Most algae will not grow in temperatures above 35°C, and to keep the algae growing the cultivation units must be cooled. A high light surface to reactor footprint ratio helps to keep the cultivation temperature at ambient temperature, but even during summer in central Europe additional cooling (e.g. by spraying cooling water at the outer wall of the reactors) is necessary (Borowitzka & Moheimani, 2013).

4.5 Light

Generally, the amount of light energy received and stored by algae has a direct relationship with the carbon-fixation capacity, which in turn determines the productivity in the biomass and cell growth rate (Jacob-Lopes et al., 2009). Therefore, it is important to optimize the light utilization efficiency in order to obtain a high CO_2 fixation capacity. General approaches to enhance light utilization relies on increasing the surface area and shortening the light path and layer thickness. Current PBR designs aim at having a high surface to volume ratio (Ho et al., 2011). The duration of the light cycles (night/day) is a fundamental criterion when assessing carbon dioxide uptake and biomass production by microalgae and cyanobacteria. In addition, genetic engineering is employed to improve photosynthetic efficiency. Normally, cell growth is directly proportional to the light intensity/light period until a certain threshold in illumination level is reached that can damage the photosystem (photo-inhibation). In natural solar energy, the photosynthesis of most microalgae is saturated at about 30% of solar

radiation, in the range of 1700-2000 µE/m/s (Pulz, 2001). Mixing of the culture is important in order to make sure that all of the cells get similar amounts of light.

4.6 Nutrients

Nitrogen is the most important element required for microalgal nutrition in addition to CO_2. Since nitrogen is a building block of both nucleic acids and proteins it is part of the primary metabolism of microalgae (Kumar et al., 2010). Fast-growing microalgal species prefer ammonium rather than nitrate as their primary nitrogen source. When ammonium or nitrate is used as the nitrogen source, the pH of the medium changes with the growth of algae. Absorption of NO_3^- ion leads to an increase in the pH of the medium, whereas consumption of NH_4^+ ion leads to a decrease in pH (Borowitzka & Borowitzka, 1988).

The third most important nutrient for microalgal growth is phosphorus, and is typically supplied as phosphates. In the case of marine microalgae, seawater supplemented with commercial nitrate and phosphate fertilizers is commonly used for production of microalgae. Trace elements, such as metals (Mg, Ca, Mn, Zn, Cu and Mb) and vitamins, are typically added for effective cultivation (Kumar et al., 2010).

5 CO_2 supply systems

Under natural growth conditions, microalgae use CO_2 dissolved into water from air (air contains about 400 ppmv CO_2). CO_2 is poorly soluble in water and therefore algae have developed different mechanisms to maximize CO_2 uptake under these low CO_2 concentrations. However, most microalgae can tolerate and utilise substantially higher levels of CO_2. At typical flue gas CO_2 concentrations (10-15 vol-%), microalgae show no signs of significant growth inhibition. On the contrary, microalgae respond better to increased carbon dioxide concentrations, outgrowing those exposed only to ambient air. Therefore, microalgal cultures must be supplied with additional CO_2 to be productive. As pH of the cultivation medium raises as CO_2 is consumed by the algae, CO_2 injection is also used as a means for controlling the pH of the culture and maintaining optimal conditions for the algal species being grown.

The main concern in CO_2 supply to the algal cultivation is to maintain a CO_2 concentration suitable for the algae to feed on. Although often marketed as a benefit, the need to dissolve large amounts of CO_2 in the algae growth medium is an energy-intensive and expensive requirement of mass algal cultures. Also, large-scale cultivation plants need to be located next to a relatively large CO_2 emitting facility, such as a power plant or other CO_2-emitting industry.

According to Borowitzka & Borowitzka (1988) carbonation, i.e. CO_2 supply, of the cultivation is one of the most difficult processes in micro-algal cultivation. The transfer of CO_2 through a neutral gas-liquid interface is so slow that special methods must be devised to provide the lengthy time and wide surface area required to maximize transfer. Packed-column carbonation, often used in industry, is discouraged because its low pH frequently harms or disrupts algal cells. According to Borowitzka & Borowitzka the most effective compatible method available to transfer CO_2 to algal cultures is counter current carbonation, where gas is injected as minute bubbles into a column of water. The water velocity is adjusted so that the small bubbles of CO_2 rising against the current essentially hang suspended in the water until fully absorbed.

CO_2 transfer into ponds and utilization by the algae is sufficiently well understood (e.g. Benemann et al. 2003). However, engineering designs for CO_2 injection have yet to be demonstrated at the large scales required.

The following possible methods for transferring the CO_2 in flue gases to the algae have been identified.

- Direct injection: Flue gas (or pure CO_2 mixed with air) is injected and dispersed into the cultivation water. In open ponds this normally takes place from gas distributors placed on the bottom of the pond. In PBRs, the injection method is typically counter-current bubble carbonation.
    - In case pure CO_2 is used as the CO_2 supply it must first be separated from flue/vent gas. The CO_2 gas is mixed with air in order not to cause acidification of the cultivation media.
- Scrubbers/absorbers using cultivation water
    - CO_2 is absorbed into water in a separate absorber (e.g. bubble column). The algae are then grown in the water containing dissolved CO_2.
- Chemical solvent scrubbers and cultivation in the solvent
    - CO_2 is absorbed into an aqueous solution containing sodium/ammonium carbonate or amines, in which the algae are subsequently grown. This method could be suitable for species that feed on bicarbonate.

5.1 CO_2 supply for open ponds

5.1.1 Direct gas injection

The simplest CO_2 supply system is to bubble CO_2 containing gas through the cultivation medium. However, bubbling gas through a shallow pond transfers only a small amount of CO_2 contained in the gas, since the residence time of the bubbles in the media is brief as the bubbles travel a relatively short path from the bottom of the pond to the surface. Therefore, a major drawback of this type of CO_2 supply is that 80-90% of the CO_2 is lost to the atmosphere (Becker, 1994; Richmond and Becker, 1986). In order to minimise the CO_2 loss, injection of CO_2 is regulated by monitoring the pH level. The transfer of CO_2 through the gas-liquid interface can be described by the following equation (Borowitzka & Moheimani, 2013):

$$Q = kA(C_s - C_d) \quad (7)$$

where Q = the mass flow of CO_2 (mM/L), k = the mass transfer coefficient (M/min), A = the gas-liquid interface area (m^2), C_s = the saturation concentration of dissolved CO_2 in the liquid in equilibrium with the partial pressure of CO_2 in the gas phase (mM/L), and C_d = the instantaneous concentration of dissolved CO_2 in the liquid (mM/L). Since in most CO_2 containing industrial waste gas streams the CO_2 partial pressure is relatively low and thus C_s will also be low. The gas transfer efficiency can be improved by using smaller bubbles, resulting in a larger gas-liquid interface area compared to large bubbles. Smaller bubbles can be achieved using sintered gas diffusers. However, gas diffusers get rapidly fouled and require frequent cleaning. The residence time of the bubbles can also be increased by locating the diffusers just upstreams of the paddle wheel, so that the bubbles are dragged along horizontally by the flow of water under the paddle wheel. Another option is to make the pond deeper around the injection pipes, so that length that the bubbles travel is increased (Figure 10). Raising the concentration of CO_2 is also a possibility but is generally considered expensive and impractical in an algae-for-biofuels process.

