Microalgae removal of CO_2 from flue gas

Xing Zhang

April 2015

Microalgae removal of CO_2 from flue gas

Author: Xing Zhang

IEACCC Ref: CCC/250

ISBN: 978–92–9029–572-3

Published Date: April 2015

IEA Clean Coal Centre
14 Northfields
London SW18 1DD
United Kingdom

Telephone: +44(0)20 8877 6280

www.iea-coal.org

Preface

This report has been produced by IEA Clean Coal Centre and is based on a survey and analysis of published literature, and on information gathered in discussions with interested organisations and individuals. Their assistance is gratefully acknowledged. It should be understood that the views expressed in this report are our own, and are not necessarily shared by those who supplied the information, nor by our member countries.

IEA Clean Coal Centre is an organisation set up under the auspices of the International Energy Agency (IEA) which was itself founded in 1974 by member countries of the Organisation for Economic Co-operation and Development (OECD). The purpose of the IEA is to explore means by which countries interested in minimising their dependence on imported oil can co-operate. In the field of Research, Development and Demonstration over fifty individual projects have been established in partnership between member countries of the IEA.

IEA Clean Coal Centre began in 1975 and has contracting parties and sponsors from: Australia, Austria, China, the European Commission, Germany, India, Italy, Japan, New Zealand, Poland, Russia, South Africa, Thailand, the UK and the USA. The Service provides information and assessments on all aspects of coal from supply and transport, through markets and end-use technologies, to environmental issues and waste utilisation.

Abstract

CO_2 forms the largest component in coal combustion flue gas. With fossil fuels currently meeting over 80% of global energy demand and as much as 85 GW of additional capacity expected to be needed in Europe alone in the future, carbon capture and storage (CCS) is vital in meeting greenhouse gas reduction targets. Various technologies have been developed to capture CO_2 from coal-fired power plants, one of which is biological post-combustion CO_2 capture. Microalgae's ability to photosynthesise and grow rapidly has resulted in the possibility of using them for CO_2 bio-fixation. A number of studies have been carried out to determine the ability of microalgae to withstand the high CO_2 concentrations present in flue gas, as well as the potentially toxic accompanying SOx and NOx gases. Thus, a lot of work has been carried out to isolate microalgal strains that are especially suitable for this application. Most of the research on algae bio-fixation has been concerned with carbon fixation strategy, photobioreactor design, conversion technology from microalgal biomass to bioenergy, and economic evaluations of microalgal energy. A review of the effect of process characteristics, especially in the complex coal combustion flue gas environment, has not yet been reported. This report attempts to fill this gap by looking at the current progress in the field of algal technology and product utilisation, together with an analysis of the advantages and the challenges of the technologies. The report begins with a brief introduction to the algae bio-fixation theory and factors affecting its efficiency especially in terms of flue gas characteristics, and then discusses culturing, processing technologies and the applications of bio-fixation by-products, finally summarising the current algae-based CO_2 capture demonstration projects at coal-fired power stations around the world.

Acronyms and abbreviations

ARRA	American Recovery and Reinvestment Act
ATP	adenosine triphosphate
CA	carbonic anhydrase
CAER	University of Kentucky Center for Applied Energy Research, USA
CCM	carbon concentration mechanism
CCS	carbon capture and storage
CCU	carbon capture and utilisation
CFD	computerised fluid dynamics
ESP	electrostatic precipitator
FGD	flue gas desulphurisation
IGCC	integrated gasification combined cycle
PAHs	polycyclic aromatic hydrocarbons
PCM	phase change material
ppm	parts per million also can be expressed as milligrams per litre (mg/L)
PUFA	polyunsaturated fatty acids
$SCCO_2$	supercritical carbon dioxide
SCR	selective catalytic reduction
SNCR	selective non-catalytic reduction
vvm	volume per volume per minute (aeration rate)

Contents

List of Figures

List of Tables

1 Introduction

Burning fossil fuels to generate electricity produces flue gas. Flue gas emitted from coal combustion mostly contains carbon dioxide (CO_2), nitrogen (N_2), oxygen (O_2), and water vapour. It also contains minor amounts of substances, such as carbon monoxide (CO), nitrogen oxides (NOx), sulphur oxides (SOx), unburned hydrocarbons (CxHy), heavy metals, halogen acids and particulate matter (PM). Emissions of many these compounds, namely SOx, NOx, PM and mercury, are regulated or in the process of being regulated. The concentration of these compounds in flue gas depends not only on the fuel type, but also on the combustion process and system. The current trend towards zero emissions presents a challenge to power station operators to minimise the environmental effects of coal combustion. Various air pollution control systems have been installed to reduce SOx, NOx, CO_2 and other greenhouse gas emissions. For example, some power plants have flue gas desulphurisation (FGD) systems to remove SO_2, and/or selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) to remove nitrogen oxides. Electrostatic precipitators (ESPs) are also widely installed to control particulate matter. The composition of the flue gas from coal-fired power plants after passing through electrostatic precipitators and desulphurisation units generally consists of 4–14% of CO_2 and up to 200 ppm of NOx and SOx depending on the type of fuel and the combustion process (Kumar and others, 2011; Maeda and others, 1995; Yamasaki, 2003).

CO_2 forms the largest component of flue gas and, with as much as 85 GW of additional power generation capacity needed in Europe alone in the future, carbon capture and storage (CCS) is vital in meeting greenhouse gas reduction targets. Described in detail by Davidson for the IEA Clean Coal Centre (2007, 2009, 2010, 2011, 2012), CO_2 capture techniques applied to coal-fired power plants are classified into three categories:

- pre-combustion capture when an integrated gasification combined cycle (IGCC) is employed;
- post-combustion capture which is similar to conventional pollutant control systems;
- oxy-combustion which involves burning coal in an oxygen rich environment to produce a concentrated steam of CO_2.

Post-combustion capture can be roughly categorised as chemical absorption, physicochemical adsorption, membrane, cryogenics, chemical looping combustion and biotechnology (such as terrestrial vegetation or hydroponic algae). From a technical point of view, all of these methods are feasible in spite of the differences in capture efficiency and capture capability. However, from an economic point of view, methods mentioned above face serious challenges such as the cost of equipment, high energy consumption for regeneration (for example with amine solvents), and large space requirements. In order to encourage CO_2 capture, scientists have been researching ways to reduce the costs and energy consumption as well as to improve the capture efficiency.

Biological post-combustion CO_2 capture has attracted attention in recent years due to its advantage of producing biofuel/biomass as a by-product. Bio-fixation of CO_2 includes fixation in plants and microalgae.

Microalgal species offer particular advantages for carbon mitigation. Microalgae are prokaryotic or eukaryotic photosynthetic microorganisms that can grow much faster than terrestrial plants and live in harsh conditions due to their unicellular or simple multicellular structure. Examples of prokaryotic microorganisms are cyanobacteria (*Cyanophyceae*) and eukaryotic microorganisms are microalgae, for example green algae (*Chlorophyta*) and diatoms (*Bacillariophyta*) (Mata and others, 2010). Cyanobateria were originally grouped with the eukaryotic microorganisms as blue algae. However, it was subsequently realised that they belong to the bacterial domain. During photosynthesis, microalgae use CO_2 from the atmosphere as a carbon source to grow and reproduce. Microalgae cells contain approximately 50% carbon, in which 1.8 kgCO_2 can be fixed to produce 1 kg of microalgae biomass. The CO_2 fixation efficiency for microalgae is about 10–50 times higher than terrestrial plants (Chisti, 2007; Costa and others, 2000).

The advantages of using microalgae to capture CO_2 from coal combustion flue gas are:

1. High purity CO_2 gas is not required for algal culture. Flue gas containing varying amounts of CO_2 can be fed directly to the microalgal culture. This simplifies CO_2 separation from flue gas significantly;
2. Some combustion products such as NOx or SOx can be effectively used as nutrients for microalgae. This could potentially negate the use of flue gas scrubbing systems for power plants;
3. The microalgae could yield high value commercial products. The sale of these high value products could offset the capital and operating costs of the process; and
4. The envisioned process is a renewable cycle with minimal negative impacts on the environment.

Figure 1 is a flow chart of microalgae capturing CO_2 from coal combustion flue gas. The concept of using microalgae to ameliorate CO_2 emissions from stationary combustion sources is not new (Kadam, 1997; Oswald and Golueke, 1968; Sheehan and others, 1998). A number of studies have been carried out to determine the ability of microalgae to withstand the high CO_2 concentrations present in flue gas (Hanagata and others, 1992; Yun and others, 1997), as well as the potentially toxic accompanying SOx and NOx gases (Lee and others, 2002; Negoro and others, 1991). Thus, much work has been carried out to isolate microalgal strains that are especially suitable for this application (Bhatti and others, 2014; Dawson and Wilson, 2014; Maeda and others, 1995; Murakami and Ikenouchi, 1997).

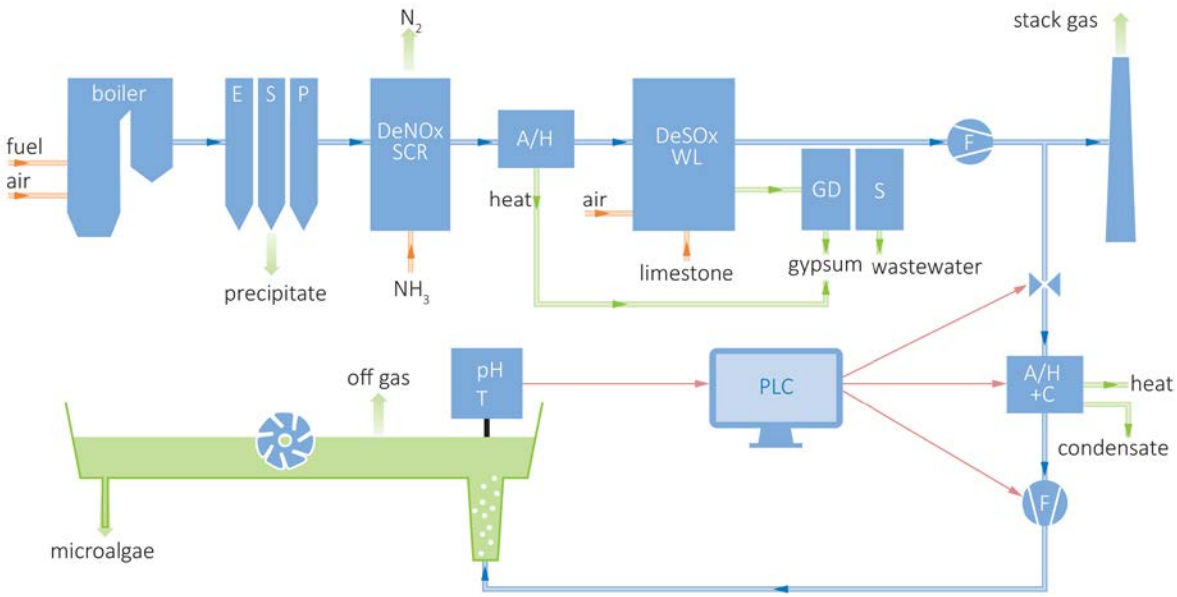

Figure 1 Flow chart of process of microalgae capturing CO_2 from coal combustion flue gas (Van Den Hende and others, 2012)

Most of the research on algae bio-fixation has been concerned with carbon fixation strategy, photobioreactor design, conversion technology from microalgal biomass to bioenergy, and economic evaluations of microalgal energy. A review regarding the effect of process characteristics, especially in the complex coal combustion flue gas environment, has not yet been reported (Zhao and Su, 2014). This report fills the gap by looking at current progress in the field of algal technology and product utilisation, together with an analysis of the advantages and the challenges of the technologies. The report begins with a brief introduction to the algae bio-fixation theory and factors affecting its efficiency especially in terms of flue gas characteristics, and then discusses culturing, processing technologies and the applications of bio-fixation by-products, finally summarising the current algae-based CO_2 capture demonstration projects at coal-fired power stations around the world.

2 Theory

Microalgae's ability to photosynthesise and grow rapidly means they may be suitable for CO_2 fixation. An understanding of photosynthesis and the factors affecting its efficiency, especially in terms of flue gas characteristics is important, as is the selection of an appropriate algal strain.

2.1 Photosynthesis

Photosynthesis has existed and shaped the environment on earth for more than 3.5 billion years, providing the foundation for all aerobic forms of life. Using the following reaction, plants and photosynthetic microorganisms (including microalgae and cyanobacteria) convert carbon dioxide into organic compounds with the aid of light energy, and release molecular oxygen, as follows:

$$6CO_2 + 6H_2O \xrightarrow{\text{light energy}} C_6H_{12}O_6 + 6O_2$$

Photosynthesis is a physicochemical process and consists of two steps:

1. light dependent reaction, which only takes place in the presence of light, and
2. light independent reaction, which takes place under both the absence and presence of light.

The first step is catabolic, which involves the release of energy. This energy is stored in organic form in the second step. Proper cycling of these two steps is important for fixing carbon. Excess exposure to light and oxygen rich environments may lead to photo inhibition, which reduces the efficiency of the photosynthetic process. When photo inhibition occurs, CO_2 may actually be released into the environment.

2.2 Species

Microalgae are present in all existing earth ecosystems, not just aquatic but also terrestrial, representing a large variety of species living in a wide range of environmental conditions. It is estimated that more than 50,000 species exist, but only around 30,000, have been studied and analysed (Mata and others, 2010). Numerous species of eukaryotic microalgae and prokaryotic cyanobacteria have been identified that are able to fix the dissolved inorganic carbon and CO_2 in the aquatic environment.

Most microalgal species isolated from natural streams, lakes or oceans have been pre-adapted for the living environment through artificial domestication. They have been successfully used for fixation of atmospheric CO_2. However, unlike atmospheric air, which has low CO_2 content (about 0.038% volume concentration v/v), post-combustion flue gas typically contains 4–14% or more v/v CO_2 concentration and possibly toxic compounds (SOx, NOx and trace elements) in a high flow rate, high temperature (80-120°C or above) stream. This means that the microalgal species need to be able to tolerate the harsh flue gas conditions in order to capture CO_2 (Zhao and Su, 2014).

Some microalgal species can be adapted to endure the rigorous flue gas conditions and continue growing. Few microalgae are able to bear CO_2 concentrations of up to 70% or even 100%, high aeration rates of 2 volume per volume per minute (vvm), low pH values of less than 3.5 and 100 ppm SO_2 and NOx. The

effects of nutrient source, light intensity, and culture temperature on microalgal growth depend on the microalgal species. Optimal ranges or values of these parameters for achieving high CO_2 fixation rates and biomass production are usually different for each microalgal species. However, the general microalgal species for industrial applications are obtained using natural breeding methods. Usually, they do not have an outstanding performance (Zhao and Su, 2014).

Microalgae and cyanobacteria species commonly used for CO_2 mitigation include *Botryococcus braunii*, *Chlorella vulgaris*, *Chlorella kessleri*, *Chlorella sp.*, *Chlorocuccum littorale*, *Chlamydomonas reinhardtii*, *Scenedesmus obliquus*, *Scenedesmus sp.*, *M. minutum*, *Tetraselmis sp.*, and *Spirulina sp.* (Ho and others, 2011; Kumar and others, 2014; Lam and others, 2012). Table 1 lists the microalgal species that are tolerant to high temperatures, high CO_2 concentrations and NOx and SOx. It shows that a few *Chlorella* and cyanobacteria species could grow well and achieve a high CO_2 fixation (500–1800 mg/L/d) with a relatively high tolerance for temperature and CO_2 concentration. Compared with other species, for example *Cyanophytes* and *Chrysophyte*, *Chlorella* was observed by Zhao and Su (2014) to have a better performance in capturing CO_2. Its biomass production rate and carbon fixation rates were up to 1060 mg/L/d and 1992 mg/L/d, respectively. *Chlorella kessleri* and *Scenedesmus obliquus* were isolated from the waste treatment pond of the Presidente Medici coal-fired power plant in the southernmost Brazilian state of Rio Grande do Sul. Their growth when exposed to different concentrations of CO_2 was investigated (De Moriais and Costa, 2007). It was found that these two microalgae grew well when the culture medium contained up to 18% CO_2. The Israeli company, Seambiotic, also found that *Nannochloropsis sp.* grows better on coal FGD flue gas than on pure CO_2 (Burgess and others, 2011). In their trials, Seambiotic achieved an average growth rate of 20 g/m^2/d, but claim a long-term theoretical maximum of 25 g/m^2/d. Some strains have considerable CO_2 fixation ability, for example *Chlorella vulgaris* (6240 mg/L/d), *Aphanothece microscopica Nageli* (5435 mg/L/d), and *Anabaena sp.* (1450 mg/L/d). Apart from CO_2 fixation, some species can potentially also remove sulphur dioxide, nitrogen oxides, and volatile organic compounds. Application of such strains may minimise the costs of pretreating the flue gas. More details will be discussed in Section 2.3. It should be noted that the performance of the microalgal strains mentioned above may have been obtained under different culture or experimental conditions, such as CO_2 concentration, temperature, cultural medium, light intensity, and photobioreactor design. The variation in those conditions may affect the CO_2 fixation efficiency of the strains. Hence, the information provided in Table 1 is not a strict comparison of the performance among those strains, but rather a literature survey of the types of microalgal strains that have been used to develop strategies for CO_2 emissions mitigation under the specific culture and operating conditions for each microalgal strain.

Table 1 Growth characteristics and CO_2 fixation performance of microalgal strains under different CO_2 concentration, temperature, and NOx/SOx contents [Ho and others, 2011]

Microalgal species	CO_2, %	Temperature, °C	NOx/SOx, mg/L	Biomass productivity, mg/L/d	CO_2 consumption rate, mg/L/d
Chlorella sp.	15	25	0/60	1000	1880[a]
Chlorella sp.	20	40	–	700	1316[a]
Chlorella sp.	50	25	–	500	940[a]
Chlorella sp.	50	25	–	386	725[a]
Chlorella sp.	50	35	60/20	950	1790
Chlorogleopsis sp.	5	50	–	40	20.45
Hot spring algae	15	50	–	266.7	501.3[a]
Nannochloris sp.	15	25	0/50	350	658
Nannochloropsis sp.	15	25	0/50	300	564

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

A multi-faceted effort was carried out to select high performance species by:

- isolating microalgae from a variety of habitats;
- screening those isolates for the ability to grow under a variety of conditions;
- analysing the biochemical components of the strains; and
- determining the effects of environmental variables on the growth and lipid composition of the selected strains (Sheehan and others, 1998).

It is also important to modify the high performance microalgal species using advanced breeding methods to enhance and improve microalgal CO_2 bio-fixation and biomass production. The methods include physicochemical mutation, cell fusion, genetic improvement, and crossbreeding.

2.3 Effects of the photosynthesis process

Microalgal CO_2 bio-fixation is a complex physicochemical process. Apart from microalgal species, the process is also influenced by physicochemical and other culture parameters (such as CO_2 concentration, pollutants in the flue gas, initial inoculation density, culture temperature, light, nutrients and pH) and hydrodynamic parameters (for example, flow, mixing and mass transfer). Microalgal growth under coal combustion flue gas is usually more complex than that under atmospheric conditions. Details of these parameters are discussed below.

2.3.1 Physicochemical parameters

CO_2 concentration

Generally, algal cells can tolerate CO_2 only up to a certain level after which it becomes detrimental for the growth of the cells because of two reasons. Firstly, environmental stress induced by the higher CO_2 concentration causes biological reduction in the capacity of algal cells for CO_2 capture. Secondly, the

culture pH decreases due to the formation of large amounts of bicarbonate buffer (Kumar and others, 2011).

Essentially, microalgal growth and its CO_2 fixation are strongly related to the carbon concentration mechanism (CCM). High CO_2 concentration significantly inhibits carbonic anhydrase (CA) activity and CCM microalgae cell formation has a significant negative effect on CA activity. As the CO_2 concentration rises, the hydrolysis of CO_2 results in an increase in HCO_3^- and H^+ concentrations. This decreases the pH value of the medium. A low pH value may inhibit the activity of CA, which plays an important catalytic role in the interchange between CO_2 and HCO_3^-, and is regarded as an important factor of CCM. As a result, the microalgal performance of carbon bio-fixation is weakened (Zhao and Su, 2014).

However, when a high CO_2 concentration decreases the pH value of the growth medium, some microalgal cells are able to adapt by, for example, gene regulation and increasing the energy allocation proportion. These methods can temporarily reduce the synthesis of organic carbon and simultaneously provide more adenosine triphosphate (ATP) to maintain the pH stability inside the cell, enabling it to tolerate extremely high CO_2 concentrations (Zhao and Su, 2014). Solovchenko and Khozin-Goldberg (2013) reviewed the high CO_2 tolerance of microalgae. They concluded that CO_2 tolerance in microalgae is achieved via several mechanisms. These include the responses preventing acidification of the chloroplastic stromal compartment and cytoplasm to maintain sufficient activity of the Rubisco, an enzyme involved in the first major step of carbon fixation. First, state transition of the photosynthetic apparatus increases ATP generation which is spent on maintaining a suitable pH by active transport. Second, the ability to rapidly and reversibly shut down the CCMs operating under atmospheric CO_2 levels but facilitate the pH drop in microalgal cells under elevated CO_2 seems to be of considerable importance. Third, various adjustments in lipid metabolism provide for optimal balance of source and sink under stressful conditions, as well as for swift rearrangements of photosynthetic apparatus membranes. Van Den Hende and others (2012) summarised another set of reasons for the ability of certain microalgae to tolerate high CO_2 concentrations which are similar to those above:

- firstly – when low gas flow rates are applied, even high CO_2 concentrations in the gas phase can lead to low inorganic carbon loading in the liquid phase and low concentrations of dissolved inorganic carbon in the reactor. Therefore, the concentrations of dissolved CO_2 that the microorganisms encounter should be considered.
- secondly – CCM may play a role. Inhibition of Rubisco through acidification under high CO_2 conditions may be prevented by CA.
- thirdly – with certain algal species, the addition of bases to compensate for CO_2 acidification enhances CO_2 tolerance. Microalgal growth can be sustained even at 100% CO_2, suggesting that it is mainly acidification that inhibits microalgal growth.

In aqueous environments, inorganic carbon may exist in several alternative chemical forms, such as CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-}, which are interconvertible via reactions controlled by temperature and pH. As the interconverting reaction is sufficiently fast, the form of carbon microalgae consumed is not a critical

issue. Microalgal cells preferentially uptake HCO_3^- over CO_2 despite the fact that the former is a poorer source of carbon than the latter (Carvalho and others, 2006).

Biomass productivity increases with increasing CO_2 concentration in the gas mixture up to a certain percentage (v/v) beyond which productivity decreases (De Morais and Costa, 2007; Kumar and others, 2011; Lam and others, 2012). Kumar and others (2011) summarised CO_2 capture experiments conducted by several authors and found that at a flow rate of 0.25 vvm, 2% (v/v) of CO_2 is optimum for the growth of *Chlorella,* while at 10% (v/v) CO_2 the specific growth rate becomes insignificant. Kumar and others (2014) own experiments show that high concentrations of CO_2 had an inhibitory effect on the growth of *Chlorella sorokiniana*. Lam and Lee (2012) reviewed a few studies and reported that *Chlorella sp.*, *Scenedesmus sp.*, and *Botryococcus braunii* are among the microalgae strains that have shown promise to bio-mitigate CO_2 emissions with typical CO_2 consumption rates of 200–1300 mg/L/d. The effect of CO_2 concentration on the growth of *Chlorella vulgaris* was studied by Yun and others (1997). The growth was somewhat inhibited at 15% (v/v) CO_2 with air. The highest growth was achieved at 5% CO_2 with air.

Some species were tested by using flue gas directly as a CO_2 source. Yoo and others (2010) demonstrated that *Botryococcus braunii* and *Scenedesmus sp.* could grow using flue gas as the carbon source. With flue gas containing 5.5% CO_2, *Botryococcus braunii* and *Scenedesmus sp.* showed higher and similar growth rates compared to those with air enriched with 10% CO_2. A similar result was also reported by Li and others (2011) in which *Scenedesmus obliquus* was able to tolerate industrial flue gas with a CO_2 concentration up to 12% with an optimal removal efficiency of 67% in the pilot plant system.

Experiments carried out by Maeda and others (1995) on the capture of CO_2 from flue gas emitted by a coal-fired power plant confirm that *Chlorella sp.* can tolerate up to 100% CO_2 concentration, but the maximum growth rate was obtained when using 10% CO_2. There was with no significant decrease in the growth rate up to 50% CO_2 concentration.

As discussed above, most of the microalgae grow only at low CO_2 concentration levels, and their growth is inhibited by CO_2 concentrations higher than 5% (v/v). Some microalgae can grow under higher flue gas CO_2 concentrations (typically 10–15%), but the carbon fixation and biomass production rates are reduced. Few microalgal species are able to tolerate extremely high CO_2 levels up to 70% or even 100%. Therefore, for most of the algae species, adaptation to higher CO_2 concentrations is required for the direct use of flue gas. Isolation of microalgal strains from lakes or ponds in the vicinity of coal-fired power plants is a useful strategy to obtain microalgae tolerant to the conditions prevalent in the area, as such organism tend to have the ability to grow in the presence of the combustion gases produced by the power plants. Another advantage of isolating microalgae from the vicinity of a coal-fired power plant is that any process developed is not dependent on a strain supplier or on the adaptation of exotic strains to the novel cultivation conditions present in a power plant. De Morais and Costa (2007) isolated the microalgae *Scenedesmus obliquus* and *Chlorella kessleri* from the waste treatment ponds of the Presidente Me´dici coal-fired power plant in the Brazilian state of Rio Grande do Sul and investigated their growth characteristics when exposed to different concentrations of CO_2. When cultivated with 6% and 12% CO_2,

Chlorella kessleri showed a high maximum specific growth rate of 0.267g/d, with a maximum biomass productivity of 0.087 g/L/d at 6% CO_2. For *Scenedesmus obliquus*, the highest maximum dry weight biomass value was 1.14 g/L/d with 12% CO_2. These two microalgae also grew well when the culture medium contained up to 18% CO_2.

It was found that a gradual increase in CO_2 concentration gave a better growth rate (Razzak and others, 2013). High density of cell inoculums in microalgae also lead to higher tolerance towards CO_2 and a faster growth rate. This is because the high density of inoculums could minimise the initial lag phase resulting in an immediate exponential growth of microalgae in the presence of a high concentration of CO_2 (Chui and others, 2008). Overall, the CO_2 tolerance of microalgae is dependent on cell density, pH, nutrients, light and species selection.

Light

Light is the basic energy source for microalgae. Generally, the amount of light energy received and stored by the cells has a direct impact on the carbon fixation capacity, consequently determining the cell growth rate and the microalgae productivity. Light influences not only the algal productivity but also its biochemical profile. The culture systems can be illuminated by sunlight, artificial light or both. Natural sunlight is applied in both open and closed cultivation systems. Artificial light is mainly applied in closed systems (Pires and others, 2012; Yen and others, 2014; Zhao and Su, 2014).

There is a complex relationship between light and microalgae growth. Usually, the effect of light on microalgae growth is presented in two ways:

- light intensity;
- light-dark period cycle.

In general, the light intensity effect can be classified into three phases: light limitation, light saturation, and light inhibition (Ogbonna and Tanaka, 2000). The light limitation phase is also called compensated light intensity. Below this, light becomes the limiting factor for algae productivity. The maximum photosynthesis rate is reached and algae growth rate is stabilised in the light saturation phase. Saturation light intensity is an important parameter which determines the light utilisation efficiency and overall photosynthesis efficiency. Photosynthesis can be weakened and inhibited with increased light intensity due to damage of the repair mechanism of photosystem II, that is, the first protein complex in the light-dependent reactions of oxygenic photosynthesis. This leads to inactivation of other systems including the oxygen evolving systems, electron carriers and the associated D1/D2 proteins. Therefore, this phase is called light inhibition (*see* Figure 2). The most often employed light intensities range between 100 to 210 $\mu E/m^2/s$ and the saturation light intensity typically varies from 140 to 210 $\mu E/m^2/s$ (Kumar and others, 2011; Zhao and Su, 2014).

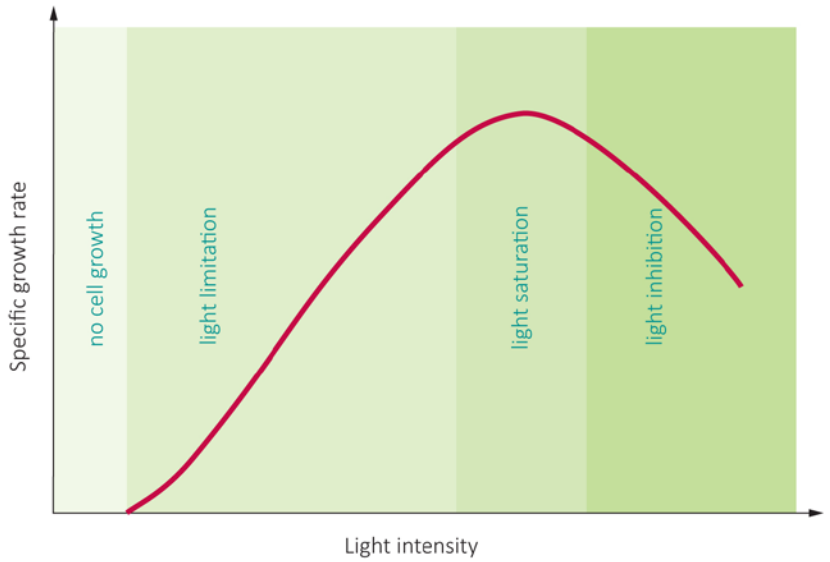

Figure 2 Effect of light intensity on microalgae growth under phototrophic cultivation (Ogbonna and Tanaka, 2000)

Like plants, microalgae have developed several mechanisms to adjust to the changes in the quality of light and light intensity. However, the adjustment capacities vary from species to species. Algae with phycobilisomes may prefer low light intensities. Some other algal strains often need higher light intensities. Colourless algae, such as *Astasia*, *Polytomella* and *Prototheca*, are best kept in a closed cupboard away from the light. Otherwise these algae have the same maintenance requirements as their photoautotrophic relatives (Razzak and others, 2013). Attenuation of light intensity depends on its wavelength, cell concentration, culture density, penetration distance of light and the geometry of the photobioreactor. For example, according to Hanagata and others (1992) saturation light intensity of *Chlorella sp.* and *Scendesmus sp.* is around 200 $\mu E/m^2/s$. Light intensity at the depth of dense algal suspension is greatly reduced because of the absorption and scattering (shading) of light, especially when the cell concentration is high or when significant biofilm formation on the surface of the reactor vessel occurs (Yen and others, 2014). Therefore, the light irradiance should be regulated according to the culture density. For lower culture densities, high light intensities can cause photoinhibition and for high culture densities, the light penetration is limited. Thus, the intensity of light supplied should increase progressively with increasing culture density. Since blue and red light are mostly consumed by the microalgae, they penetrate a shorter distance in the microalgae suspension than green light. This effect is more pronounced in dense cultures. From an engineering point of view, the reactor geometry can reduce the attenuation of light in microalgal suspensions. Fernandes and others (2010) studied the effect of circular and plane geometries. For similar microalgae cell concentrations, the circular geometry allowed a better light penetration than the plane geometry enabling a higher volume fraction of the reactor to receive sufficient amounts of light. However, the plane geometry gave a more uniform distribution of light. In outdoor conditions, light availability is the dominant factor determining photosynthetic productivity. In addition, the effect of light intensity on microalgal growth must take into account the interactions between the various factors. For example, culture temperature is able to adjust the required light

intensity by influencing the metabolic reaction of microalgal cells. Specifically, under higher culture temperatures, microalgae may grow well with a lower light intensity requirement. Microalgal photosynthesis can also be enhanced as the nutrient concentration increases with a high light intensity; it can be weakened when cell density increases under low light intensity (Kumar and others, 2010; Pires and others, 2012).

Besides light intensity, the light-dark period cycle can also influence microalgal growth significantly. During the dark period, algae can repair the damaged mechanism of photosystem II. The light-dark periods for most microalgal cultivation include 24:0, 16:8, 12:12 (hour). For a specific microalgal species, there are different growth characteristics under different light-dark periods. An inappropriate light-dark period cycle may lead to unwanted photoperiodic effects. For example, a short day length may cause cyst formation in some species. Some microalgal species do not grow well under constant illumination. The photosynthetic efficiency can be decreased when the dark period is up to 50% of the cycle period (12:12 hour). Furthermore, due to differences in the photo-bioreactor configuration, the light distribution and light-dark cycle are influenced by fluid-cell flow, inter-cell absorption and light scattering, all of which affect the microalgal photosynthesis process (Pires and others, 2012; Razzak and others, 2013; Zhao and Su, 2014). Pires and others (2012) found that the photosynthetic rates increased exponentially with increasing light-dark frequencies. The microalgae became progressively more efficient in the overall utilisation of light energy when the dark period was longer than the light period. However, a longer dark period relative to the light period did not mean that high photosynthetic rates can be achieved. Moreover, it was also observed that the microalgae do not acclimatise to a specific light-dark cycle. The efficiency of light utilisation by microalgae depended on its acclimatised state, the specific frequency of the light-dark fluctuations and the duration of the exposure.

The following approaches have been proposed for improving light utilisation efficiency of microalgae (Ho and others, 2011; Kumar and others, 2011):

- proper mixing of the culture for better distribution of nutrients and light to the cells;
- increasing the surface area of photo-bioreactor;
- selecting species with high saturation light intensity; and
- genetically modifying the photosynthetic systems and metabolic pathways of the microalgae to shorten the light path and layer thickness.