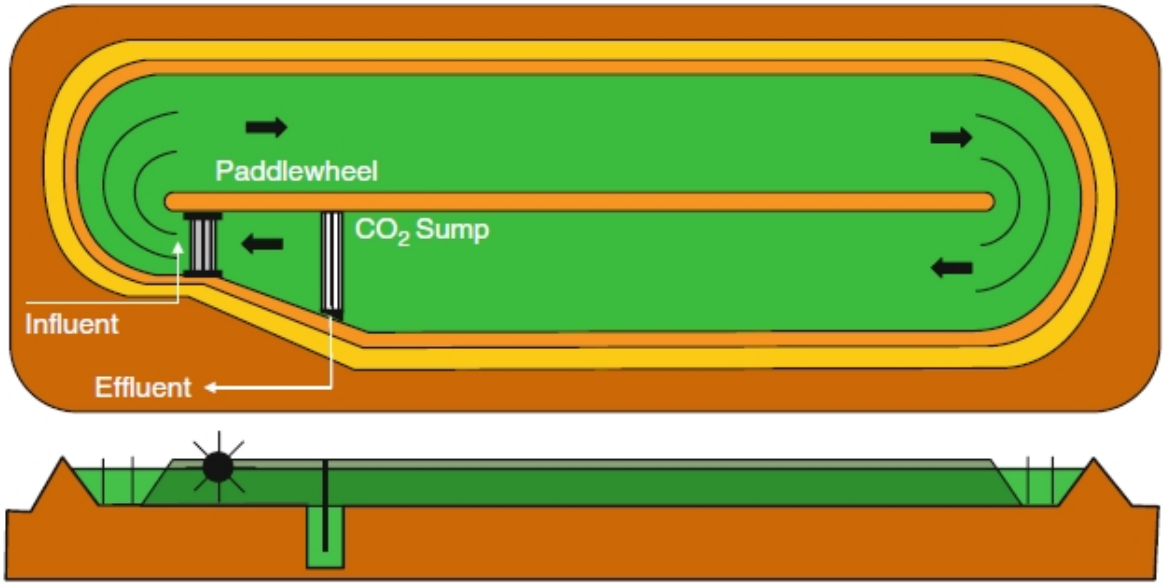

Figure 10. Plan view and side elevation of a high rate algal pond with CO_2 addition (Borowitzka & Moheimani, 2013).

Several methods have been developed to increase the efficiency of CO_2 transfer in ponds. The simplest type is gas bell, i.e an open vessel placed upside down above the gas distributor. Variation on the gas bell is a floating gas injector consisting of a plastic sheet, which gets inflated by the CO_2 released from diffusers. The plastic sheet has a frame equipped with a spoiler downstream of the injector to produce a high turbulence for increasing the gas transfer into the liquid. According to Vasquez & Heussler (1985), using this type of floating injector system, an injector area covering 4 % of the pond is required to maintain a minimum concentration of 10 mg/L dissolved CO_2.

5.1.2 Separate absorbers

Instead of directly injecting the CO_2 containing gas into ponds the cultivation water could be led into separate absorber for absorbing the CO_2. Using a separate absorber allows for better process control. For instance, CO_2 uptake can be maximized by designing the absorber so that the flue gas residence time and contact surface are maximized and the desired CO_2 concentration in the cultivation water is achieved. Examples of absorbers are packed bed towers, spray towers, bubble columns and hollow fibre modules. Also, having a separate absorber enables the flue gas to be returned to the flue gas stack, so that only the dissolved CO_2 (and other dissolved flue gas components) are transported to the open pond. This reduces the possible health risks mentioned earlier associated with injecting flue gases as such into open ponds. In addition, the cooling requirements of flue gases can be reduced, as the CO_2-lean flue gases exiting the absorption column can be used for cooling the incoming CO_2-rich flue gases. An example of this can be seen in Cyanotech's concept (see section on "Pilots").

5.1.2.1 Bubble-type absorption columns

The bubble-type absorption column seems better suited for capturing large amounts of CO_2 into water than packed beds, since absorption in a bubble-type column can be 3-10 times faster than in a packed bed column (Houghton et al., 1957). Therefore, the reactor volume required for absorbing the same amount of CO_2 using a bubble-type column is roughly one third to one tenth of that required by a packed bed column. However, using a bubble-type

column requires more energy than a packed bed column, due to the pressure drop caused by the bed of water that the gas must be pushed through. Putt et al. (2011) designed and tested a 3 m high bubble column for absorbing 90% of the CO_2 in enriched air containing 5 % CO_2. The experiments showed that a 82-83% capture efficiency could be obtained using the column. This capture efficiency is much higher than what normally can be achieved with water at such low partial pressures of CO_2. It is likely that the nutrients and additional NaOH used for maintaining the incoming water at a pH of 9-10 improves the capture efficiency and capacity of water significantly.

5.1.2.2 Hollow-fibre modules

Microporous membranes, in hollow-fiber forms, are being developed for supplying CO_2 to algal cultures. These consist of bundles of polymeric porous fibers with typical diameters of 250 µm, connected to inlet/oulet ports in their ends and contained in housings. As a result of the enormous number of fibers inside each module, the ratio between the membrane outer area and the external dimensions is quite high. These have been of particular interest when the CO_2 source is purchased CO_2 gas and hence CO_2 losses to the atmosphere need to be minimized to save feedstock costs. Better CO_2 mass transfer rates can be achieved using hollow-fiber modules in comparison to plain bubbling (e.g. Carvalho & Malcata, 2001). However, membranes are relatively expensive and are likely to be even more difficult to clean than other absorber types.

5.2 Photobioreactors

5.2.1 Direct gas injection

The most common mode of CO_2 supply for photobioreactors seems to be using direct gas injection. Direct gas injection in PBRs has the additional benefit that the flow of the gas is used for mixing the culture and removing oxygen in addition to provide CO_2 (Kumar et al. 2011). Examples of these types of PBRs are airlift reactors, bubble column reactors, tubular PBRs and flat panels (see section on “Cultivation systems”). An exception is the horizontal tubular PBR design, which suffers from oxygen buildup and high energy requirements to achieve the turbulent flow needed for mixing of the culture. The helical type PBR is likely to give the best CO_2 uptake efficiency of these systems due to its long contact time with CO_2. According to Kumar et al., the airlift reactor seems the most suitable reactor for CO_2 sequestration from the flue gas due to its high gas transfer, uniform mixing, low hydrodynamic stress, and ease of control.

5.2.2 Separate absorbers

Similarly as for open ponds, separate CO_2 absorbers can also be used for PBRs. The expected advantages are lower energy requirements and simpler reactor design, as the flue gas stream does not need to be driven through the PBRs. The main disadvantage is likely to be the loss of mixing normally provided by the gas injection. An example of the use of a separate absorber is the RWE algae pilot at the Niederaussem power plant (see section on “Pilots”). In RWE’s pilot, the power plant flue gases are withdrawn from the flue gas desulphurisation unit, cooled and fed to a bubble reactor containing the cultivation medium (Figure 11). The CO_2-enriched algal suspension is fed into photobioreactors that are made of clear plastic hoses that are fixed in a V-shape to supports. The PBRs are stirred by blowing additional air bubbles from the bottom of the reactors.