Toxic pollutants in flue gas

Beside CO_2, flue gas also contains other compounds which influence microalgae growth, including nitrogen oxides (NOx) and sulphur oxides (SOx), and some heavy metals. The effect of NOx and SOx on microalgae growth is still not fully understood owing to different observations reported in the literature. Some researchers have found that NOx and SOx can act as nutrients for the microalgae, whilst others have found them toxic.

Nitrogen oxides

In general, the total NOx content in flue gas varies from several hundreds to thousands of ppm with more than 90–95% NO and 5–10% NO_2. After the sulphur dioxide has been removed in the flue gas desulphurisation unit, the NO level is around 50–200 ppm. Colourless NO is only partially soluble in water. NO_2, on the other hand, has a 6,000 times higher solubility than NO. When any of the NOx dissolves in water, it forms nitric acid (HNO_3) or nitrous acid (HNO_2), as follows:

$$NO + H_2O \rightarrow HNO_2$$

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3$$

$$3HNO_2 \rightarrow HNO_3 + 2NO + H_2O$$

In microalgal bioreactors, where the pH is normally higher than 4, HNO_3 and HNO_2 are mainly present as NO_3^- and NO_2^-, respectively. Microalgae can take up nitrogen in several forms: NH_4^+, NO_3^-, NO_2^-, NO and N_2. The exact mechanisms through which microalgae use NOx are still to be proven by employing more accurate techniques such as nitrogen isotopes (Van Den Hende and others, 2012). It was found that algae can take up the dissolved NO through diffusion. To some extent, the dissolved NO can be oxidised to nitrate or nitric in the culture medium before being taken up by algae as nutrients. NO was found to be used preferentially as a source for microalgal growth rather than nitrate (Nagase and others, 2001). Through this observation, it is expected that the presence of NOx in flue gas may not inhibit algal growth (Doucha, 2005; Ghorbani, 2013). Furthermore, some studies report that NOx can be regarded as an additional N-source for microalgae, therefore encouraging algae to grow (Jiang and others, 2013; Kao and others, 2014; Lam and others, 2012; Projapati and others, 2013). The presence of NO is associated with the physiological conditions of microalgae cells. Its concentration usually has a two-sided influence on microalgae growth. This influence is also closely related to the microalgal species. Although a low concentration of NO can be absorbed by the culture medium and used as a nitrogen nutrient source, this positive influence has a limit. The increased concentration results in a lower algae growth rate for most of the species. Negoro and others (1991) and Zhao and Su (2014) both reported that a concentration of more than 300 ppm NO may give rise to a decline in microalgae. However, in Jiang's study (2013), *S dimorphus* was found to grow in up to 500 ppm NO.

Sulphur oxides

SOx is a mixture of SO_2 and about 2–4% of SO_3. SO_2 is a colourless gas with a high solubility in water, where it forms bisulphite (HSO_3^-) and can be further converted to sulphite (SO_3^{2-}) and sulphate (SO_4^{2-}) at certain pH levels. SO_3 quickly reacts with water to form sulphuric acid (H_2SO_4). At pH above 1.9, SO_4^{2-} is the major species.

$$SO_2 + H_2O \rightarrow H_2SO_3$$

$$H_2SO_3 + SO_2 \rightarrow H_2SO_4$$

$$SO_3 + H_2O \rightarrow H_2SO_4$$

The presence of SO_2 inhibits microalgae growth. Although some microalgal species are able to grow in high SO_2 concentrations, they have a longer lag phase than those grown without SO_2 present. It is almost impossible for most microalgae to grow when the SO_2 concentration exceeds 100 ppm, (Jiang and others, 2013; Zhao and Su, 2014). Seambiotic (Ben-Amotz, 2008) have conducted several trials of microalgal production using coal-fired flue gas for their commercial process and reported an even lower toxic SOx limit, 60 ppm, for microalgae to grow. Jiang and others (2013) summarised Lee's research (2002) that growth of *Chlorella KR-1* was totally inhibited by 150 ppm SO_2 and Westerhoff's research (2010) that *Scenedesmus*, *Chlorella* or a mixture of the two cultures died almost immediately upon gaseous addition of 313 ppm SO_2 in 20% CO_2. Negoro and others (1991) evaluated the SOx and NOx effects on the growth of ten strains of marine and halotolerant microalgae. The growth of *Nannochloris sp.* and *Nannochloropsis sp.* was not affected by 50 ppm of SO_2 when the CO_2 concentration was 15%. However, at 400 ppm SO_2, the pH dropped and growth ceased after 20 hours of cultivation. It was concluded that any inhibitory effects may have been attributable to rapid drops in pH due to excessive rates of flue gas delivery.

Both pH and HSO_3^- play a role in the tolerance of microalgae to SO_2 (Lam and others, 2012; Van Den Hende and others, 2012; Zhao and Su, 2014). Due to the hydrolysis of SO_2, H^+ is released. This causes a drop in the pH of the culture medium, thereby indirectly affecting the normal conduct of the CCM and even killing the microalgae cells when the pH is below 3. A recent study (Kao and others, 2014) showed that when using industrial flue gas to cultivate microalgae, only a slight pH decrease in the broth was observed; the lowest pH was ~ 6.4. This indicates the negative effect of SO_2 on microalgal growth was not very significant. In the conversion of HSO_3^- into SO_4^{2-}, highly oxidative molecules are produced, such as superoxide anions, hydroxyl radicals and hydrogen peroxide. These molecules can cause cell membrane lipid peroxidation and bleaching of chlorophyll, consequently damaging their pigments and proteins, and thus inhibiting microalgae growth.

The effect of SOx and NOx on microalgae CO_2 fixation depends on algae cell density, SOx and NOx concentration, gas flow rate, reactor type and species (Van Den Hende and others, 2012). Of these, species is the most important factor. Some algae can tolerate higher levels of SOx and NOx. For example, *Chlorella caldarium* has the ability to grow in highly acidic media and at elevated temperature. *Dunaliella tertiolecta* can grow even when the NOx level is 500 ppm (Pires and others, 2012). Maeda and others (1995) have shown that *Chlorella sp. T-1* can produce sufficient biomass under flue gas containing up to 10 ppm SOx and 150 ppm NOx. Ben-Amotz (2008) found that *Nannochloropsis sp.* grows better on coal combustion flue gas than on pure CO_2. In such cases, flue gases from power plants can be directly utilised as the CO_2 source in algal production, without prior need of upstream separation of CO_2 from the flue gas.

Mercury and nickel

Van Den Hende and others (2012) summarised the effects of heavy metals in the flue gas. Microalgae possess high metal uptake capacities (uptake and adsorption) and can detoxify a wide range of heavy metals. Although traces of heavy metals are essential as co-factors for many enzymatic processes in microalgae, higher concentrations are toxic. For example, Ghorbani and others (2014) reviewed Matsumoto's study (1997) which reported that nickel (Ni) and vanadium (V) above 1.0 and 0.1 ppm,

respectively, decrease algal productivity. As one of the most important trace heavy metals in flue gas, the effect of mercury (Hg) on algae growth has been studied (Ghorbani and others, 2014; Van Den Hende and others, 2012; Zhao and Su, 2014). Mercury exists in coal combustion flue gas in a variety of forms depending on the coal type and combustion conditions. The primary forms are elemental, oxidised and particulate. Particulate mercury in the flue gas can be removed using air pollution control devices such as electrostatic precipitators and fabric filters (baghouses). Elemental mercury is often oxidised and captured by FGD scrubbers. The effect of oxidised mercury has been experimentally investigated but with conflicting results. Some work suggests that Hg has no detrimental effects on microalgal growth, and some algae may convert Hg between forms representing a possible route to toxic remediation (Ghorbani and others, 2014). Others (Zhao and Su, 2014) think that microalgae growth rate can be inhibited even though Hg^{2+} concentration is at an extremely low level. With increasing concentration of Hg^{2+}, the chlorophyll content decreased gradually, directly causing a reduction in photosynthetic efficiency. Mercury is especially detrimental for microalgae in reactors sparged with untreated flue gas (Douskova and others, 2009).

Initial inoculation density

Theoretically, microalgal biomass production or corresponding carbon fixation increases as the initial inoculation concentration rises under given conditioning factors and culture time. In the microalgal growth process, a higher initial microalgae cell concentration can reduce CO_2 load and enhance the tolerance to CO_2 and even toxic compounds such as SO_2 and NO, leading to increased biomass production. Zhao and Su (2014) summarised a collection of work and reported that when the initial culture density increased to 0.3 g/L, *Chlorella sp.* cells could grow well with 100 ppm SO_2 and 300 ppm NO. Additionally, for some microalgal species, the short and steep lag phase could be observed with a high initial concentration.

However, initial cell concentration usually has an interactive influence on the microalgal growth with other conditioning factors, such as C source, N source, light intensity and temperature, which are decisive to the special growth characteristics. Increasing initial cell concentration can intensify the competition among microalgae for nutrients, light, and other conditioning factors when these are insufficient. In contrast, high initial biomass concentration increases the carbon fixation and biomass production, while nutrient source and light conditions are sufficient. This increased speed of microalgae growth may create self-shading, which in turn slows growth. Therefore, there is a complex relationship between initial inoculation density and special growth (Zhang and others, 2001; Zhao and Su, 2014).

pH

The pH is an important factor in culture media. Besides chemical properties of the culture medium, pH changes are attributed to the hydrolysis of CO_2 and water-soluble pollutants such as SOx from flue gas. Therefore, the effects of pH on microalgal growth mainly depend on the CO_2 and SO_2 concentration in the culture medium. For atmospheric CO_2, there is no significant pH change in the culture medium. However, for combustion flue gas, the pH sharply reduces to about 5.5 with a CO_2 concentration of 14% or more. Additionally, the presence of 100–250 ppm SO_2 reduces the pH value to about 3.5–2.5 at an aeration rate

of 0.25 vvm (Zhao and Su, 2014). With elevated CO_2 concentrations, pH drops to pH 5 and, with higher SOx concentrations, a pH of 2.6 has been reported (Maeda and others, 1995).

Usually, a low pH inhibits microalgal growth. Whereas the pH change due to the CO_2 has just a minor influence on algal growth, the strong pH change caused by SOx inhibits all growth. The pH drop could be prevented with buffered medium and active pH control. Maeda and others (1995) added $CaCO_3$ to the culture medium to prevent the drop in pH and microalgae death. Most microalgal species have their own optimal pH ranges under which they grow. However, after being habituated in the changed culture medium, some microalgal species may be able to tolerate extremely low pH values. For example, *Chlorella sp.KR-1* can grow at pH below 4.0 (Sung and others, 1998). Rachlin and Grosso (1991) measured the effects of pH on *Chlorella vulgaris* growth. They found that acidic (3.0–6.2) and alkaline (8.3–9.0) pH values retarded its growth. Optimal growth occurred when the pH of the medium was adjusted to values of 7.5 and 8.0. Their results (*see* Table 2) show that when the pH was at 6.9, *Chlorella vulgaris* gained 100% growth, while under acidic conditions (pH 3–5), the growth was reduced to 27.3–55% compared to the growth at pH 6.9. In addition, at an alkaline pH of 8.3–9.0, growth was reduced from 46% to 37.2% of the growth reference values. Of particular interest is that at the alkaline pHs of 7.5 and 8.0, the growth exceeded the reference growth, indicating optimum growth conditions within this narrow pH range.

Table 2 pH effects on the growth of *Chlorella Vulgaris* (Rachlin and Grosso, 1991)

Initial pH	Growth, %	Final PH
3.0	27.3 ± 0.16	2.8
4.0	36.3 ± 0.17	4.0
5.0	55.6 ± 0.18	4.9
6.2	91.9 ± 0.10	6.2
6.9	100	6.9
7.5	124.9 ± 0.20	6.9
8.0	120.0 ± 0.18	7.8
8.3	46.1 ± 0.18	7.9
8.5	49.7 ± 0.18	8.1
9.0	37.2 ± 0.17	8.5

Temperature

Culture medium temperature is an important limiting factor for microalgae growth as photosynthesis is a series of temperature dependent physicochemical reactions. Microalgae can tolerate a range of temperatures and their response to temperature variations can affect the following (Richmond, 2008):

- nutritional requirements;
- rates and nature of metabolism; and
- cell compositions.

Low temperature decreases the ratio of O_2 to CO_2 solubility causing reduced amounts of O_2 fixation by oxygenase activity of RuSisCO carbon fixation; thereby the process of photosynthesis and CCM will not be accelerated. A high temperature inhibits the microalgal metabolic behaviour and respiration intensity. It

also causes low CO_2 solubility in water (Zhao and Su, 2014). Therefore, there is an optimum temperature value or range for microalgal growth. Zhao and Su (2014) summarised the range for the most common microalgal species as 15–26°C, while Ghorbani and others (2014) and Pires and others (2012) report 25–35°C. An intermediate value of 18–20°C, close to room temperature, is often recommended due to high growth rates in this range. The optimum temperature for microalgae to grow varies with microalgal species and culture medium composition. Many microalgae can easily tolerate temperatures up to 15°C lower than their optimal, although temperatures lower than 16°C will slow microalgal growth. However, exceeding the optimum temperature by only 2–4°C may result in total culture loss. Temperatures higher than 35°C are usually lethal for a number of species although several species have been identified which can tolerate temperatures up to 60°C (Kumar and others, 2011; Mata and others, 2010; Zhao and Su, 2014). However, the tolerance and adaptability of some species to high temperature can be improved by induced acclimation technology.

Generally, the temperature of flue gas from coal-fired power plant is around 65-120°C (Kumar and others, 2011; Kvamsdal and others, 2011). In many cases, additional heat is recovered from the flue gases leaving a gas turbine or the boiler house through the application of waste heat boilers. Hence the temperature of the gas stream partly depends on the components installed in the power plant. A post-cooling system usually cools the flue gas temperature to 20–30°C, which is acceptable for most microalgae species. In addition, the selection of appropriate microalgae strains that can tolerate high temperatures is important to reduce the cost of cooling the flue gas. Thermal-tolerant species have been identified. The optimal growth temperature for *Chlorella sp. MTF-7* is 30°C and its growth rate and productivity at higher temperatures (35°C and 40°C) remain high (Chiu and others, 2011). *Chlorella sp. T-1* had an optimal temperature of 35°C, while *Chlorella KR-1* and *ZY-1* are able to grow rapidly at temperatures up to 40°C (Zhao and Su, 2014). Two thermal-tolerant mutants of *Chlorella sp. MT-7* and *MT-15* can grow at 40°C and *Chlorella sorokiniana UTEX1230* at 42°C. Thermophilic cyanobacteria *Chlorogleopsis sp.* can survive 50°C (Pires and others, 2012).

Nutrients

Beside trace metals (Na, Mg, Ca, Mn, Zn, Cu, Fe, Si and Mo) and vitamins, nitrogen and phosphorus are the two most important nutrients in the culture medium to maintain microalgal growth. As a component of both nucleic acids and proteins, nitrogen is directly associated with the primary metabolism of microalgae. Usually, the nitrogen source exists in the forms of nitrate (NO_3^-), nitrite (NO_2^-) and ammonia salt, such as ammonium (NH_4^+) in the culture medium. Fast-growing microalgal species prefer ammonium rather than nitrate as the primary nitrogen source. Adding nitrate will enhance microalgal growth if the medium lacks nitrates. Under partial nitrogen deprivation, microalgae grow at lower rates, but produce significantly more lipids, which are reserve compounds synthesised under stress conditions, even at the expense of lower productivities. Phosphorus needs to be supplied in the forms of phosphate, hydrogen phosphate (HPO_4^{2-}) and dihydric phosphate ($H_2PO_4^-$). Other forms of phosphorus may combine with metal ions and be precipitated, thus becoming unavailable to the algae (Kumar and others, 2010; Prajapati and others, 2013; Zhao and Su, 2014).

Extremely low N and P concentrations inhibit microalgal growth, whilst high concentrations decrease the microalgae growth rate and can even kill them. The form of nutrients also affects microalgae growth. For example, when culturing *Isochrysis galbana* in nitrate, and nitrite and ammonium, it was found that ammonium cultures gave significantly higher growth rates, as well as more lipids, than the nitrate and nitrite medium (Fidalgo and others, 1998). In addition, a high N/P ratio can increase the growth rate. Moreover, N sources can influence other process factors, particularly the C source (Zhao and Su, 2014).

These nutrients normally come from chemical or inorganic fertilisers. The use of chemical fertiliser has the advantage of reducing contamination in the culture medium and thus promotes water reutilisation to re-culture microalgae (Lam and Lee, 2012). Some researchers suggest using wastewater to culture microalgae as secondary and tertiary wastewaters usually contain significant amount of nitrate and phosphate, which are not removed during primary treatment (Gonçalves and others, 2014; Lam and Lee, 2012). As mentioned earlier, NOx and SOx in coal combustion flue gas can also be utilised as N and S sources for microalgae growth.

2.3.2 Hydrodynamic parameters

Flow and mixing

Microalgae are usually cultivated in either open or closed containers (*see* Chapter 3). Appropriate turbulent flow and mixing are necessary and important to homogenise the cells, light, heat, nutrients, and distribution of metabolites, to enhance mass transfer and to prevent microalgal aggregation and sedimentation. Mixing also takes advantage of the flashing light effect, which increases algal productivity (Grobbelaar, 1994; Kumar and others, 2011; Zhao and Su, 2014). Excessive turbulent flow and mixing may damage the microalgae cells, besides requiring a large energy input, as not all the microalgae species can tolerate vigorous shear stress. Optimum levels of flow and mixing rate are needed.

The most common methods of mixing are (Kumar and others, 2010; Zhao and Su, 2014):

- jet pumping, which offers a fair mixing efficiency, but low gas transfer rate. The associated hydrodynamic stress increases with the rotation speed of the pumps, or the number of passes of the microalgal suspension through the pump units. It is often employed in open systems;
- mechanical stirring, which offers good mixing efficiency and gas transfer. It is likely to produce significant hydrodynamic stress, which can be managed via adequate use of baffles to create a controlled turbulence pattern. The effect is directly associated with stirring speed. Shear stress near the impeller may cause significant damage to microalgal cells; and
- gas aerating (bubbling), which offers reasonable mixing efficiency and gas transfer with low hydrodynamic stress. Aeration rate is an important parameter, as well as bubble size. It is defined as the gas volumetric flow rate per unit volumetric culture medium (vvm).

Zhao and Su (2014) summarised recent research developments on mixing in bioreactors. An appropriate turbulence effect caused by an appropriate aeration rate is helpful to increase microalgal production. But an extremely high aeration rate increases shear stress, especially in the processes of bubble generation,

bubble deformation and gas-liquid interface formation. Furthermore, cell damage in sparged cultures increases as the biomass concentration increases, because exponentially higher degrees of stirring are needed to maintain a high density culture at a predefined level of mixing. One approach to minimise this problem is to maintain a low gas input per nozzle, so as to reduce shear stress and consequent cell damage. Moreover, the flow pattern caused by aeration can be improved by optimising the bioreactor configuration, such as using horizontal and vertical baffles in a flat plate airlift. Also, turbulent mixing by aeration can be controlled via adequate use of baffles. Recently, computerised fluid dynamics (CFD) techniques have been employed to optimise flow and mixing in a bioreactor. Usually, performance of microalgal CO_2 fixation and biomass production have a nonlinear relationship with aeration rate. For most closed cultivation, the recommended aeration rate is 0.1-1. The optimum aeration rate varies with microalgal species and bioreactor configuration. For example, 0.025–1 vvm was proposed to be cost effective for 5% or 10% (v/v) CO_2 aeration and 0.05 vvm for a flat panel bioreactor. The aeration strategy is another factor. Gradual increase of CO_2 supply could enhance the microalgae growth rate and CO_2 fixation rate compared with constant CO_2 supply. This is because microalgae can adapt to the new CO_2 concentration and enhance their CO_2 tolerance when the CO_2 supply slowly increases. This is especially the case under relatively high concentrations of CO_2.

Mass transfer

Mass transfer is a complex process in microalgal culture, involving three-phase mass transfer:

- gas (CO_2) – liquid (culture medium);
- gas (CO_2) – solid (microalgae); and
- liquid (culture medium) – solid (microalgae).

As CO_2 has a low mass transfer coefficient, the mass transfer from gas to liquid phase is the major limiting step in cultivation of microalgae. The oxygen produced by photosynthesis inhibits microalgae growth. A common solution is to supply the gas with high flow rates to work in a turbulent regime. Another solution is to strip the culture medium with air or inert gases, such as argon (Pulz, 2001). In the gas aerating method, the mass transfer performance and biochemical reaction rate depend on bubble size, gas holdup, gas-liquid contact area, CO_2 concentration and gas-liquid ratio (Zhao and Su, 2014).

New methods to increase mass transfer include enhancing the CO_2 concentration gradient and expanding the contact area. The former involves using $NaHCO_3$ as an additive to generate a chemical reaction. The latter involves using hollow fibre membranes (Zhao and Su, 2014). Cheng and others (2006) evaluated the performance of a photobioreactor with a hollow fibre membrane for CO_2 fixation by *Chlorella vulgaris*, aimed at enhancing CO_2 and O_2 mass transfer. The membrane was used for CO_2 supply and for removing the oxygen produced by photosynthesis. The CO_2 fixation capacity increased more than 3 times. However, this process caused fouling deposition, which increased the pressure drop, reduced the mass transfer and increased the power consumed for gas transport.

2.4 Summary and comments

Beside the culture conditions, the microalgal species is important as it directly influences the photosynthesis efficiency, and hence, the performance of carbon fixation and biomass production. The selection, isolation and culture of microalgal species with a fast growth rate, high photosynthesis rate, strong environmental tolerance/adaptability and a high lipid content will need more research and development. Efforts to find the 'ideal' microalgae species for CO_2 capture, which have commercial value and grow well under a wide range of thermal conditions and various ranges of CO_2 concentration will continue.

Microlagal CO_2 fixation is a complex process, especially in a flue gas environment. Usually, most of the physicochemical and hydrodynamic process parameters have important nonlinear effects on microalgal growth. However, their detailed reaction mechanisms, especially the impact on the activity of CA and CCM, have not yet been completely understood and still need to be explored (Zhao and Su, 2014). Also, these parameters are related and interact with each other. It is crucial to comprehensively consider the effects of all process factors to improve the microalgal growth and the tolerance to the culture environment. Previous studies mainly focused on the independent effect of a single factor or the interactive effects of two factors. Up to now, there have been few investigations involving the comprehensive relationship between microalgal CO_2 fixation/biomass production kinetics and process parameters. The related issues about multi-objective optimisation are also rarely reported (Zhao and Su, 2014).

3 Microalgae cultivation

Microalgae growth takes place by photoautotrophic or heterotrophic production. Some algae strains can combine autotrophic photosynthesis and heterotrophic assimilation of organic compounds in a mixotrophic process. Under natural growth conditions, phototrophic algae absorb sunlight, and assimilate carbon dioxide from the air and nutrients from the aquatic habitats. Therefore, as far as possible, artificial production should replicate and enhance the optimum natural growth conditions. The use of natural conditions for algae production has the advantage of using sunlight as a free natural resource. However, this may be limited by availability of sunlight due to diurnal cycles and seasonal variations. To address this, artificial fluorescent lamps are almost exclusively used for the cultivation of phototrophic algae at pilot scale facilities. Artificial lighting enables continuous production, but at significantly higher energy input (Brennan and Owende, 2010).

Currently, photoautotrophic production is the only method which is technically and economically feasible for large scale production of algae. Two types of microalgae cultivation systems that have been deployed based on open pond and closed photobioreactor technologies. These two systems are well documented by Yen and others (2014), on whose work this chapter is based.

Since most microalgae production is photoautotrophic, the light regimen is crucial. Generally, the light regimen itself is influenced by light intensity, light incident angle, surface area, cell density, and cell composition. Furthermore, the light regimen in an outdoor environment is significantly influenced by geographic location, day period and weather conditions (Ho and others, 2011). Other factors that need to be considered when designing cultivation systems are efficient mixing and rapid gas transport (Signh and Sharma, 2012). Basically, the key factors for the design and operation of microalgae cultivation systems are as follows (Yen and others, 2014):

- how to use appropriate light sources (intensity and wavelength);
- how to enhance light conversion efficiency;
- how to maintain an appropriate microalgae biomass concentration during prolonged operation; and
- how to maintain the stability of a continuous culture of microalgae.

These design principles will be discussed, alongside an introduction to microalgae culture systems, in this chapter.

3.1 Open systems

Microalgae cultivation in open pond production systems has been used since the 1950s. Open systems can be divided into natural waters (lake, lagoons, ponds) and artificial ponds or containers. Among the various sizes and shapes of open systems, the most commonly used ones include large ponds, tanks, circular ponds, and raceway ponds. Open pond systems are cheaper and easier to construct and operate than closed systems, at the minimum requiring only a trench or pond. Large ponds have the largest production capacities relative to other systems of comparable cost. Also, open pond cultivation can

exploit unusual conditions that suit a specific algae. For instance, *Spirulina* sp. thrives in water with a high concentration of sodium bicarbonate, whilst *Dunaliella salina* grows in extremely salty water. Open culture can also work if there is a system of culling the desired algae and inoculating new ponds with a high starting concentration of the culled algae. The biggest advantage of these open ponds is their simplicity, resulting in low production and operating costs. However, major limitations in open ponds include poor light utilisation by the cells, evaporative water losses, diffusion of CO_2 to the atmosphere, and the requirement for large areas of land. The ponds are usually shallow to ensure sufficient light exposure for the microalgae, because sunlight can only penetrate the pond water to a limited depth. In addition, temperature and lighting cannot be controlled. The growing season is largely dependent on location and, aside from tropical areas, is limited to the warmer months. Bad weather can often stunt algae growth. Furthermore, contamination by predators, alien microalgae species, and other fast-growing microorganisms restrict the commercial production of algae in open culture systems. Due to inefficient stirring mechanisms, mass gas transfer rates are relatively low compared with those of closed systems. All these limitations lead to lower biomass productivities for open systems compared with closed systems. Nevertheless, the simple operation and easy scale-up for mass cultivation make open systems the first-choice option for microalgae cultivation in industrial applications (Brennan and others, 2010; Singh and Sharma, 2012; Yen and others, 2014).

The same limitations apply to using algae to capture CO_2 from a coal-fired power plant. Burgess and others (2011) summarised Benemann's (2011) key economic issues for open pond algae CO_2 fixation at a power plant:

- cost of transport of CO_2 from the facility to the capture plant, including the need to store CO_2 at night when the algae are inactive, and to design the pipeline and infrastructure for the highest CO_2 consumption rate in the summer;
- loss of CO_2 during transfer to the algal pond and through out-gassing for open ponds;
- inefficiencies mean that only 40–60% of the CO_2 actually fixed by the algae is present in the final algal oil; and
- the 'maximum plausible' CO_2 final capture in open ponds is only 10% of that emitted by the power plant.

To capture the quantities of CO_2 emitted from a large coal-fired power plant requires an area of some hundreds of square kilometres and, for cost reasons, this dictates a need for systems based on open pond culture. High productivity algal ponds require enrichment of the culture media by CO_2. In the context of industrial fixation this requires either the separation of CO_2 from the process or the transport of flue gas to the algal facility. In the former case, the algal facility may be separated from the industrial facility by some distance if the CO_2 is compressed and piped. In the latter case, it is not practicable to duct flue gases for long distances due to the large volumes involved. Therefore the algal facility must be located within close proximity of the power plant.

3.1.1 Simple ponds

The marked advantage of these open ponds is their simplicity, resulting in low production and operating costs. Operation is simple for this system, which only has a giant rotating mixer at the centre of the pond to avoid precipitation of algal biomass. Circular ponds have a rotating arm to provide agitation, while in inclined systems mixing is achieved through pumping and gravity flow. Although this is indeed the simplest among all the microalgae cultivation techniques, it has a major drawback: the environment in and around the ponds is not completely under control. Adverse weather conditions can stunt algal growth. For example, high temperatures as well as insufficient or excessive sunlight intensities are critical factors affecting the efficiency of microalgae growth. In addition, contamination from bacteria or other foreign microorganisms often results in the predominance of undesirable species over the desired algae growing in the pond. Rain is a common source of contamination, since it can flush microorganisms into the ponds from the air. Therefore, finding an appropriate cultivation location is crucial to the success of open systems. Despite the disadvantages of the simple pond system, the simple operation and high scale-up availability are attractive factors and these ponds are often utilised for industrial production of microalgae (Mata and others, 2010; Yen and others, 2014).

3.1.2 Raceway ponds

Raceway ponds are a modified version of the simple open pond system that have a different flow pattern. In raceways, the water flow direction is controlled by the rotation speed of paddlewheels, in contrast to only coaxial mixing in conventional open ponds. In raceway systems, the microalgae, water, and nutrients are continuously circulated around a racetrack, following the same direction as the paddlewheel (*see* Figures 3 and 4). In this way, the circulation rate around the racetrack can be adjusted by the paddle speed. Paddlewheels provide the driving force for liquid flow, so the microalgae are kept suspended in the water and are regularly circulated back to the surface. Raceway ponds are usually shallow, operating at a water depth of 15–20 cm, in order to expose the algae to sunlight (Yen and others, 2014).

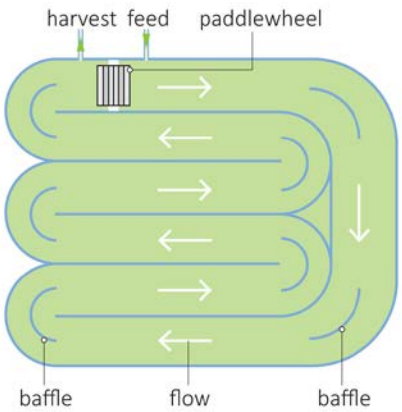

Figure 3 A raceway pond (Singh and Sharma, 2012)

Figure 4 Seambiotics open pond 2009 (Ben-Amotz, 2011a)

Raceways are typically made from poured concrete or dug into the earth and lined with a plastic liner. Baffles in the channel guide the flow around bends in order to minimise space. The system is often operated in a continuous mode, where the fresh feed (containing nutrients such as nitrogen, phosphorus and inorganic salts) is added in front of the paddlewheel. The algal broth is harvested behind the paddlewheel after it has circulated through the loop. Depending on the nutrients required by algal species, several sources of wastewater can be used for algal culture. For some marine-type microalgae, seawater or high salinity water can be used (Singh and Sharma, 2012).

The same drawbacks observed in the operation of conventional open ponds are also found in raceways. Furthermore, the requirement for large areas for microalgae cultivation is another barrier for commercialisation of microalgae systems. Nevertheless, control of environmental factors (such as mixing) in raceways is easier than in conventional open ponds, making the use of raceways for the cultivation of microalgae attractive.

3.2 Closed systems – Photobioreactors

The idea behind the closed pond is to cover an open pond with a transparent or translucent barrier, which turns it into a greenhouse. The term closed systems refers to photobioreactors (PBR) which have no direct exchange of gases and contaminants between the cultivation systems and the outside environment. A photobioreactor can be described as an enclosed, illuminated culture vessel designed for controlled microalgae cultivation. The necessary gas exchange is performed through a sterilised gas filter, thus avoiding contamination inside the culture system. Besides the typical drawback of high equipment cost, closed system photobioreactors have several major advantages over open systems (Singh and Sharma, 2012) as they:

- minimise contamination and allow axenic algal cultivation of monocultures;

- offer better control over conditions such as pH, temperature, light, CO_2 concentration, and so on;
- lead to less CO_2 loss;
- prevent water evaporation;
- permit higher cell concentrations; and
- allow the production of complex biopharmaceuticals.

Singh and Sharma (2012) summarise suggestions given by Tsoglin and others (1996) for the design of the photobioreactor, namely:

- it should permit the cultivation of various microalgal species universally;
- the design must provide for uniform illumination of the culture surface and the fast mass transfer of CO_2 and O_2;
- cells of microalgae are highly adhesive which results in rapid fouling of the light transmitting surfaces of the reactor. This leads to frequent shutdown for mechanical cleaning and sterilisation. The design must therefore prevent or minimise fouling of the reactor, particularly its light transmitting surfaces;
- high rates of mass transfer must be attained by methods that neither damage cultured cells nor suppress their growth;
- the photobioreactor must work under conditions of intense foaming, which often occur with high rates of mass transfer; and
- the non-illuminated part of the reactor should be minimised.

The capital cost of construction is the primary economic variable for photobioreactors. The cost of the land, site preparation, earthworks and levees, geo-textiles and materials are all dependent on the site and the chosen project execution plan.

There are several types of closed systems for the cultivation of microalgae, including vertical (tubular) columns, flat plate photobioreactors, and horizontal tubular photobioreactors. These are described in the following sections. In addition, their advantages and limitations are summarised in Table 3.