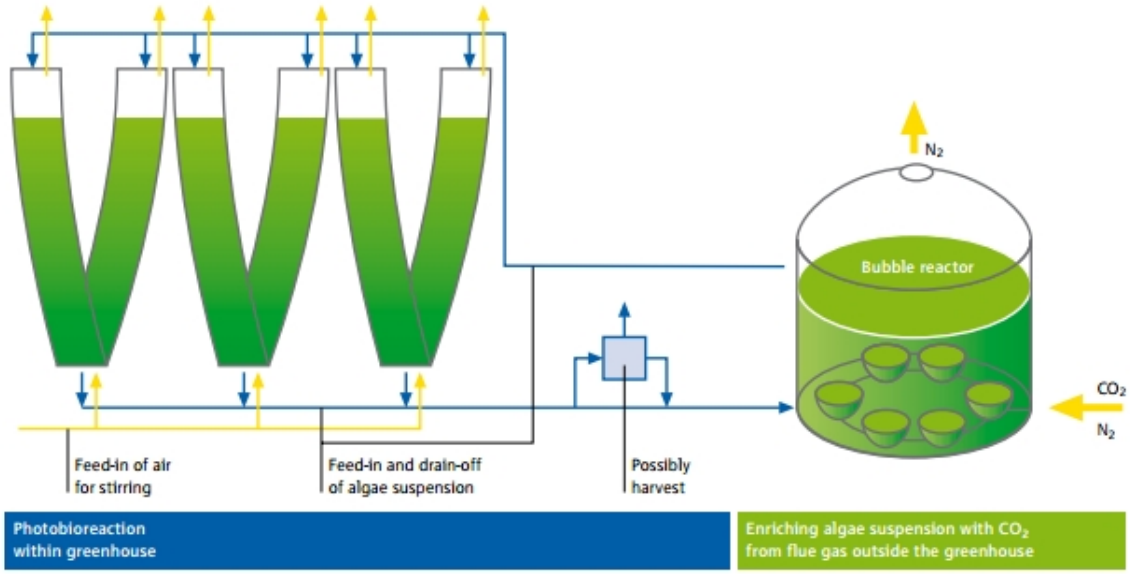

Figure 11. Process diagram of photobioreactor with separate bubble reactor for CO_2 absorption into cultivation media (RWE Power, 2009).

5.3 Chemical solvent scrubbers and cultivation in the solvent

For a chemical absorbent liquid, like an amine or amino acid solutions, the solubility of CO_2 is tenfold to that of CO_2 in water.

According to Goetheer et al. (2011) *Spiruina Platensis, Neochloris oleoabundans, Chlorella vulgaris,* and *Scenedesmus obliquus* could be suitable for these types of systems, since these can tolerate pH values higher than 8. Fernandéz et al. (2009) tested cultivation of *Anabaena, Synechocystis, Chlorococcum, Botryococcus, Spirulina* and *Chlorella* in sodium carbonate/bicarbonate solutions for this particular purpose, with *Synechocystis* and *Chlorococcum* showing best performance. Goetheer et al. (2011) tested the growth of micro-algae in 0.1-1 M solutions of amino acids (β-alanine, sarcosine, 6-amino-hexanoic acid, taurine, and L-glutamic acid), amines (monoethanolamine, diethanolamine, and methyl diethanolamine) and carbonates (K_2CO_3, Na_2CO_3, NH_4HCO_3).

It is known that bicarbonate salts (e.g. $NaHCO_3$) can be used instead of CO_2 to provide additional inorganic carbon to algae (Borowitzka & Moheimani, 2013). The addition of bicarbonate salts has a small effect on the pH of the cultivation medium (in contrast to bubbling CO_2), but it increases the ionic strength of the medium which may lead to problems over longer time in freshwater algae culture.

Using a chemical solvent to increase the solubility of CO_2 in the cultivation water not only restricts the cultivation to algal species that can tolerate these chemicals but it is also likely to increase the operational costs due to requirements for make-up chemicals.

5.4 Separation of CO_2

Many algal cultivations use pure CO_2 and mix it with air. Various processes are available to separate CO_2 from flue gas streams and produce pure CO_2 that can be easily transported in pipelines and tanker trucks & ships (IPCC, 2005). However, these processes require a lot of energy. Also, as algal cultivations anyway are normally fed with a diluted stream of CO_2, the

only reason to separate CO_2 from a flue gas stream for use in a large-scale algae cultivation would be if the CO_2-emitting facility is located far away (tens to hundreds of kilometres) from the algal cultivation. Still, the cost for the CO_2 capture and transport system is likely to be a significant share of the total cost for the algal cultivation so it is probably wiser to place the algal cultivation near the industrial CO_2 source so that direct injection or cheap water scrubbers can be employed.

6 Pilots

In this section, micro-algal pilots aiming at CO_2 capture are identified and reviewed. Numerous pilot and commercial demonstration projects are currently underway (reportedly 200 or more ventures exist); including retrofitting algal cultivation systems to power station exhausts (GCCSI, 2011). This overview focuses on pilot projects, where 1) flue gas is used, 2) maximization of CO_2 capture is targeted, and 3) cultivation is carried out at a larger scale (i.e. not lab-scale).

6.1 Cyanotech (USA)

Although most commercial algae facilities use pure CO_2 gas for feeding the algae, Cyanotech, based in Hawaii, uses flue gas as a source of CO_2 for producing various types of Spirulina and Astaxanthin that is sold as natural health products[6]. Cyanotech's patented concept uses a fossil fuel-motor that generates electricity (Jensen & Reichl, 1996). The hot exhaust gas is used for drying algae, while the carbon dioxide is recovered for feeding the microalgae. The electricity produced is used at the plant for driving motors, pumps and artificial illumination. According to the patent, the hot flue gases go first through a system of heat exchangers, a cyclone and a condenser, which utilize the heat in flue gases for spray draying the algae (Figure 12). Cooled flue gases are fed to a CO_2 scrubber, where aqueous filtrate from the pond absorbs CO_2 from the flue gases. The aqueous stream containing dissolved CO_2 is fed back to the culture pond.

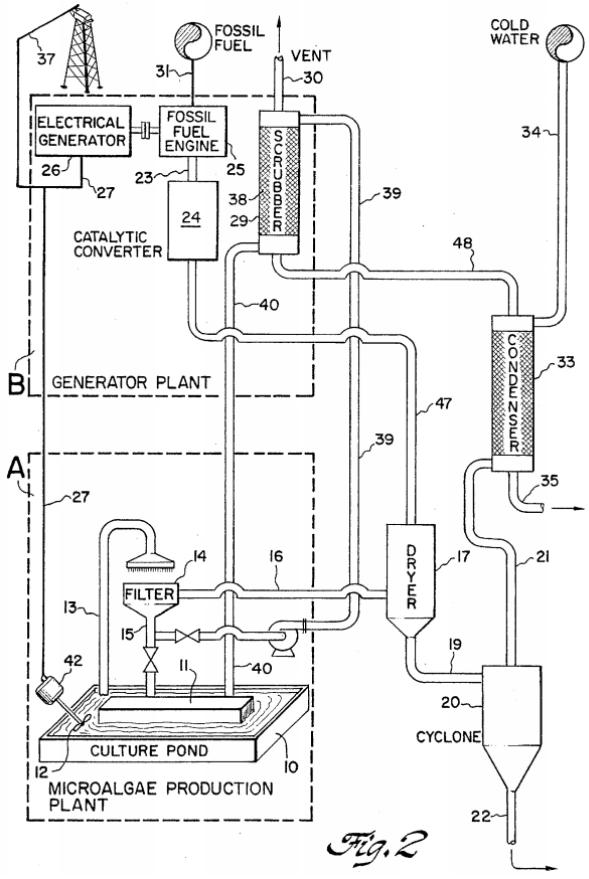

Figure 12. Cyanotech's patented concept for integrated microalgae production and electricity cogeneration (Jensen & Reichl, 1996).

[6] http://www.cyanotech.com/pdfs/Cyanotech_AR_7-12-13_SECURED.pdf

6.2 The RITE Biological CO_2 Fixation Programme (Japan)

In 1990 an R&D programme was launched in Japan to develop methods for CO_2 fixation by biological micro-organisms including projects at Research Institute of Innovative Technology for the Earth (RITE). The focus was on culture systems using closed photobioreactors with or without solar collectors to transmit light into the reactors (Borowitzka & Moheimani, 2013). Almost all of the studies were on small lab-scale. Some small-scale pond studies were also carried out near Sendai by Mitsubishi Heavy Industries and several electric utilities. These studies showed that microalgae could be grown on untreated CO_2-containing flue gas from power stations.

6.3 Laboratory for Microalgal Culture (Czech Repbulic)

The Laboratory of Microalgal Culture has been developing algal cultivation pilots since 1960 (Borowitzka & Moheimani, 2013). Doucha et al. (2005) successfully tested the use of flue gas containing 6-8 vol-% CO_2 for cultivating *Chlorella* sp. in the laboratory's outdoor photobioreactor, having a 55 m^2 culture area. The pilot is a thin-layer, open, inclined cultivation system, developed for large-scale cultivation. The utilisation of CO_2 was also monitored and reported. The degree of CO_2 flue gas decarbonization in the algal suspension

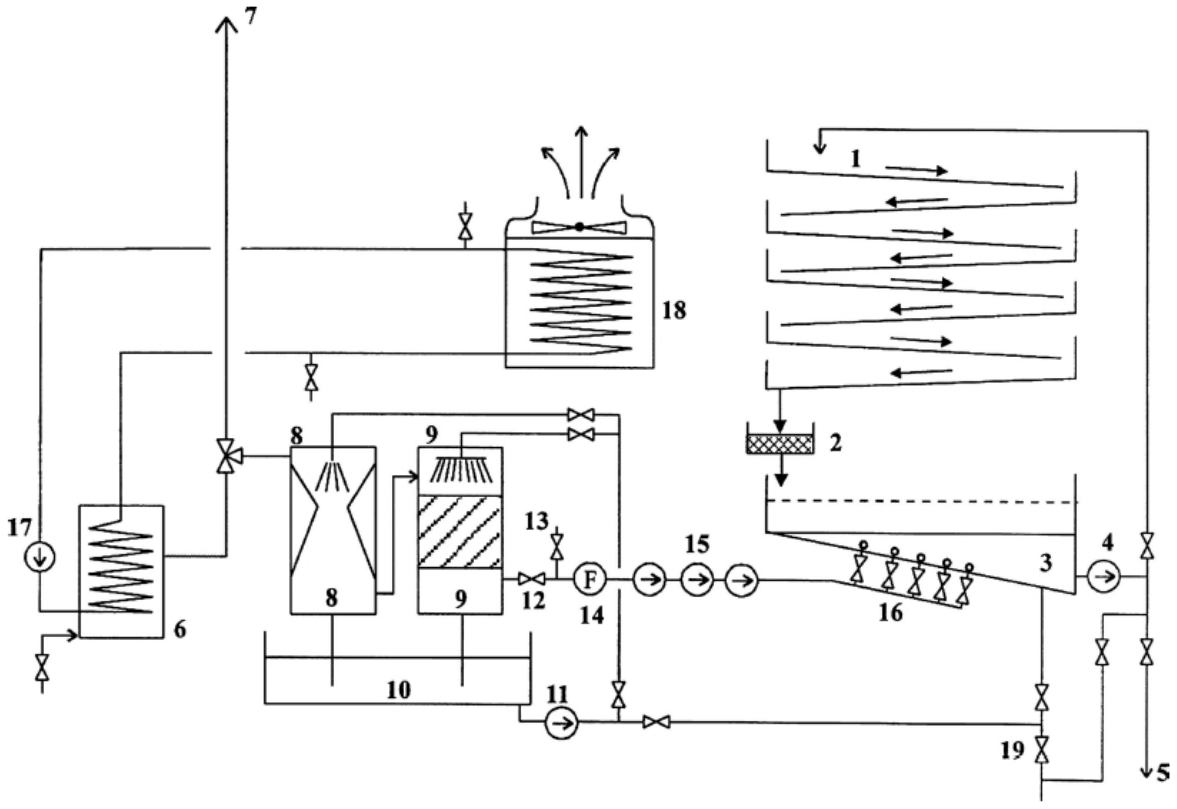

Figure 13. Schematic diagram of an experimental photobioreactor for cultivation of microalgae using flue gas. (1) cultivation lanes; (2) sieve filter; (3) retention tank; (4) circulation pump; (5) harvesting of algae; (6) gas boiler; (7) chimney; (8) flue gas cooler; (9) flue gas scrubber; (10) cooling water tank; (11) water circulation pump; (12) flue gas valve; (13) air valve; (14) gas flow meter; (15) gas blower set; (16) saturation/aeration system; (17) hot water pump; (18) air cooler; (19) water in/out (Doucha et al., 2005).

achieved was 10–50%. In this system, flue gas from a natural gas combusted boiler was transported by blowers via a Venturi gas cooler (Figure 13; 8) and scrubber (Figure 13; 9) to the saturation system (Figure 13; 16). Flue gas was fed through porous ethylpropylenedimer (EPDM) membrane tubes placed at the bottom of a retention tank and saturated the suspension with CO_2. At night the suspension was kept in the retention tank and aerated. To minimize losses of dissolved CO_2 from the algal suspension into the atmosphere, the partial pressure of dissolved CO_2 at the end of the culture area was maintained at a minimum pCO_2 of 0.1–0.2 kPa, which was necessary for non-limited algal growth.

6.4 GreenFuel Technologies (USA)

GreenFuel Technology was started in 2001 as one of the first algae-to-biofuel companies in the world[7]. Their first pilot plant for biofuel production was built around MIT's 21 MW power plant – the first one ever to recycle CO_2 and nitrogen effluents into biodiesel. Larger pilot units were tested from 2005 onwards at Arizona Public Service (APS) Company's Redhawk power plant in Arizona[8]. The first pilots used the inclined air-lifted photobioreactor technology tested at MIT (also presented earlier) and ran for 15 months[9]. In these, flue gas is introduced at the bottom of the reactors, in which algae are suspended in a media, with nutrients added to optimize the growth rate (Figure 14). A portion of the media is withdrawn continuously from

Figure 14. Greenfuel Technologies GEN3 bioreactors at Arizona Public Service Company

[7] http://www.algaeindustrymagazine.com/aim-interview-dr-isaac-berzin/

[8] http://thefraserdomain.typepad.com/energy/2006/12/arizona_public_.html

[9] http://www.nrel.gov/biomass/pdfs/sun.pdf

the bioreactor and sent to dewatering to harvest the algae. A blower pulls the flue gas through the bioreactor. Using an induced draft fan provides several operating advantages, including ensuring minimal disruption to power plant operations, simplifying retrofits to existing facilities. In 2007, vertical “v”-shaped thin film reactors were installed at APS Redhawk (that are visually very similar to those tested at RWE).

In 2007, the company had to shut down its third-generation bioreactor facility in Arizona after the plant produced more algae than the company’s equipment could handle. At the same time, the company found that its algae harvesting system would cost twice as much as expected[10]. According to the founder of GreenFuel Technology, the process was not economically viable – the price was about 800 USD per barrel.

6.5 Seambiotic (Israel)

Seambiotic Ltd.’s pilot facility for the cultivation of marine microalgae was established in 2006. It is located at the Israel Electric Corporation’s (IEC) Rutenberg coal-fired power station, Israel[11]. The algae are cultivated in open ponds using flue gas from

Figure 15. Seambiotic’s algae pilot plant in Israel.