Table 3 Advantages and limitations of different photobioreactors (Brennan and Owende, 2010; Yen and others, 2014)

Photobioreactors	Advantages	Limitations
Vertical column (tubular)	Compact, high mass transfer, good mixing with low shear stress, low energy consumption, high potentials for scalability, easy to sterilise, readily tempered, good for immobilisation of algae, reduced photo-inhibition and photo-oxidation	Small illumination surface area, construction requires sophisticated materials, stress to algal cultures, decrease of illumination surface area upon scale-up, expensive compared to open ponds
Flat panel	Large illumination surface area, suitable for outdoor cultures, good for immobilisation of algae, good light path, high biomass productivities, relatively cheap, easy to clean up, readily tempered, low oxygen build-up	Scale-up requires many compartments and support materials, difficulty in controlling culture temperature, some degree of wall growth, possibility of hydrodynamic stress to some algal strains
Horizontal tubular	Large illumination surface area, suitable for outdoor cultures, good biomass productivities, relatively cheap	Gradients of pH, dissolved oxygen and CO_2 along the tubes, fouling, some degree of wall growth, requires large land space

3.2.1 Vertical column (tubular) photobioreactors

A vertical column (also called tubular) photobioreactor is made up of vertical tubing (glass or acrylic) that is transparent to allow the penetration of light for autotrophic microalgae cultivation. A gas sparger system is installed at the bottom of the reactor, which converts the inlet gas into tiny bubbles. Sparging with the gas mixture provides the driving force for mixing, mass transfer of CO_2, and removing O_2 produced during photosynthesis (*see* Figure 5). Normally, no physical agitation system is required. Vertical tubular photobioreactors can be categorised as bubble column or airlift reactors based on the liquid flow patterns inside the photobioreactor (Singh and Sharma, 2012; Yen and others, 2014).

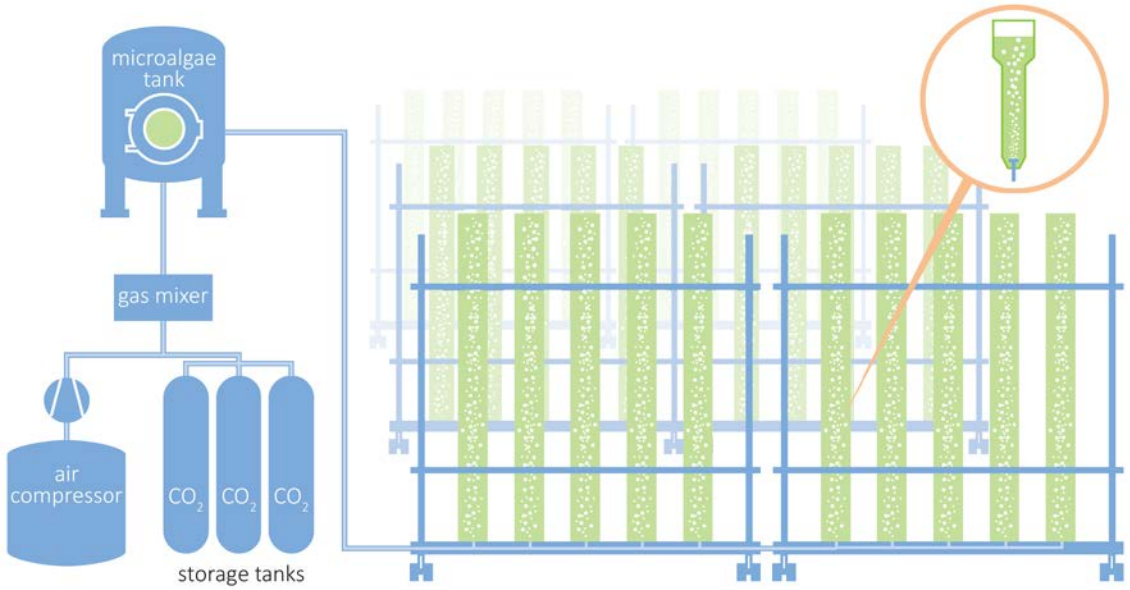

Figure 5 Vertical column photobioreactors (Yen and others, 2014)

Bubble column photobioreactors

Bubble column reactors are cylindrical vessels with a height greater than twice their diameter. They have the advantages of low capital cost, high surface area to volume ratio, lack of moving parts, satisfactory heat and mass transfer, relatively homogenous culture environment, and efficient release of O_2 and residual gas mixture. The gas bubbling upward from the sparger provides the required mixing and gas transfer. Therefore, the sparger's design is critical to the performance of a bubble column. Perforated plates are used as the sparger in tall bubble columns to break up and redistribute coalesced bubbles (*see* Figure 5). The light supply often comes from outside the column. Nevertheless, an inner-illumination design is used due to higher light-penetration efficiency and more uniform light distribution. Photosynthetic efficiency largely depends on the gas flow rate as well as the light and dark cycle created when the liquid is circulated regularly from the central dark zone to the external zone at a higher gas flow rates. A circulation flow pattern is not created when the gas flow rate is less than 60.01 m/s due to the lack of back mixing. The photosynthetic efficiency can be increased by increasing the gas flow rate as this leads to shorter light and dark cycles (Singh and Sharma, 2012; Yen and others, 2014).

Airlift photobioreactors

Airlift reactors, common in traditional bioreactor designs, are made of a vessel with two interconnecting zones. One of the tubes, called a gas riser, is where the gas mixture flows upward to the surface from the sparger. The other region, called the downcomer, does not receive the gas, but the medium flows down toward the bottom and circulates within the riser and the downcomer (Singh and Sharma, 2012; Yen and others, 2014).

Based on the circulation mode, the design of an airlift reactor can be further classified into one of two forms: internal loop or external loop. In the internal loop reactor, regions are separated either by a draft tube or a split-cylinder. The internal loop reactor can be further classified into an internal loop split airlift reactor and an internal loop concentric tube reactor. In the external loop reactor, the riser and downcomer are separated physically by two different tubes. Mixing is achieved by bubbling gas through the sparger in the riser tube without any physical agitation (Singh and Sharma, 2012; Yen and others, 2014).

The riser is similar to those used in a bubble column, where the gas moves randomly and haphazardly upwards. This decreases the density of the riser enabling the liquid to move upwards. The upward movement is assisted by the gas holdup of the riser. The gas leaves the liquid in the disengagement zone with the performance dependent on the design and operating conditions. The amount of gas which does not disengage in this zone becomes trapped by the liquid moving downwards in the downcomer. Gas holdup in the downcomer has a significant influence on the fluid dynamics. Degassed liquid moves downwards in the annular space in a laminar fashion with a defined and oriented motion. Increasing the gas hold-up difference between the riser and downcomer is an important criteria to take into account when designing an airlift reactor (Singh and Sharma, 2012).

An airlift reactor has the advantage of creating a flow circulation where the liquid culture passes continuously through dark and light phases, giving a flashing-light effect to the microalgal cells. The residence time of gas in the various zones controls performance, affecting parameters such as gas–liquid mass transfer, heat transfer, mixing, and turbulence. It can be improved by, for example, putting a sparger into the annular tube. A rectangular airlift photobioreactor is also suggested to have better mixing characteristics and high photosynthetic efficiency, but the design complexity and difficulty of scale-up are drawbacks (Singh and Sharma, 2012).

3.2.2 Flat panel photobioreactors

The flat panel reactor has a cubic shape with a minimal light path (*see* Figure 6). It can be made from transparent materials like glass, plexiglass, optical light film, and polycarbonate. It has a high surface area to volume ratio, and an open gas disengagement system. Light is evenly emitted from a flat transparent surface screen or from lamps above the culture. Agitation is provided either by bubbling air from one side through a perforated tube or by rotating it mechanically using a motor.

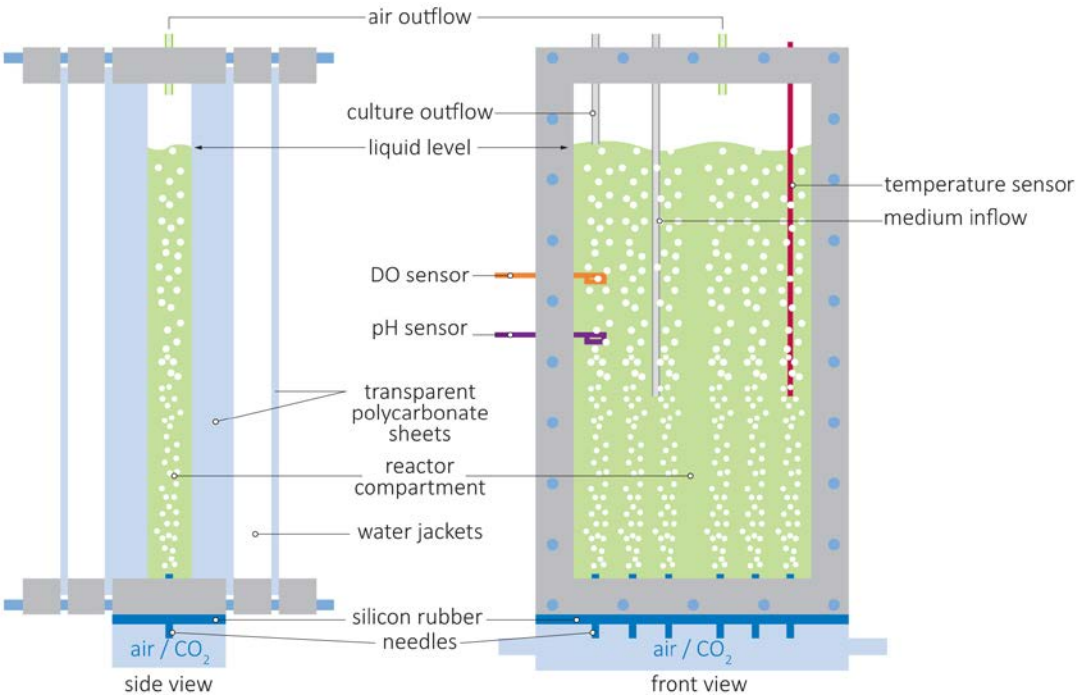

Figure 6 A flat panel photobioreactor (Singh and Sharma, 2012)

A number of flat panels can be easily combined to provide a reactor with the desired light path. However, flat plate systems may experience problems with relatively high space requirements, high light energy requirements, difficulties in cleaning, and possible low efficiency in terms of mass production per unit of space. Productivity is highly dependent on the space between the panels and the areal productivity constraint for outdoor application. On the other hand, if flat plate systems are to be operated indoors, then certain crucial factors are involved, including distance of light sources from panels, temperature effects, illumination of one or both panel sides, and light path. Scale-up of the flat plate system is potentially difficult due to the increase in hydrostatic pressure with increasing volume. In general, the structure of flat plate systems cannot tolerate very high pressure. Moreover, as discussed in Chapter 2, the hydrodynamic stress on microalgae cells may affect their growth. In addition, the biomass productivity in parallel flat panels is strongly influenced by shading and light penetration between the panels. To reduce the equipment cost, a novel design of a vertical flat panel photobioreactor, consisting of a transparent bag, for example plastic, located on a rigid frame, has been proposed. This could enhance the economic feasibility (Yen and others, 2014).

Singh and Sharmar (2012) briefly describe a number of different flat panel photobioreactors designs. A flat panel was built by Barbosa and others (2005) from a polycarbonate sheet held together with stainless steel. The surface area to volume ratio was 0.34 cm^{-1}.The mixture of CO_2 and air was sparged through 17 needles with a diameter of 0.8 mm punched through a piece of silicon placed at the bottom of the reactor. The reactor was illuminated at one surface with 10 fluorescent tubes having total light intensity of approximately 1000 µmol photons/m^2 s. Iqbal and others (1993) modified a flat panel reactor by including some more engineering features like giving it a V shape to obtain a high mixing rate, eliminating escape corners which minimises shear stress and cell adhesion to the walls of the reactor. Tredici and

Zittelli (1998) designed a near horizontal flat panel, which was divided longitudinally into five channels with two plexiglass manifolds at the top and at the bottom. The surface area to volume ratio was 40 m^{-1} with a gas holdup capacity of 10.3%. A CO_2 gas mixture was injected axially through the bottom tubular plexiglass manifolds. A photosynthetic efficiency of 4.8%, less than an inclined tubular reactor (5.6%), was achieved when kept outdoors and using Arthrospira (Spirulina) platensis M2. This may be due to the curved surface of the inclined tubular reactor, which reduces the light saturation effect at midday. A continuous culture of *Chlorella sorokiniana* in a flat panel with a short path length and under high irradiance conditions gave a volumetric productivity rate of 12.2 g/L/d. This is the highest productivity of green algae achieved so far under over-saturating light conditions. The reactor can be scaled up by arranging several plates over an area. Scale-up can be achieved not by lengthening the reactor but by increasing the liquid height to increase the light path. The flat panel designed by Degen and others (2001) used the airlift circulation mode. It had a smaller downcomer zone and large riser zone where the compressed air was injected. In addition, baffles were employed, attached alternatively to the front and back of the larger faces of the panel.

One successful application of a flat panel bioreactor is the BIQ algal house in Hamburg, Germany (*see* Figure 7). It has 129 bioreactors installed on the south west and south east faces of the four-storey building. The bioreactor, SolarLeaf, consists of two 2.8 m x 0.7 m vertical façade panels forming a 0.18 m thick cavity with a capacity of 24 litres for the circulation of liquids and growth of algae. For safety and thermal insulation, the bioreactor is clad on both sides with laminated safety glass. Compressed air is pumped in from the bottom of each bioreactor at certain time intervals (*see* Figure 8). The gas emerges as large air bubbles visible to the naked eye and generates an upstream water flow and turbulence to stimulate the uptake of CO_2 and light by the algae. At the same time, the inner surfaces of the façade panels are washed by a mixture of water and air.

Figure 7 BIQ algal house in Hamburg, Germany

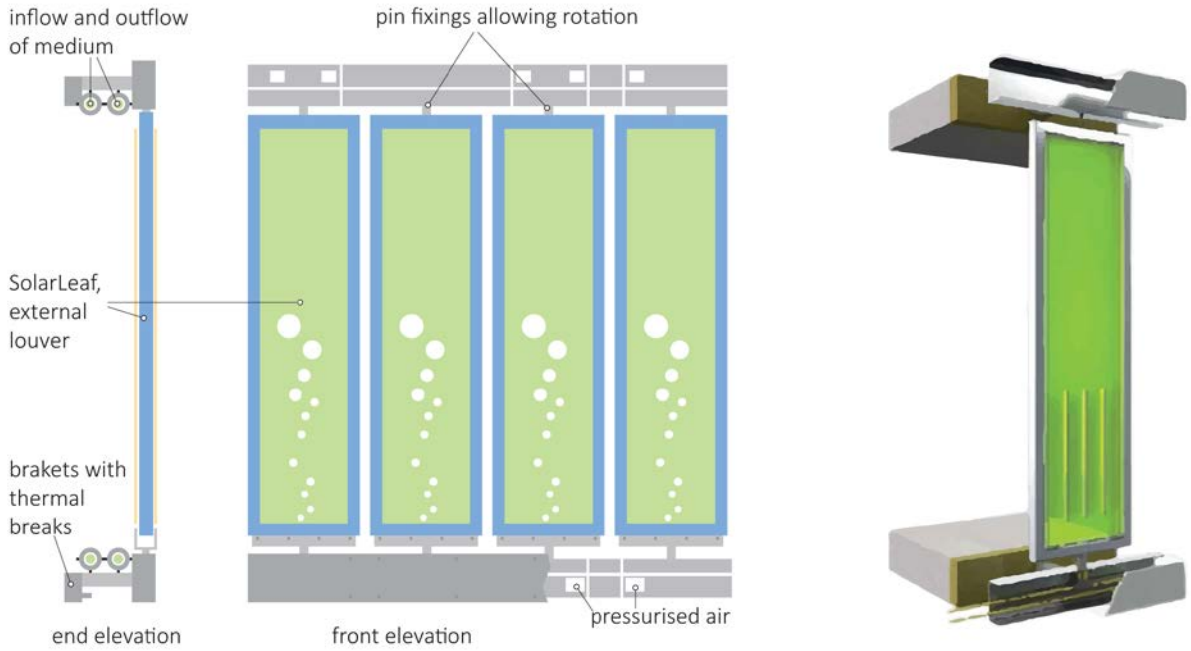

Figure 8 Principal construction methodology of the flat panel photobioreactor, SolarLeaf (Colt, 2014)

3.2.3 Horizontal tubular photobioreactors

Tubular photobioreactors are made of transparent polypropylene acrylic or polyvinylchloride pipes with small internal diameters to increase the penetration of light. Mixing and agitation of the culture are maintained by an air pump to provide circulation (*see* Figure 9). Horizontal tubular photobioreactors are placed horizontally in various designs, including parallel sets of tubes, a loop shape, an alpha shape, an inclined tubular shape or horizontal tubular reactor. The various shapes provide advantage in outdoor

culture due to their orientation towards sunlight, which results in high light conversion efficiency (Singh and Sharma, 2012; Yen and others, 2014).