[10] http://en.wikipedia.org/wiki/GreenFuel_Technologies_Corporation

[11] http://www.seambiotic.com/uploads/Seambiotic%20Ltd.%20-%20Algae%20Pilot%20Plant%20white%20paper.pdf

the power station for providing CO_2 enrichment. The total area of the plant is 1,600 m^2, of which the open pond surface area is about 1,000 m^2. Flue gas at ambient temperature and a CO_2 content of 12% is dispersed into the pond water by underwater bubble aerators or diffusers. The flue gas diffusers are placed in the liquid culture about 20 cm deep. Diffusing flue gas usually dissolves CO_2 in the liquid medium to the somewhat acidic pH level of 5.2. According to Seamiotic, carbonic acid is added to control the pH of the culture at approximately 7 while maintaining the total dissolved carbon (TDC) at 2–5 mM. The algal growth rate using flue gas desulphurization (FGD) gases was found to be about 50% higher than when using pure food-grade CO_2 and fossil oil. The FGD gases contain a range of heavy metals essential for algal growth, such as vanadium, strontium, mercury, and zinc, in ppb concentrations. The algae are cultivated using seawater. No fresh water is needed. As most species of the marine unicellular algae can withstand a wide range of salinities, the water can be recycled for a few growth cycles.

6.6 University of Almeria (Spain)

The serpentine reactors developed at the Department of Chemical Engineering of the University of Almeria (Spain) are a two-layer, 4,000-L horizontal tubular PBR, made of 10 cm diameter Plexiglas ® tubes connected by U-joints to form a single 400 m long loop. This pilot has been used for production of lutein-rich biomass of freshwater microalgae *Scenedesmus*

Figure 16. Tubular photobioreactor pilot at University of Almeria[12].

[12] http://www.southampton.ac.uk/engineering/research/facilities/algal_facilities.page

almeriensis. Adopting a dilution rate of about 35%, a mean volumetric productivity of 0.4 g L^{-1} day^{-1} (corresponding to an areal productivity of about 20 g m^{-2} day^{-1}) was attained in winter with *Nannochloropsis*. The biomass production cost in this plant was estimated to be around 25 €/kg.

6.7 RWE (Germany)

RWE Power constructed and operated an algae pilot at the Niederaussem power plant location for binding carbon dioxide from the power station's flue gases between 2008-2011. According to RWE, micro-algae grew just as well with flue gases from the lignite-fired power plant as with pure CO_2.[13]

In RWE's pilot the flue gas was withdrawn downstream of the FGD system. Since the flue gas contained a high proportion of water vapour, the flue gas was dried before being transported. The flue gas was then propelled with the aid of a fan through a PE pipe (to prevent corrosion) to the algae cultivation (Figure 17).

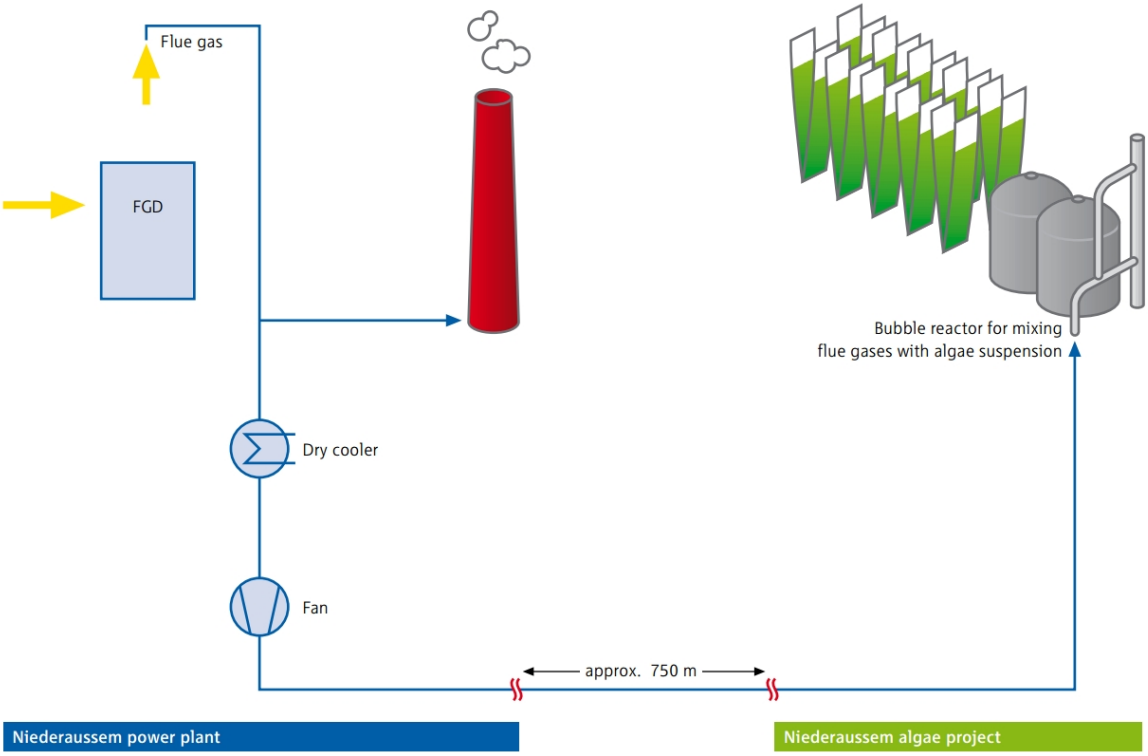

Figure 17. Schematic diagram of the flue-gas link-up from the power plant to the algae pilot.

The flue gases were fed into a bubble reactor, which contained an algae suspension consisting of saltwater and the micro-algae. The flue gases mixed with the suspension, absorbing CO_2 from the flue gas up to saturation of the solution and the gas exited the reactor at the top. Thanks to the bubble-reactor, no flue gas, but only the CO_2 dissolved in the algae suspension. This is likely to be a less energy-intensive solution than leading the

[13] https://www.rwe.com/web/cms/en/213188/rwe-power-ag/innovations/coal-innovation-centre/rwes-algae-project/

flue gas through the reactors. It also put less demand on the PBR system, as it did not need to be designed to channel large amounts of flue gases through the PBR.

The CO_2-enriched algae suspension was fed into photobioreactors developed by Novagreen Projekt-management GmbH. These consist of clear plastic tubes that were fixed in V shape to supports. The production capacity of the pilot was 6,000 kg algae per year.

6.8 EniTecnologie

In 2007, EniTecnologie in Italy conducted a field experiment of CO_2 uptake by algae in a raceway pond. The strains were supplied with CO_2 from natural gas turbine flue gas. *Tetraselmis suecica*, a marine algal, was used for this study. EniTecnologie reported growth rates as mass of dry algae produced each day per square meter of raceway, the productivity ranged between 10 and 30 g/m^2/day.[14]

6.9 Solix BioSystems (USA)

Solix BioSystems, Inc, founded in 2006, has developed and deployed a low-cost proprietary algal growth system (AGS) that is based on extended-surface area closed photobioreactor panels. The technology is applicable to a broad range of microalgae species. The company

Figure 18. Solix Biosystems photobioreactor system.[15]

[14] http://www.powerplantccs.com/ccs/cap/fut/alg/alg_proj_eni.html

[15] http://www.fleetsandfuels.com/studies/2012/10/algae-fuels-pose-concerns-says-nas/

has operated its demonstration facility in southwestern Colorado for several years. The system consists of a series of vertical panels made of welded flexible plastic film, which are submerged in a shallow water basin to provide mechanical support and temperature control. Carbon dioxide enriched air is bubbled through sparging tubes to regulate pH, remove dissolved oxygen and provide adequate mixing of the algal suspension. The vertical orientation of Lumian panels increases the surface area illuminated by both direct and diffuse light, while the water basin provides structural support and improved temperature control to optimize algal growth. According to the company, the results from the demonstration facility demonstrate that the system can deliver a high productivity, superior crop protection, improved process control, and rapid scale up[16]. The cost of large-scale oil production with the current AGS technology has been estimated at 1 USD/L.

6.10 Algenol

Algenol is developing an algal technology platform for production of ethanol and other biofuels. The company was started in 2006, but their patented technology has been developed since 1984[17]. A central component is a proprietary flexible plastic film photobioreactor that facilitates product generation and collection. The plastic is specifically engineered for the purpose and enhanced with resins and other features designed to optimise its performance. Each individual PBR consists of ports for ethanol and biomass collection and the introduction of CO_2 and nutrients. Gravity facilitates the collection of the ethanol and spent algae from the PBRs. The company finished constructing an integrated biorefinery pilot in 2013 that has the capacity to produce up to 38,000 litres of ethanol per year. Ethanol is the primary product, being produced at 473 litres/tonne of CO_2. The other

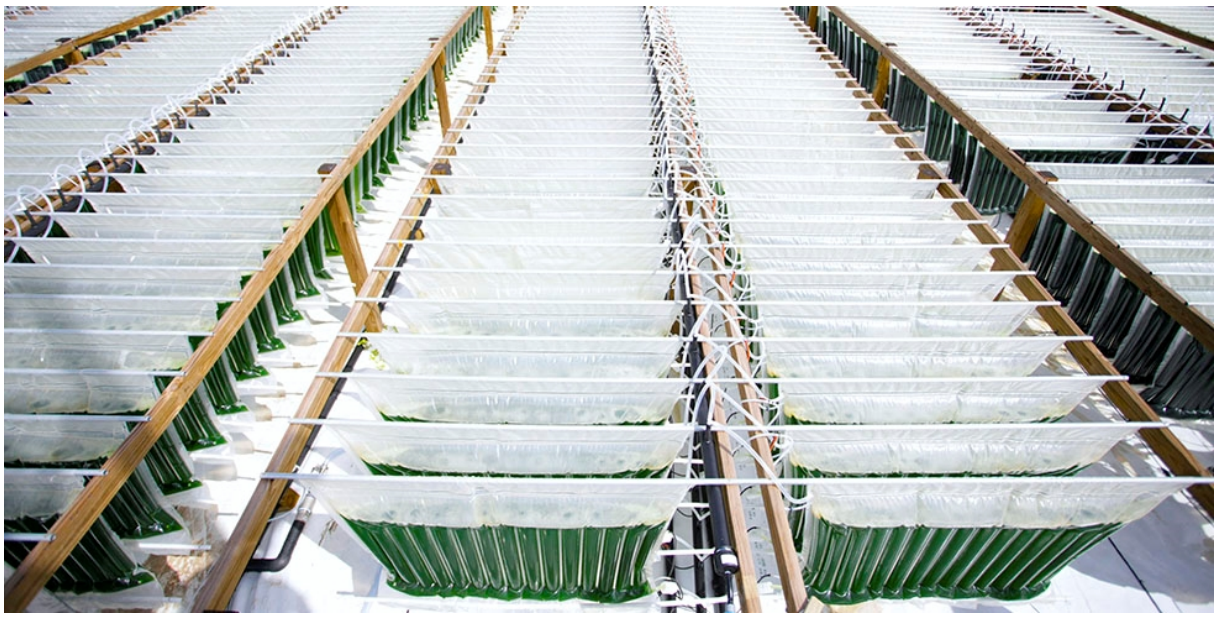

Figure 19. Algenol's plastic photobioreactors (source: Algenol)

[16] http://solixbiosystems.com/

[17] http://www.algenolbiofuels.com/

fuels produced from the process are diesel, gasoline and jet produced at 30, 23 and 19 litres per tonne of CO_2, respectively. According to Algenol, pure CO_2 is not needed for the process: "concentrations of carbon dioxide in air below 50% are suitable for use". The company claims it is the only renewable fuel production process that can convert more than 85% of its CO_2 feestock into the four most important fuels.

6.11 E.ON Hanse

E.On Hanse established in 2008 a pilot plant in Hamburg for consuming CO_2 using microalgae.[18] The cultivation system is based on Subitec's 180 L flat panel airlift-photobioreactors. The total volume is 1.44 m^3 (2 modules consisting of 4 reactors each). The pilot uses flue gases from a natural gas driven combined heat and power unit.

Figure 20. Outdoor plant at E.ON Hanse in Hamburg/Reitbrook (Source: http://subitec.com)

6.12 Algae.Tec pilot plant studies

The McChonchie-Stroud system presented earlier has according to Algae.Tec been developed over a seven year period[19]. A pilot plant test was conducted over a 4 month period, using a pilot plant volume of 76 m^3. On average, 11 kilos of dry algae was grown on the equivalent of one square meter of water surface area every 30 days.

6.13 Endesa

Endesa (Spain) claims to have built the biggest pilot using microalgae for CO_2 fixation in Europe, with a capacity to capture up to 20 tonnes of CO_2 a year. The pilot plant is located at the Almeria thermal power facility and is currently operative. The plant consists of 12 lanes of photo-bioreactors (bag-type open vertical panels angled at 60º north-south). In the second

[18] http://subitec.com/en/eon-hanse

[19] http://algaetec.com.au/wp-content/uploads/2011/01/AlgaeTec_Prospectus.pdf

phase of the project, new types of photobioreactors will be developed and evaluated. They also plan to test genetically modified microalgae later in the Almeria pilot plant. In addition to using real combustion gases, seawater will also eventually be used in the plant. The long term goal is to increase the concentration of microalgae sustained in the culture and hence its capacity to capture CO_2, and to increase the production of bioethanol and lipids for products such as biodiesel.[20] Unfortunately, very little public information is available about the pilot.

6.14 Duke Energy / University of Kentucky (USA)

Researchers at the University of Kentucky's Centre for Applied Energy Research (CAER) are demonstrating a system to capture CO_2 from Duke Energy's East Bend power station emissions through algae absorption. This gas is pumped into a liquid filled tank containing microalgae. The algae circulate through a photobioreactor exposed to sunlight while absorbing the CO_2, a process which is repeated several times. The resulting biomass is dried and formed into sheets, which could be further used for a variety of purposes, for example as a biofuel. The by-products of this process are touted as potential revenue streams. The pilot will be expanded into a 50,000 gallon photobioreactor to demonstrate the feasibility of an algae based CO_2 mitigation process.[21]

7 Conclusions

Using algal cultivation for CO_2 capture is not a straightforward process. Both overfeeding and underfeeding CO_2 can be harmful to the algae, so a careful balance must be upheld. The most promising systems for CO_2 capture seems to be the use of separate, bubbling, carbonation columns, both for open ponds and closed photobioreactors. Using a separate bubbling column makes the design of the photobioreactors simpler, as CO_2 is fed readily dissolved by recycling the cultivation water through the bubbling columns. Using separate bubbling columns for open ponds enables a higher CO_2 concentration in the ponds than what can be achieved by direct injection, and reduces the risk for release of gaseous harmful flue gas components into the area surrounding the ponds. While the capacity of pure water to dissolve CO_2 is poor, the addition of alkaline salts can significantly improve the CO_2 uptake of water as well. As algae can thrive using CO_2 from desulphurized flue gases injected into the cultivation water, there is no need for using costly CO_2 separation processes, as long as the algal cultivation unit is built next to a suitable industrial CO_2 source.