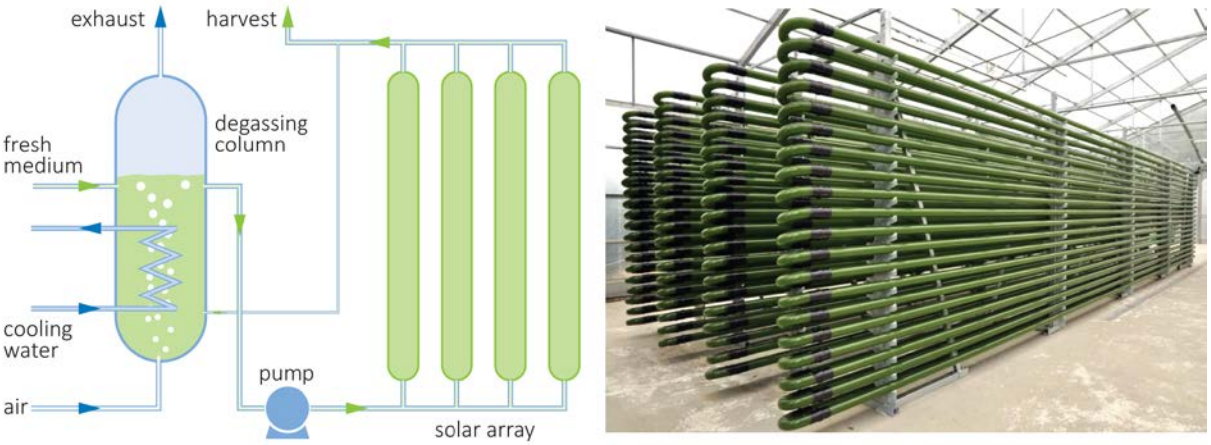

Figure 9 A horizontal tubular photobioreactor (Singh and Sharma, 2012)

The most significant characteristic of a tubular system, that is different from the vertical column bioreactor, is the improvement of air-residence time inside the tubular bioreactor. This can provide more dissolved CO_2. These systems could use artificial light, but they are also designed for natural light (sunlight). The hydrodynamic stress on the algae varies, depending on the flow characteristics of each system, for example turbulent flow or pump type. Likewise, the gas transfer to the culture can vary from low to high, depending on the flow characteristics and the air-supply technique adopted.

The operational difficulties are similar to other systems, including growth of microalgae on the wall of the tubes, thus blocking light penetration, high oxygen concentration that can inhibit photosynthesis, and limits on the length of the tube in a single run. Oxygen build-up during photosynthesis causes photobleaching and reduces photosynthetic efficiency. Methods adapted for cooling the system include spraying water on the surface of the tubes, overlapping of tubes, placing the light harvesting unit inside a pool of temperature controlled water, and regulating the temperature of the feed or recirculation stream. A major drawback is the high energy consumption of about 2000 W/m^3 compared with 50 W/m^3 for bubble column and flat plate photobioreactors. This high energy input is necessary to reach high linear liquid velocities of about 20–50 m/s for achieving turbulent conditions with sufficient short light/dark cycles. The inclined tubular system is similar to the horizontal tubular reactor; however, it has an inclination of a few degrees towards the sun. This inclination helps in harnessing sunlight more efficiently. Singh and Sharma (2012) describe the reactor designed by Tredici and Zittelli in 1995. This was made up of plexiglass tubes with 3.4 cm internal diameters placed side by side without any space between the tubes. The tubes were connected at the top and bottom ends by tubular plexiglass manifolds. The reactor was laid on a wooden framework facing south with an inclined angle of 5 degrees horizontally. Surface area to volume ratio was maintained at 70 m^{-1}, however, gas holdup was kept to 10.3% of the total volume occupied by the gas bubbles. An automatic evaporative cooling system was used for temperature control. Volumetric productivity and photosynthetic efficiency were higher than those of a flat reactor (Singh and Sharma, 2012).

A helical type photobioreactor (also called coil type) is a special form of a horizontal bioreactor. It consists of a small diameter coiled transparent and flexible tube, and a separate or attached degassing unit. A centrifugal pump drives the culture through the long tube to the degassing unit (*see* Figure 10). The CO_2 gas mixture and culture medium can be circulated from either direction, but injection from the bottom gives a better photosynthetic efficiency.

Most coil type systems have a larger ratio of surface area to culture volume to receive illumination effectively, as well as easy control of temperature and contaminants. They also have the advantage of good balance between energy input and photosynthesis efficiency. This type of system requires less energy for its operation and imposes less mechanical stress to the microalgal cells. The cleaning problems of tubular systems are not easy to overcome due to the small internal tube size; there is no ready mechanical way to clean the inside of a long tube. The scale-up of these systems is relatively easy compared with other photobioreactor designs. The tubular photobioreactor working volume can easily be increased by simply extending the tube length to the designed volume, provided the air pump can provide enough power to pump in air bubbles (Yen and others, 2014).

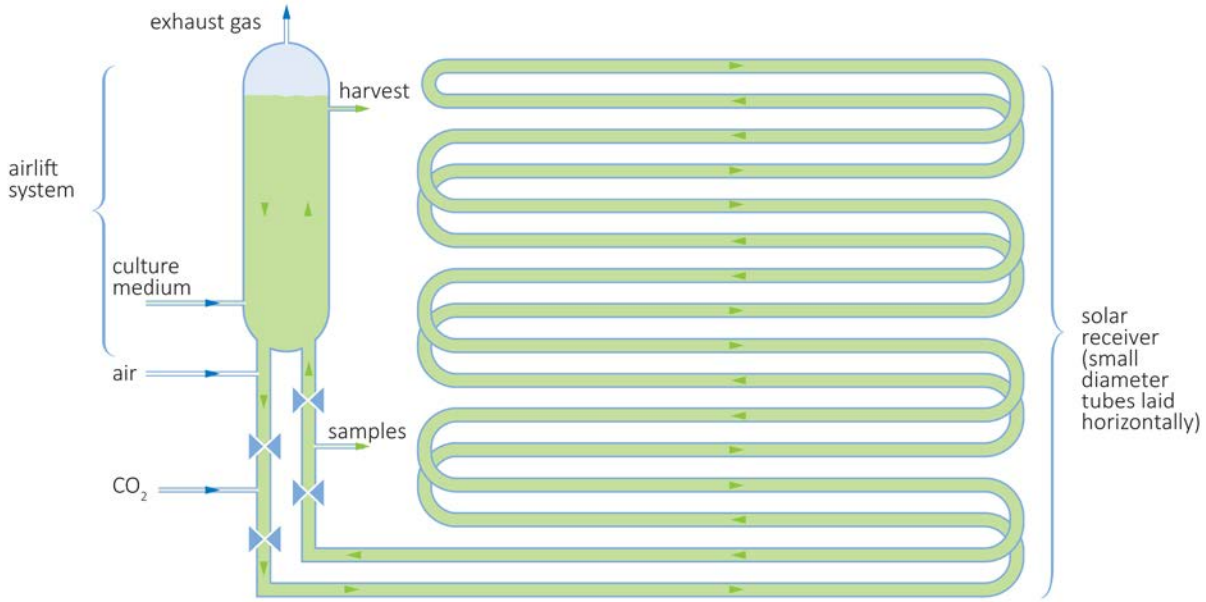

Figure 10 A helical type of photobioreactor (Singh and Sharma, 2012)

3.2.4 Other types of photobioreactors

Singh and Sharma (2012) describe another two types of systems, namely stirred tank and hybrid type photobioreactors.

Stirred tank photobioreactor

For a stirred tank reactor, the agitation is provided mechanically with the help of impellers of different sizes and shapes. Baffles are used in order to reduce the vortex (*see* Figure 11). The CO_2 enriched air is bubbled through the bottom to provide the carbon source for algae growth. This type of bioreactor has been turned into a photobioreactor by illuminating it externally with fluorescent lamps or optical fibres. The main drawback of the system is the low surface area to volume ratio, which, in turn, decreases the

light harvesting efficiency. The use of optical fibres has also been tried but can hinder the mixing pattern. The New Brunswick Bioflo 115 and Bioengineering fermentors are commercially available photobioreactors having external light systems. A large disengagement zone separates the unused sparged gas and produced oxygen during photosynthesis from the liquid gas to gas phase.

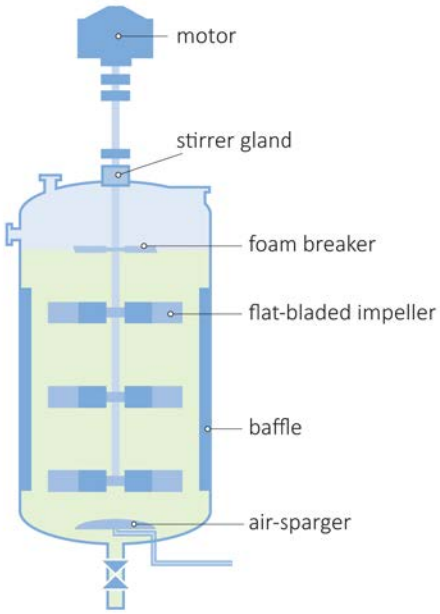

Figure 11 Stirred tank photobioreactor (Singh and Sharma, 2012)

Hybrid type photobioreactor

The widely used hybrid type of photobioreactor exploits the advantages of the two different types of reactor used, and one overcomes the disadvantage of the other. Fernandez and others (2001) employed an integrated airlift system with an external tubular loop system placed horizontally in a thermostatic pond of water. The hybrid reactor had a total volume of 200 litres. On one hand, the external loop acts like a light harvesting unit as it gives a high surface area to volume ratio and controls the temperature of the culture. On the other hand, the airlift system acts as a degassing system where probes can also be integrated in order to regulate the other culture variables. The advantages include a better control over culture variables, enabling higher productivities and reducing power consumption. Grima and others (1994) and Richmond and others (1993) have developed a similar type of integrated system but the external light harvesting unit of the former used horizontal parallel sets of tubes rather than a loop like structure developed by the latter. The temperature was controlled by water sprayed over the external light harvesting unit (Frima and others; 1994). The advantages of horizontal tubes were the photosynthetic efficiency and low cost. The main disadvantages were the large occupied land area and a very narrow light harvesting unit. It was not economically feasible because of the cost associated with the required land area and bundle of tubes. The alpha shaped reactor is another type of hybrid system developed by Lee and others (1995) and designed and constructed based on algal physiology and sunlight. In this reactor, the culture is lifted 5 m by air to a receiver tank. The culture then flows down an inclined PVC tube (2.5 cm ID x 25 m), making a 25° angle with the horizontal, to reach another set of air riser tubes. The process is repeated for the next set of tubes. The unidirectional and high liquid flow rate can be

achieved at relatively low air flow rates. Also photosynthetic efficiency is high due to the large area to volume ratio.

3.3 Comments

Table 4 compares open and closed algae culture systems. In addition, since outdoor open ponds and photobioreactors usually utilise natural solar light and without additional temperature control, the growth of biomass greatly depends on weather conditions and ambient temperatures. Due to these limitations, in most regions of the world it is not feasible to have stable microalgal biomass production through outdoor mass cultivation. Futhermore, the potential contamination is also a serious threat to the operational success of outdoor open ponds or raceways. In contrast, closed system photobioreactors have the advantages of better operational stability and conditions control. However, the high equipment and process costs of closed photobioreactors are still barriers impeding the mass cultivation of microalgae.

Table 4 Comparison of selected parameters for open and closed algae culture systems (Ho and others, 2011; Mata and other, 2010)

Selected parameters	Open system	Close system
Process control	difficult	easy
Temperature and pH control	difficult	easy
Evaporation losses	high	low
Light utilisation efficiency	low	high
Gas flow control	low	high
CO_2 diffusion to air	yes	no
O_2 inhibition	no	yes
mixing	difficult	easy
Species control	difficult	easy
Contamination control	difficult	easy
Growth control	difficult	easy
CO_2 fixation ability	low	high
Specific growth rate control	low	high
productivity	low	high
Investment	low	high
Cost	low	high
Operation cost	low	high
Life span	high	low
Space required	big	small
Scale-up	easy	difficult

The major advantages associated with bubble column bioreactors are the low capital costs, high surface area to volume ratio, lack of moving parts, satisfactory heat and mass transfer, efficient release of O_2 and residual gas mixture. The flat panel bioreactor has the highest productivity under over-saturating light conditions. Volumetric mass productivity is higher than that of a similar bubble column reactor. The shape of a horizontal tubular bioreactor is advantageous in outdoor culture with orientation towards light resulting in high light conversion efficiency. Also the photosynthetic efficiency and volumetric

productivity are higher than those of a flat panel bioreactor. A helical type photobioreactor also has the advantages over other bioreactors of low land requirement, and a better CO_2 transfer from the gas phase to liquid phase. But its major disadvantages are fouling of the reactor, and the energy required by the centrifugal pump for recirculating the culture and the associated shear stress. This limits its commercial use.

Despite the progress that has been made in developing photobioreactors for mass production of microalgae, more effort is still required for further improvements and the development of more efficient methods, especially regarding cost reduction. High cost is the main constraint which limits microalgae CO_2 mitigation and production at a large scale; this is especially true for photobioreactors. Finding more rigid, reliable, and transparent materials with lower costs for the design of closed photobioreactors is crucial to enhance cultivation efficiency and to reduce the cost of photobioreactors. The large area of land requirement for large scale outdoor CO2 fixation is a critical issue.

4 Product harvesting and processing

Microalgae, especially when used to capture CO_2 from coal combustion flue gas, are typically cultured in highly diluted water suspensions. Separating algae from its culture medium is known as harvesting. The harvested algae are then dried and further processed to obtain the desired products.

Efficient harvesting and processing of microalgae from the cultivation broth is essential for mass production as the costs of these processes can be high. The method chosen depends principally on the final product and hence the microalgae strains. The characteristics of microalgae, such as size and density, affect the harvesting processes. Certain algae species are much easier to harvest. For example, *Cyanobaterium spirumlina* has a long spiral shape and is suitable for the cost- and energy-efficient micro-screening method of harvesting (Brennan and Owende, 2010).

4.1 Harvesting

Microalgae harvesting is based on the principle of solid-liquid separation processes. Thickening of loose algae suspension until a thick algal slurry or cake forms is a vital stage of harvesting. In other words, the water content of algae suspension must be reduced as far as possible to enable practical harvesting and downstream processing. Brennan and Owende (2010) describe microalgae harvesting as a two-stage process, involving:

- bulk harvesting – to separate microalgae from the bulk suspension. By this operation, the total solid matter can reach 2-7% using flocculation, flotation, or gravity sedimentation; and
- thickening – to concentrate the slurry through techniques such as centrifugation, filtration and ultrasonic aggregation. Hence, this is generally a more energy intensive step than bulk harvesting.

Show and Lee (2014) describe the most common harvesting processes as screening, coagulation, flocculation, flotation, sedimentation, filtration, and centrifugation. Other harvesting techniques such as electrophoresis, electro-flotation, and ultrasound are used to a lesser extent. Although Brennan and Owende (2010) classified harvesting as a two-stage process with flocculation as the first stage, Show and Lee (2014) think that the harvesting process may include thickening, dewatering, and/or drying. This section introduces some harvesting processes but not necessarily in a working stage order.

In essence, the choice of technology for algae harvesting must be energy-efficient and relatively inexpensive for viable production. The final slurry concentration will depend on the extraction methods employed and will impact the required energy input. The final slurry concentration also affects plant location because of transportation, water quality, and recycling issues. A feasible algae utilisation strategy must, therefore, consider the energy cost and issues associated with harvesting and dewatering (US DOE, 2010).

4.1.1 Screening

According to Show and Lee (2014), screening is the first operation used in most algae harvesting. This involves straining the algae suspension through a screen with a particular pore size. The efficiency of the operation depends on the spacing between the screen openings and the algal particle size. For algae harvesting, micro-strainers and vibrating screens are common screening devices.

Micro-strainers

Micro-strainers consist of a rotary drum covered by a straining fabric, typically stainless steel or polyester. The partially submerged drum rotates slowly in a trough of suspended algal particles. The screen is a fine mesh that captures only fairly large particles such as algae. As the mesh moves to the top, a water spray dislodges the drained particles. Micro-strainers have several advantages, such as simple function and construction, easy operation, low investment, negligible abrasion due to absence of fast moving mechanical parts, low energy consumption, and high filtration ratios. Problems encountered with micro-strainers include low harvesting efficiency and difficulty in handling particle fluctuations. Smaller algae can pass through the screen and are therefore not harvested. The problems may be overcome, in part, by varying the drum rotation speed. Another problem associated with micro-straining is the build-up of bacterial and algae biofilm slime on the fabric or mesh. Ultraviolet irradiation, in addition to periodic fabric or mesh cleaning, may help to inhibit the biomass growth. Successful removal of *Micractinium* and *Scenedesmus* from ponds and lagoons has been reported (Chen and others, 2011; Show and Lee, 2014).

Vibrating screens

The harvesting of *Coelastrum* algae by a vibrating screen was reported in 1980. A higher algae solids concentration of 7–8% has been achived under batch operations in comparison with lower algal solids contents of 5–6% when operated in a continuous mode. In a study by the Food and Agriculture Organization of the United Nations in 2008, vibrating screens were used for harvesting *Spirulina*, which are multicellular and filamentous blue-green microalgae. In the commercial production of *Spirulina* as food for humans and domestic animals and fish, vibrating screen filtration achieved a very high algal biomass removal efficiency of up to 95% for harvesting up to 20 m^3/h, from which algal slurries of 8-10% biomass solid contents were produced. Compared with the inclining screens counterpart with a filtration area of 2-4 m^2/unit, the vibrating screens required only one-third of the area (Show and Lee, 2014).