[20] http://www.endesa.com/en/saladeprensa/noticias/microalgae

http://www.endesa.com/en/aboutEndesa/businessLines/principalesproyectos/CapturadeCO2

[21] http://www.caer.uky.edu/factsheets/biofuels_Crocker_Algae-Demo-Project_Eastbend-1-07-13.pdf

8 References

Acién-Fernández, F.G., Férnandez-Sevilla, J.M., Egorova-Zachernyuk, T.A., Molina-Grima, E. 2005. Cost-effective production of ^{13}C, ^{15}N stable isotope-labelled biomass from phototrophic microalgae for various biotechnological applications. Biomol. Eng. 22, 193-200.

Alías, C.B., López, M.C.G.M., Fernández, F.G.A., Sevilla, J.M.F., Sánchez, J.L.G., Grima, E.M. 2004. Influence of power supply in the feasibility of *Phaeodactylum tricornutum* cultures. Biotechnol. Bioeng. 87, 723-733.

Beardall, J., Giordano, M. 2002. Ecological implications of microalgal and cyanobacterial CO_2 concentrating mechanisms, and their regulation. Funct. Plant Biol. 29, 335–347.

Becker EW (1994) Microalgae. Biotechnology and Microbiology. Cambridge University Press, Cambridge, p 293.

Benemann, J.R. 1993. Utilization of carbon dioxide from fossil fuel-burning power plants with biological systems. Energy Conversion & Management 34 (9-11) 999-1004.

Benemann, J., Pedroni, P.M., Davison; J., Beckert, ., Bergman, P. 2003. Technology roadmap for biofixation of CO_2 and greenhouse gas abatement with microalgae. In: Proceedings of Second Annual Conference on Carbon Sequestration, May 5-8, Alexandria, VA. http://www.netl.doe.gov/publications/proceedings/03/carbon-seq/PDFs/017.pdf

BIOREF-INTEG, 2009. Overview innovative biorefinery concepts. Development of advanced biorefinery schemes to be integrated into existing industrial fuel producing complexes. (EU BIOREF-INTEG project, http://www.bioref-integ.eu). Deliverable 4.5, internal report (not published).

Burlew, J. (Ed.) 1953. Algae Culture: From Laboratory to Pilot Plant. Carnegie Institute, Washington D.C.

Borowitzka, M.A., Borowitzka, L.J. (Eds.) 1988. Micro-algal biotechnology. Cambridge Univeristy Press, Cambridge. ISBN 0-521-3249-5.

Borowitzka, M.A., Moheimani, N.R. (Eds.) 2013. Algae for Biofuels and Energy. Developments in Applied Phycology, Vol. 5. 288 p. DOI 10.1007/978-94-007-5479-9

Carvalho, A.P., Meireles, L.A., Malcata, F.X. 2006. Microalgal Reactors: A Review of Enclosed System Designs and Performances. Biotechnology Progress 22(6) 1490–1506. DOI: 10.1021/bp060065r

Carvalho, A.P., Malcata F.X. 2001. Transfer of carbon dioxide within cultures of microalgae: plain bubbling versus hollow-fiber modules. Biotechnol Prog. 17(2) 265-272.

Chrismada, T.; Borowitzka, M.A. 1994. Effect of cell density and irradiance on growth, proximate composition and eicosapentaenoic acid production of Phaeodactylum tricornutm grown in a tubular photobioreactor. J. Appl. Phycol. 6, 67-74.

Chen, F.; Johns, M.R. 1995. A strategy for high cell density culture of heterotrophic microalgae with inhibitory substrates. J. Appl. Phycol. 7, 43-46.

Chen, C.-Y., Yeh, K.-L., Aisyah, R., Lee, D.-J.,Chang, J.-S. 2011. Cultivation, photobioreactor design and harvesting of microalgae for biodiesel production: A critical review. Bioresource Technology 102, 71-81.

DOE, 2010. National Algal Biofuels Technology Roadmap. U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Biomass Program. http://www1.eere.energy.gov/bioenergy/pdfs/algal_biofuels_roadmap.pdf

Doucha, J., Straka, F., Lívanský, K. 2005. Utilization of flue gas for cultivation of miroalgae (*Chlorella* sp.) in an outdoor open thin-layer photobioreactor. Journal of Applied Phycology 17, 403-412. DOI: 10.1007/s10811-005-8701-7

Fernandéz, F.G.A, Grima, E.M., Sevilla, J.M.F., López, C.V.G., Moya, B.L., Aparicio, J.C.B. 2008. Liquid-phase gas collection. Patent Application, International Publication Number WO 2009/112624.

Giordano, M., Beardall, J., Raven, J.A. 2005. CO2 concentrating mechanisms in algae: mechanisms, environmental modulation, and evolution. Annu. Rev. Plant Biol. 56, 99–131. doi: 10.1146/annurev.arplant.56.032604.144052

Goetheer, E.L.V., van den Broeke, L.J.P., Jahn, J., van den Bos, W.A.P., Roelands, C.P.M. 2011. Combining Algae Cultivation and CO_2 capture. Patent Application, International Publication Number WO 2013/022349 A1.

Grima, E.M.; Pérez, J.A.S.; Camacho, F.G.; Sánchez, J.L.G.; Fernández, F.G. A.; Alonso, D. L. Outdoor cultivation of *Isochrysis galbana* ALII-4 in a closed tubular photobioreactor. J. Biotechnol. 1994, 37, 159-166.

Harmelen, T., van, and H. Oonk, 2006, Microalgae biofixation processes: applications and potential contributions to greenhouse gas mitigation options. TNO Built Environment Geosciences.

Ho, S.-H., Chen, C.-Y., Lee, D.-J., Chang, J.-S. 2011. Perspectives on microalgal CO_2 emission mitigation systems – A review. Biotechnology Advances 29, 189-198.

Houghton, G., McLean, A.M., Ritchie, P.D. 1957. Absorption of carbon dioxide in water under pressure using a gas-bubble column. Chemical Engineering Science 7(1-2) 26-39.

Huntley, M.E. & D.G. Redalje. 2007. CO_2 mitigation and renewable oil from photosynthetic microbes: a new appraisal. Mitigation and Adaptation Strategies for Global Change 12, 573–608. DOI: 10.1007/s11027-006-7304-1

IPCC, 2005. IPCC Special Report on Carbon Dioxide Capture and Storage. Prepared by Working Group III of the of the Intergovernmental Panel on Climate Change. Metz, B., Davidson, O. de Coninck, H.C., Loos, M., Meyer, L.A. (Eds.). Cambridge University Press, Cambridge.

Jacob-Lopes, E., Scoparo, C.H.G., Lacerda, L.M.C.F., Franco, T.T. 2009. Effect of light cycles (night/day) on CO_2 fixation and biomass production by microalgae in photobioreactors, Chemical Engineering and Processing: Process Intensification 48(1) 306-310, http://dx.doi.org/10.1016/j.cep.2008.04.007.

Jensen, G., Reichl, E.H. 1996. Integrated Microalgae Production and Electricity Cogeneration. Patent application, patent number US 5659977.

Kastanek, F., Sabata, S., Solcova, O., Maleterova, Y., Kastanek, P., Branyikova, I., Kuthan, K., Zachleder, V. 2010. In-field experimental verification of cultivation of microalgae Chlorella sp. using the flue gas from a cogeneration unit as a source of carbon dioxide. Waste Management & Research 28(11) 961–966.