4.1.2 Flocculation

Flocculation causes algal cells to aggregate into larger clumps, which are more easily filtered and/or settle more rapidly to facilitate their removal in downstream processes. Flocculation on its own is not effective for harvesting in large scale open pond systems (Ho and others, 2011). Optimising flocculation methods, type, mixtures, concentrations, and chemistry to maximise algae recovery depends on strain selection, the mechanism of algae flocculants interactions, and on empirical determinations in particular processes. Therefore, culture manipulation techniques may be useful for promoting flocculation (US DOE, 2010).

Auto-flocculation

Auto-flocculation occurs as a result of the precipitation of carbonate salts with algal cells in an elevated pH, a consequence of photosynthetic CO_2 consumption by algae. Hence, prolonged cultivation under sunlight with limited CO_2 supply assists auto-flocculation of algal cells for harvesting. Laboratory experiments also revealed that auto-flocculation can be stimulated by adding NaOH to achieve certain pH values (Chen and others, 2011; US DOE, 2010).

Chemical coagulation

Adding chemicals to microalgal culture to induce flocculation is a common practice in various solid-liquid separation processes as a pre-treatment stage. It is applicable to the treatment of large quantities of numerous kinds of microalgal species. Chemicals that have been used as algal coagulants can be broadly grouped into inorganic and long-chain organic coagulants. Some also combine inorganic and organic coagulants together (Chen and others, 2011; Show and Lee, 2014).

Inorganic coagulants

Microalgal cells are negatively charged, as a result of the adsorption of ions originating from organic matter and dissociation or ionisation of surface functional groups (Uduman and others, 2010). Adding a coagulant, such as iron- or aluminium-based coagulants, will neutralise or reduce the surface charge allowing algae to coalesce into a floc. Aluminium sulphate was used when harvesting *Scenedesmus* and *Chlorella* via charge neutralisation (Molina Grima and others, 2003). Microalgae can also be aggregated with inorganic flocculants at a sufficiently low pH (Uduman and others, 2010). However, coagulation using inorganic coagulants suffers from the following drawbacks (Chen and others, 2011):

- a large concentration of inorganic flocculants is needed to obtain a solid–liquid separation of the microalgae, thereby producing a large quantity of sludge;
- the process is highly sensitive to pH level;
- although some coagulants may work for some microalgal species, they do not work for others; and
- the end product is contaminated by the added aluminium or iron salts.

Organic coagulants

Organic coagulants, also called polyelectrolytes, can exist as anionic, cationic, non-ionic synthetic or natural polymeric substances. In examining various organic polymers as algal coagulants, it was reported that only the cationic polyelectrolytes were found to be efficient coagulants (Show and Lee, 2014). Polymer molecular weight, charge density of molecules, dosage, concentration of microalgal biomass, ionic strength and pH of the broth, and the extent of mixing in the fluid have all been found to affect flocculation efficiency (Molina Grima and others, 2003). High molecular weight polyelectrolytes are generally better bridging agents. A high biomass concentration in the broth also helps flocculation due to the frequent cell–cell encounters. Thus mixing at a low level is useful, as it helps bring the cells together, but excessive shear forces can disrupt flocs. In addition functional groups on microalgal cell walls are important, because they stimulate the formation of negative charge centres on the cell surfaces (Uduman and others, 2010).

Combined flocculation

A combined flocculation process is a multistep system that employs more than one type of flocculant. Studies revealed that while anionic polyelectrolytes enhanced lime flocculation, most polyelectrolytes can be used in conjunction with aluminium sulphate or ferric sulphate as coagulant aids to strengthen the flocs, thus enhancing algae harvesting. When used as coagulant aids, the polyelectrolytes can be applied at lower dosages than they would have been when used alone. This can lower chemical costs (Show and Lee, 2014).

Bio-flocculation

Bio-flocculants have emerged as a new research trend in flocculation technology. Generally, bio-flocculation is a dynamic process resulting from the synthesis of extracellular polymer substances by living cells. Up to now, bacteria, fungi and antinomies have been identified as bio-flocculants-producing microorganisms. These microorganisms are able to produce extracellular polymer substances, such as polysaccharides, functional proteins and glycoprotein, which act as bio-flocculants. A recent report has underlined that bio-flocculants from *Pseudomonas stutzeri* and *Bacillus cereus* were effective in flocculating marine microalgae, *P. carterae*. In the study, microalgae cells were not damaged even after flocculation. However, the study showed that adequate mixing was essential to provide sufficient contact between extracellular polymer substances and microalgae. The estimated cost for this process was 79% lower than conventional flocculants. Also, a flocculated culture medium can be effectively reused without retarding microalgae growth, thereby significantly reducing the cost for water treatment and purification (Lam and Lee, 2012). Show and Lee (2014) outlined a study on the effect of various cultural conditions on pelletisation of an *Aspergillus sp.-Chlorell vulgaris* fungi-algae complex. The results showed that pH was the key factor affecting formation of fungi-algae pellet, and pH could be controlled by adjusting the glucose concentration and number of added fungal spores.

Electrolytic process

Electrolytic and ultrasound processes are also used to perform flocculation. Electro-coagulation mechanisms involve three consecutive stages:

1. generation of coagulants by electrolytic oxidation of the sacrificial electrode;
2. destabilisation of particulate suspension and breaking of emulsion; and
3. aggregation of the destabilised phases to form flocs.

Electrolytic flocculation differs from electrolytic coagulation in that it does not require the use of sacrificial electrodes. It is based on the movement of microalgae to the anode in order to neutralise the carried charge and then forms aggregates. The efficiency of algal removal is 80–95% when electrolytic flocculation is applied (Chen and others, 2011). Vandamme and others (2013) report electro-coagulation-flocculation as a method for harvesting fresh water *Chlorella vulgaris*. Using an aluminium anode is more efficient than using an iron anode. The process can be substantially improved by reducing the initial pH and by increasing the turbulence in the microalgal suspension.

Ultrasonic aggregation

Brennan and Owende (2010) summarised research which successfully used ultrasound to optimise the aggregation efficiency and concentration factor. They achieved a 92% separation efficiency. The main advantages of ultrasonic harvesting are that it can be operated continuously without inducing shear stress on the biomass, which could destroy potentially valuable metabolites, and it is a non-fouling technique.

4.1.3 Gravity sedimentation

Gravity sedimentation is the most common harvesting technique for algae biomass in wastewater treatment because of the large volumes treated and the low value of the generated biomass. It is used for algae separation where the clarity of overflow is of primary importance and algal feed suspension is usually diluted, or where a thickening of the underflow and the algae feed slurry is usually more concentrated. The success of solids removal by gravity settling depends on the density and radius of the microalgal particles. Low density microalgal particles do not settle very well and cannot be separated successfully by settling (Chen and others, 2011; Show and Lee, 2014).

Microalgal harvesting by sedimentation can be achieved through lamella separators and sedimentation tanks or ponds (Uduman and others, 2010). To enhance algae settling, flat inclined plates are incorporated in a settling tank to promote solids contact and settling along and down the plates. The slope of the plates allows the settled algal particles to glide down into the sump from which they are removed by pumping. Algae concentrated to 1.6% solids content has been achieved. Coagulant dosing is required if the suspension of tiny algae such as *Scenedesmus* is fed to the system. Operational reliability of this method is reasonable, but further thickening of the algae slurry is needed. For clarification in simple sedimentation tanks or ponds, secondary ponds are often used for algae settling from high rate oxidation pond effluent. Well-clarified effluent and algae slurry of up to 3% solids content have been achieved at the secondary ponds attributable to algae auto-flocculation, which enhanced the settling (Show and Lee, 2014).

Flocculation is frequently used to increase the efficiency of gravity sedimentation. It is often followed by gravity sedimentation for algae separation. The process can achieve up to 85% removal of the algal biomass using alum as a coagulant when treating high rate oxidation pond effluent. Various algae species can be separated to achieve algae slurry of 1.5% solids content (Show and Lee, 2014).

4.1.4 Flotation

An alternative to gravity sedimentation is flotation, which is particularly effective for light algae suspensions. Whereas gravitation separation works best with thick algae suspension, flotation is used when suspended particles have a settling velocity so low that they are not able to settle in sedimentation tanks. Flotation is simply gravity thickening upside down. Instead of waiting for the sludge particles to settle to the bottom of the tank, flotation methods are based on the trapping of algae cells using dispersed micro-air bubbles injected near the bottom of a flotation tank. The bubbles attach themselves to the

particulate matter, and their combined buoyancy encourages the particles to rise to the surface. Once the particles have floated to the surface, a layer of thickened slurry is formed that can be collected by a skimming operation. The air-to-solids ratio is probably the most important factor affecting flotation performance. Some strains naturally float on the surface of the water as the microalgal lipid content increases. The principal advantage of flotation over sedimentation is that small or light algal particles can be harvested in a much shorter time. Flotation systems also offer higher solids concentrations and low initial equipment cost. Although flotation has been mentioned as a potential harvesting method, there is very limited evidence of its technical or economic viability (Brennan and Owende, 2010; Show and Lee, 2014).

Based on bubble sizes, the process can be divided into dissolved air flotation (DAF), dispersed flotation and electrolytic flotation. There is also a study on using ozone as dispersal gas.

Dissolved air flotation

In the dissolved air flotation system, a liquid stream saturated with pressurised air is added to the flotation unit, where it mixes with the incoming feed. As the pressure returns to atmospheric pressure, the dissolved air comes out of the liquid, forming fine bubbles that bring the small particles with them as they rise to the surface, where they are removed by a skimmer.

Factors influencing the flotation system's performance include the bubble size and bubble distribution through the suspension, the pressure of the tank, recycle rate, hydraulic retention time, and the floating rate of the particle. The slurry concentration depends on the skimmer speed and its distance above water surface. The process can be operated in conjunction with flocculation (Show and Lee, 2014; Uduman and others, 2010; US DOE, 2010).

Dispersed air flotation

A variation of dissolved air flotation is dispersed-air flotation, where air is directly introduced to the flotation tank. Large bubbles of about 1 mm are generated by agitation combined with air injection (froth flotation) or by bubbling air through the porous media (foam flotation). In froth flotation, the cultivator aerates the water into a froth, and then skims the algae from the top. Medium pH, aeration rate, aerator porosity, feed concentration, and the height of foam in the harvesting column affect the performance of the process. Dispersed air flotation efficiencies for microalgae using three collectors were compared and results showed that the cationic N-cetyl-N-N-N trimethylammonium bromide (CTAB) effectively removed *Scenedesmus quadricauda*, while the nonionic X-100 and anionic sodium dodecylsulphate did not. They attributed these differences to changes in surface hydrophobicity with collector adsorption (Chen and others, 2011; Ho and others, 2011; Show and Lee, 2014).

Electrolytic flotation

In electrolytic flotation, fine gas bubbles are formed by electrolysis. The generated hydrogen gas formed attaches to the fine algal particles, which float to the surface, where they are removed by a skimmer. Instead of a saturator, a more expensive rectifier that supplies 5-20 DC volts at approximately 11 Amperes per square meter is required. The voltage required to maintain the necessary current density for

bubble generation depends on the conductivity of the feed suspension. A wide range of microalgae species have been recovered by electrolytic flotation with up to 5% solids in the harvested algae. Decantation after a further day increased the solids concentration to 7–8%. The energy needs of the electrolytic flotation process are generally high, but for small units (<5 m^2 area) electrolytic flotation operating costs are less than those of dissolved air flotation units (Show and Lee, 2014).

Ozone flotation

An injected air stream containing ozone gas was used to separate microalgae from high rate oxidation pond effluent. The ozone gas promotes cell flotation by modifying the algae cell wall surface and by releasing some surface active agents from the algae cells. Although it was demonstrated to be effective, this method is currently considered too expensive for commercial use (Ho and others, 2011; Show and Lee, 2014).

4.1.5 Centrifugation

Centrifugation is widely used in industrial suspension separation and has been investigated for algal harvesting. The efficiency is dependent on the selected species (as related to size). Laboratory centrifugation tests showed that about 80–90% microalgae can be recovered within 2–5 minutes (Chen and others, 2011). Centrifugation is preferred for harvesting high value metabolites and extended shelf-life concentrates for hatcheries and nurseries in aquaculture. The process is rapid and energy intensive; biomass recovery depends on the settling characteristics of the cells, slurry residence time in the centrifuge, and settling depth. The disadvantages of the process include high energy costs and potentially higher maintenance requirements (Brennan and Owende, 2010). The centrifuge systems used for algae separation include hydro-cyclone, tubular centrifuge, solid-bowl decanter centrifuge, nozzle-type centrifuge, and solid-ejecting disc centrifuge (Show and Lee, 2014).

4.1.6 Filtration

Solid-liquid filtration technologies are well studied, and filtration without prior flocculation can be used to harvest and dewater algae. Filtration is carried out by forcing an algal suspension to flow across a filter medium using a suction pump. The algae are retained and concentrated on the filter medium and are then harvested. The main advantage of filtration is being able to recover very low density microalgae. The main problems are a relatively low efficiency and a tendency to clog easily. Filtration is conceptually simple but potentially very expensive. The process could be optimised through further understanding of several issues (Ho and others, 2011; Show and Lee, 2014; US DOE, 2010):

- the filter pore size is critically important as it is defined by the size of the algae species and algae aggregation rate. Small algae pass through larger pores, thus decreasing filter efficiency. Decreasing the pore size, however, leads to blinding, the blocking of filter pores, and reduction of filtering rates. Culture purity becomes important as the distribution of microorganism size will affect filtration efficiency and blinding rates;
- filter material also influences filtration and recovery efficiency. Materials can be used that optimise filtration and have the ability to remove the algae later. For instance, filter materials with controlled

hydrophobicity and/or algae affinity could be developed. However, durability and blinding could be issues;

- filtration design is an important variable with both static and dynamic filtering operations. Moving filters have been used in drum and cylinder press designs. Power costs will certainly influence the design;
- an important step is recovering the algal biomass from the filter. Washing the filter is one practice, but doing so leads to re-dilution of the product. Filtration designs should consider minimal or no washing requirements.

In practice, filtration is satisfactory for recovering relatively large microalgae/cyanobacteria (>70 µm), such as *Coelastrum* and *Spirulina*, but unsuitable for smaller species (<30 µm), such as *Chlorella*, *Dunaliella* and *Scenedesmus* (Molina Grima and others, 2003). Conventional filtration operates under pressure or suction. Filtration aids, such as diatomaceous earth or cellulose, can be used to improve efficiency. Filtration can achieve a concentration factor of 245 times the original concentration for *Coelastrum proboscideum* to produce a sludge with 27% solids (Brennan and Owende, 2010).

Various filtration methods have been devised, based on gravity, vacuum, pressure, or magnetism, depending on the required pressure drop. Filtration can be categorised either as surface or deep-bed filtration. In surface filtration, solids are deposited on the filter medium in the form of a paste or cake. Once an initial thin layer of cake is formed, algal cells are deposited, serving as a filter medium. As the algal deposition grows thicker, the resistance to flow across the medium increases. The filtration flux declines at a constant pressure-drop operation. In deep-bed filtration, solids are deposited within the filter-bed matrix. For the recovery of smaller algae cells (<30 µm), membrane micro-filtration and ultra-filtration (a form of membrane filtration using hydrostatic pressure) are technically viable alternatives to conventional filtration. The following section discusses the various filtration methods that have been used for algae harvesting based on Show and Lee's review (2014).

Pressure filtration

Algae can be dewatered and harvested by pressure filtration using either plate-and-frame filter presses or pressure vessels containing filter elements. In the plate-and-frame filter press system, dewatering is achieved by forcing the fluid from the algal suspension under high pressure. The filtration cycle involves filling the press, maintaining it under pressure, opening the press, washing and discharging the cake, and closing the press. Chemical conditioners such as polyelectrolytes may be used to increase the solids content of the cake.

A number of designs have been devised for pressure vessels, such as rotary-drum pressure filters, cylindrical-element filters, vertical tank vertical leaf filters, horizontal tank vertical leaf filters, and horizontal leaf filters. Of these, Chamber filter press, cylindrical sieve, and filter basket were recommended by Show and Lee (2014) for algae filtration with respect to energy consideration, reliability, and concentrating capability. A belt filter press was not recommended because of low-density algal cake if filtration was carried out without prior coagulants dosing to the feed. A pressure suction

filter was also not recommended because of a low filtration ratio, high investment costs, and unclear operational expenses.