Kumar, A., Ergas, S., Yuan, X., Sahu, A., Zhang, Q., Dewulf, J., Malcata, F.X., van Langenhove, H. 2010. Enhanced CO_2 fixation and biofuel production via microalgae: recent developments and future directions. Trends in Biotechnology 28(7) 371–380.

Manninen, K., Spilling, K. Growing algae for carbon capture: a review of available technologies and life cycle analyses. Carbon Capture and Storage Programme (CCSP), Deliverable D207.

Matsumoto H, Hamasaki A, Sioji N, Ikuta Y (1997) Influence of CO_2, SO_2 and NO in flue gas on microalgae productivity. J. Chem. Eng. Jpn. 30: 620–624.

Maxwell, E.L, Folger, A.G., and Hogg, S.E. 1985. Resource evaluation and site selection for microalgae production systems. (SERI/TR-215-2484). Golden, CO. Solar Energy Research Institute.

Milne, J.L., Cameron, J.C., Page, L.E., Benson, S.M., Pakrasi, H.B. 2009. Report from Workshop on Biological Capture and Utilization of CO_2, Charles F. Knight Center, Washington University in St. Louis, September 1-2, 2009.

Moroney, J.V., Ynalvez, R.A. 2009. Algal Photosynthesis. In: Encyclopedia of Life Sciences (ELS). John Wiley & Sons, Ltd: Chichester. DOI: 10.1002/9780470015902.a0000322.pub2

Mukherjee, B., Moroney, J.V., 2011. Algal Carbon Dioxide Concentrating Mechanisms. In: Encyclopedia of Life Sciences (ELS). John Wiley & Sons, Ltd: Chichester. DOI: 10.1002/9780470015902.a0000314.pub3

Negoro M, Shioji N, Niyamoto K, Miura Y. 1991. Growth of microalgae in high CO_2 gas and effects of SOx, NOx . Appl. Biochem. Biotechnol. 28–29: 877–886.

Negoro M, Hamasaki A, Ikuta Y, Makita T, Hirayama K, Suzuki S. 1993. Carbon dioxide fixation by microalgae photosynthesis using actual flue gas discharged from a boiler. Appl. Biochem. Biotechnol. 39–40: 643–653.

Ono, E., Cuello, J.L. 2003. Selection of Optimal Microalgae Species for CO_2 Sequestration. In: Proceedings from 2nd Annual Conference on Carbon Sequestration, Alexandria, USA.

Pearson, H.W., Mara, D.D., Mills, S.W., Smallman, D.J. 1987. Factors determining algal populations in waste stabilization ponds and the influence of algae on pond performance. Water Science and Technology 19(12) 131 – 140.

Pedroni, P.M., Lamenti, G., Prosperi, G., Ritorto, L., Scolla, G., Capuano, F. and Valdiserri, M. 2005. Enitecnologie R&D Project on Microalgae Biofixation of CO_2: Outdoor Comparative Tests of Biomass Productivity Using Flue Gas CO_2 from a NGCC Power Plant. The 7th

International Conference on Greenhouse Gas Control Technologies, 2, 1037-1042. http://dx.doi.org/10.1016/B978-008044704-9/50105-1

Perez-Garcia, O., Escalante, F.M.E., de-Bashan, L.E., Bashan, Y. 2011. Heterotrophic cultures of microalgae: Metabolism and potential products, Water Research 45(1) 11-36. http://dx.doi.org/10.1016/j.watres.2010.08.037

Pulz O., 2001, Photobioreactors: production systems for phototrophic microorganisms, Appl. Microbiol. Biotechnol., 57: 287-293.

Putt, R., Singh, M., Chinnasamy, S. 2011. An efficient system for carbonation of high-rate algae pond water to enhance CO_2 mass transfer. Bioresource Technology 102, 3240–3245.

Ras, M., Steyer, J.-P., Bernard, O. 2013. Temperature effect on microalgae: a crucial factor for outdoor production. Rev Environ Sci Biotechnol 12, 153–164. DOI 10.1007/s11157-013-9310-6

Round, F.E. 1981. The ecology of algae. Cambridge University Press. ISBN 0-521-22583.

RWE Power, 2009. RWE's algae project in Bergheim-Niederaussem - Production of micro-algae using power plant flue gases to bind CO_2. Broschure available online: https://www.rwe.com/web/cms/mediablob/en/234586/data/213188/2/rwe-power-ag/innovations/coal-innovation-centre/rwes-algae-project/Brochure-RWEs-algae-project-.pdf (accessed 29 June 2014).

Sánchez Mirón, A., García Camacho, F., Contreras Gómez, A., Grima, E.M., Yusuf, C. 2000. Bubble-column and airlift photobioreactors for algal culture. AIChE Journal 46(9) 1872-1887. http://dx.doi.org/10.1002/aic.690460915.

Shilton, A. (Ed.). 2005. Pond Treatment Technology. IWA Publishing, Cornwall, UK. ISBN: 9781843390206. 496 pages.

Singh, R.N., Sharma, S. 2012. Development of suitable photobioreactor for algae production – A review. Renewable and Sustainable Energy Reviews 16, 2347– 2353.

Stepan, D.J., Shockey, R.E., Moe, T.A., Dorn, R.2002. Carbon dioxide sequestering using microalgal systems. Report prepared for DOE: http://www.osti.gov/energycitations/product.biblio.jsp?query_id=1&page=0&osti_id=882000

Stewart, W.D.P. (ed.) 1974. Algal Physicology and Biochemistry. Botanical Monographs Volume 10. University of California Press, Jan 1, 1974, 989 p.

Styring, P., Jansen, D., de Coninck, H., Reith, H., Armstrong, K., 2011. Carbon Capture and Utilisation in the green economy – Using CO2 to manufacture fuel, chemicals and materials. The Centre for Low Carbon Futures, Report no. 501. http://www.policyinnovations.org/ideas/policy_library/data/01612

Tredici, M. R. 2003. Closed photobioreactors: basic and applied aspects. In Proceedings of Marine Biotechnology: Basics and Applications, Matalascanas, Spain, p 1.

Tredici, M. R.; Rodolfi, L. 2004. Reactor for industrial culture of photosynthetic micro-organisms. PCT WO 2004/074423 A2.

Vance, P., Spaldning, M.H. 2005. Growth, photosynthesis, and gene expression in *Chlamydomonas* over a range of CO_2 concentrations and CO_2/O_2 ratios: CO_2 regulates multiple acclimation states. Canadian Journal of Botany 83(7) 796-809. DOI: 10.1139/B05-064

Vasquez V, Heussler P (1985) Carbon dioxide balance in open air mass culture of algae. Arch Hydrobiol Ergeb Limnol Beih 20:95–113.

Vunjak-Novakovic, G., Kim, Y., Wu, X., Berzin, I., Merchuk, J.C. 2005. Air-Lift Bioreactors for Algal Growth on Flue Gas: Mathematical Modeling and Pilot-Plant Studies. Ind. Eng. Chem. Res. 44, 6154-6163.

Westerhoff, P., Qiang, H., Esparza-Soto, M., Vermaas, W. 2010. Growth parameters of microalgae tolerant to high levels of carbon dioxide in batch and continuous-flow photobioreactors. Environmental Technology 31(5) 523-532.

Wijffels, R.H., Barbosa, M.J., Eppink, M.H.M. 2010. Microalgae for the production of bulk chemicals and biofuels. Biofuels, Bioproducts and Biorefining 4(3), 287-295. doi: 10.1002/bbb.215

Yamaguchi, K. 1996. Recent advances in microalgal bioscience in Japan, with special reference to utilization of biomass and metabolites: A review. J. Appl. Phycol. 8, 487-502.