Vacuum filtration

The driving force for vacuum filtration results from the application of suction on the filtrate side of the medium. Vacuum filtration can yield algal harvests with moisture contents comparable to those of pressure filtration at a lower operating cost provided the content of large algal cells in the feed is high. Five different vacuum filters, vacuum drum filter (not precoated), vacuum drum filter precoated with potato starch, suction filter, belt filter, and filter thickener, have been tested for the harvesting of *Coelastrum*. The suspended solids content of the harvested algae was in the range of 5–37%. The precoated vacuum drum filter, the suction filter, and the belt filter were recommended based on energy consideration, reliability, and dewatering capability. The precoated filter can also be used to harvest tiny microalgae such as *Scenedesmus*. The non-precoated vacuum drum filter was ineffective and not reliable due to clogging problems. The filter thickeners were not recommended because of the low solid content (3–7%) of the algal cake, a low filtration velocity, high energy demand, and poor reliability.

Deep-bed filtration

In deep-bed filtration, algae particles are harvested in a depth filter. Algal particles that are smaller than the medium openings flow into the medium and are retained within the filter bed. Deep-bed filtration is most often operated as a batch process. When the pressure drop reaches the maximum available, the filter must be taken out of service for backwashing. Successful separation of algal cells from pond effluent with average solids concentration of 30 mg/L by intermediate sand filtration has been reported by Show and Lee (2014). The filtration systems, however, rapidly experienced a severe clogging problem and filtration flux dropped drastically.

Cross flow ultra-filtration

A cross flow ultra-filtration system was adopted for treatment of algae pond effluents to produce thickened algae for animal feed. Algae concentration of up to 20 times has been collected with very high-quality filtered effluent. The main disadvantage of this system is the high energy requirement, which rendered the process uneconomic.

Magnetic filtration

Magnetic filtration was initially used in wastewater treatment for removal of suspended solids and heavy metals. Magnetic separation using suspended magnetic particles (such as Fe_3O_4 magnetite) was subsequently used in algae removal. Algal cells and the magnetic particles were coagulated, and the fluid was passed through a filter screen encompassed by a magnetic field to retain the magnetic precipitates. Algae removal efficiency of between 55% and 94% by a commercial magnetic filter dosed with alum coagulant was reported. Higher algae removal (>90%) was achieved using 5–13 mg/L Iron (III) Chloride as the primary coagulant and 500–1200 mg/L magnetite as magnetic particles for pond algal harvesting.

4.2 Processing

Once microalgae are harvested, the algae slurry must be dried for stability, end use, extraction, or other processes.

4.2.1 Drying

Drying delicate microalgae is very challenging and requires an innovative answer. The most feasible algae drying techniques should eliminate the degradation of algal quality. Drying poses a major economic constraint on microalgae production; it may constitute 70–75% of the processing cost. The various drying systems differ both in capital investment and in energy requirements. The selection of a drying method depends on the scale of operation and the final product required. The ultimate goal is to harvest a large amount of algae cost effectively. Drying methods that have been used for microalgae include: drum drying, spray drying, solar heat drying, freeze drying, cross flow and vacuum shelf drying, fluidised bed drying, and Refractance Window™ technology drying (Brennan and Owende, 2010; Show and others, 2013). The following discusses some of the major methods.

Drum drying

Also called rotary drying, drum drying uses a sloped rotating cylinder to move the content being dried from one end to the other by gravity. Show and others (2013) summarised a collection of studies and reported that *Scenedesmus* algae produced an excellent dried algal product with the use of a thin layer drum dryer. They also reported that replacement of the electrically heated drum dryer by a steam heated counterpart could lower the processing cost by 6.8 times.

Spray drying

Spray drying involves liquid atomisation, gas/droplet mixing and drying of the liquid droplets. The atomised water droplets are usually sprayed downwards into a vertical tower through which the hot gases also pass downwards. Drying is completed within a few seconds. The dried product is removed from the bottom, and the gas stream exhausted through a cyclonic dust separator (Show and others, 2013). Spray drying is commonly used for the extraction of high value products, for example, human food. Though it is efficient, it can cause significant deterioration of some algal pigments. The main drawback of spray drying is the high operating cost (Brennan and Owende, 2010).

Solar heat drying

Solar heat drying is the cheapest dehydration method, accomplished either by direct sun radiation or by solar water heating. The main disadvantages of sun drying include long drying times, the requirement for large drying surfaces, and the risk of material loss. Sun radiation causes algal chlorophyll to disintegrate, thereby altering the texture and colour of the final product. Also, solar radiation is uncontrollable and the problem of algae overheating could occur. Therefore operational reliability is low and highly dependent on the weather and location. Using wind energy may improve the drying efficiency. Becker and Venkataraman (1982) carried out a feasibility study using direct sun radiation to dry *Spirulina* algae in which a solar dryer consisting of a wooden chamber with the internal surface painted black and the top

covered with glass plate was tested. After drying for 5-6 hours at a temperature of around 60-65°C, the product had a water content of about 4–8%.

In a solar water heating system, water is heated using solar thermal energy from proprietary designed glass panels or tubes. With proper system design, the algae drying rate is higher than sun drying and the overheating of algae could be avoided. This method is less attractive due to its higher capital cost. As a result, more energy efficient approaches, such as using waste heat from a power plant should be considered.

Other drying methods

Freeze drying is expensive, especially for large scale commercial operations, so it is only widely used in research laboratories.

Cross flow air drying and vacuum shelf drying were investigated for algae drying by Becker and Venkataraman (1982). For cross flow air drying, a wet slurry of *Spirulina* algae containing 55–66% moisture was dried for 14 hours at 62°C in a compartment dryer. A dried product that was 2–3mm thick with 4–8% moisture was obtained. The cell wall of *Chlorella* and *Scenedesmus* also remained intact after drying. In the study involving vacuum shelf-drying, *Spirulina* algae was dried to 4% moisture content in a vacuum shelf dryer at a temperature of 50–65°C and 6 kPa pressure. The dried algae developed a porous structure and became hygroscopic. This method has high capital and running costs.

4.2.2 Extraction and purification

After drying, the microalgae products are either in a powder or a compressed form as pastilles. The microalgae biomass may need further extraction and purification when used as biofuel, algal metabolites or in other applications.

Lipids are one of the main components of microalgae. Depending on the species and growth conditions, microalgae contain around 2–60% lipids of the total cell dry weight. The development of methods of lipid extraction and purification from dry biomass is critical for biofuel production from microalgae (Razzak and others, 2013). Two lipid extraction methods are commonly used: solvent extraction which is suitable for dry microalgae biomass, and supercritical fluid extraction, which is suitable for wet paste microalgae biomass (Lam and Lee, 2012). Microalgae lipids can be extracted with organic solvents, such as hexane, chloroform-methanol, ethanol, hexane-isopropanol or other polar/non-polar solvent mixtures. During lipid extraction, the microalgal biomass is exposed to an eluting extraction solvent which extracts the lipids out of the cellular matrices (Halim and others, 2012). The drying temperature during lipid extraction affects both the lipid composition and the yield from the algae biomass. Currently, other technologies such as microwave and ultrasound are coupled to solvent extraction to enhance the kinetics through speedy disruption of the cellular structures (Cuellar-Bermudez and others, 2014).

Supercritical carbon dioxide ($SCCO_2$) is the primary solvent used in the majority of supercritical fluid extractions. Its moderate critical pressure (7.38 MPa) allows a reserved compression cost, while its low critical temperature (31.1°C) enables successful extraction of thermally sensitive lipid fractions without

degradation. Also, $SCCO_2$ facilitates a safe extraction due to its low toxicity, low flammability, and lack of reactivity. Furthermore, if the microalgal cells need to be cultivated at a coal-fired power station, the CO_2 required for supercritical conversion can be conveniently obtained from the scrubbed flue gas of the station (Halim and others, 2012).

Solvents are widely used to extract metabolites, such as astaxanthin, β-carotene and fatty acids, from algal biomass (Brennan and Owende, 2010).

4.3 Comments

Technologies are available to harvest, process and make valuable applications from microalgae. However, most of the existing technologies are adapted from technologies already in use in the food, biopharmaceutical and wastewater treatment sector. They are not developed specifically for algae production and are therefore inefficient, requiring large energy inputs. For example, the physical extraction method, which is suitable for extracting oil from oil bearing crops, is not efficient in extracting lipid from microalgae since the lipid is embedded within a layer of cell wall. A cell disruption method followed by chemical solvent extraction is necessary to recover the lipid effectively. However, care should be taken as some of the cell disruption methods require large quantities of energy input could lead to a negative energy balance. In addition, it should be noted that the choice of cell disruption method, chemical solvents and extraction conditions are largely dependent on microalgae strains. In other words, there is no single method that can give optimum lipid extraction for all types of microalgae strains (Lam and Lee, 2012).

5 Product applications

Since the focus of this report is on algae CO_2 capture, although the product applications may be appealing, they are considered as by-products and their commercial value are not discussed here.

Co-firing dried microalgae with coal to produce electricity is the easiest and most obvious algae application. However, since microalgae contain lipids (7–23%), carbohydrates (5–23%), proteins (6-52%) and some fat, depending on the species, these constituents can be converted into several commercial applications, such as human food, animal feed, cosmetics, medical drugs, fertilisers, bio-molecules for specific applications and biofuel (Zhu and others, 2014). For the power generation industry, these algae applications are an extra bonus after capturing CO_2 from coal combustion because of the generated revenue. Figure 12 demonstrates microalgae production schemes. Pires and others (2012) classified the applications into fuel and non-fuel applications. The sections below will discuss algae applications under these two groups. Applications for wastewater treatment and CO_2 capture and utilisation are also described.

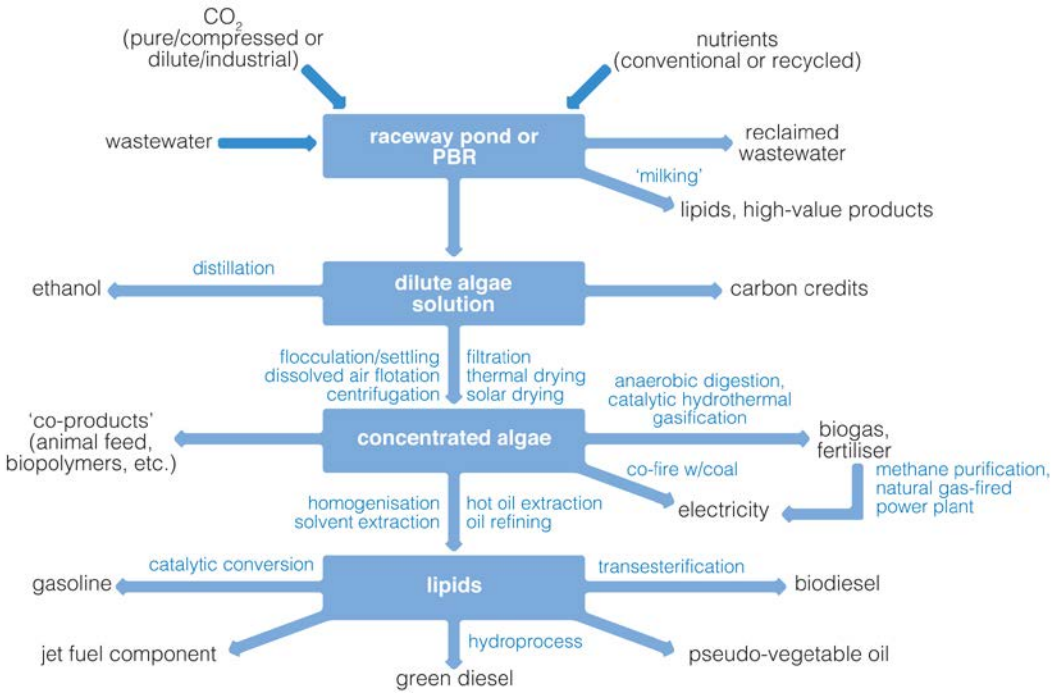

Figure 12 Microalgae production schemes (Rickman and others, 2013)

5.1 Fuel applications

Microalgae have been investigated as biofuel feedstock for the production of biodiesel, bio-hydrogen, biogas, bio-ethanol, and many other fuel types via thermochemical and biochemical conversion. Thermochemical conversion processes include: direct combustion, gasification, liquefaction, and pyrolysis. Biochemical conversion processes include: anaerobic digestion, alcoholic fermentation, and photobiological hydrogen production. Factors influencing the choice of conversion process include: the

type and quantity of biomass feedstock, the desired form of the energy, economic considerations, and the desired end form of the product (Brennan and Owende, 2010).

5.1.1 Biodiesel

Biodiesel is a mixture of monoalkyl esters of long chain fatty acids (FAME) derived from a renewable lipid feedstock such as algal oil. After the extraction and purification processes (*see* Section 4.2.2), the resulting product lipid can be converted into biodiesel through a process called transesterification. Transesterification is a chemical reaction between triglycerides and alcohol in the presence of a catalyst to produce mono-esters that are termed biodiesel. Algal oils contain a high degree of polyunsaturated fatty acids when compared to vegetable oils, and have similar physical and chemical properties to petroleum diesel which compare favourably with the International Biodiesel Standard for Vehicles (EN14214). Therefore, algal biodiesel is an accepted substitution for fossil fuels (Brennan and Owende, 2010). However, despite being technically feasible, microalgae biodiesel production needs be economically competitive.

Quantity and composition of lipids are key properties that determine biodiesel oxidative stability and performance properties (Cuellar-Bermudez and others, 2014). The lipid content and microalgae composition depend mainly on the culture conditions. Some microalgal species have a fatty acids profile that allows biodiesel production with high oxidation stability. Cuellar-Bermudez and others (2014) summarised the effect of culture conditions on lipid contents for some algae species. Nitrogen starvation increased the total lipid content in *Ulva pertusa*, *E. gracilis*, and *Botryococcus* species. The cellular content of lipids and total polyunsaturated fatty acids (PUFA) are inversely related to light intensity. In addition, a decrease in growth temperature generally increases the unsaturation degree of lipids in membrane systems. It seems that temperature, in a physiologically tolerant temperature range, may exert a more significant effect on the relative cellular content of lipid classes rather than on total lipid content in the cells. For *Chlorella kessleri*, a low CO_2 concentration in the cultures medium showed high contents of α-linolenate. In contrast, in *Chlamydomonas reinhardtii* mutant cia-3, a high content of PUFA was found in cultures with a high CO_2 concentration. Finally, pH can also affect lipid metabolism. Low pH stress in *Chlamydomonas sp.* increased the total lipid content compared with higher pH values. However in *Chlorella spp.*, an alkaline pH resulted in triacylglycerides accumulation.

5.1.2 Bio-hydrogen

According to Brennan and Owende (2010), microalgae possess the necessary genetic, metabolic and enzymatic characteristics to photo-produce H_2 gas. Under anaerobic conditions, hydrogen is produced from eukaryotic microalgae either as an electron donor in the CO_2 fixation process or evolved in both light and dark conditions.

During photosynthesis, microalgae convert water molecules into hydrogen ions (H^+) and oxygen; the hydrogen ions are then subsequently converted by hydrogenase enzymes into hydrogen gas under anaerobic conditions. Due to the reversibility of the reaction, hydrogen is either produced or consumed by the simple conversion of protons to hydrogen. Photosynthetic oxygen production causes rapid

inhibition to the key enzyme, hydrogenase, and the photosynthetic hydrogen production process is impeded. Consequently, microalgae cultures for hydrogen production must be subjected to anaerobic conditions.

Brennan and Owende (2010) and Pires and others (2012) reported that green algal, *Chlamydomonas reinhardtii*, can yield hydrogen through an aerobic-anaerobic cycle developed by Melis and others (2000). A literature review by Zhu and others (2014) found that some microalgae, such as *Scenedesmus obliquus*, *Playtmonas subcordiformis*, *Scenedesmus sp.* and *Chlamydomonas reinhardtii*, have substantial hydrogenase activity in bio-hydrogen formation. For example, the enzyme activity of *C. reindhartii* is robust. The generated oxygen has a strong inhibiting effect on hydrogenase enzyme, which can be relieved by microalgae after 2–3 days of sulphur deprivation to lead to the anaerobic conditions for bio-hydrogen production. Wecker and others (2011) successfully designed a new biosensor to grow *Rhodobacter capsulatus* and *Chlamydomonas reinhardtii* in the dark to produce H_2, while Chatzitakis (2013) employed a photo-electrocatalytic-enzymatic hybrid system for simultaneous hydrogen production and organic pollutant reduction. Lee and others (2010) collected a total of 444 ml of bio-hydrogen produced from 10 g/L of dry algae in a 100 ml of culture fluid for 62 h when marine brown algae (*Laminaria japonica*) were fed under dark fermentation conditions.

5.1.3 Biogas - methane

Microalgae or their residues after lipid extraction have potential for biogas production because of their high lipid, starch and protein contents, 70%, 50%, and 50%, respectively (Zhu and others, 2014). Microalgae biomass can be converted into biogas directly or indirectly by the anaerobic digestion of the oil cakes. Anaerobic digestion is a process by which microorganisms break down biodegradable material in the absence of oxygen. The process produces biogas, consisting of methane, carbon dioxide and traces of other gases, such as hydrogen sulphide. The process occurs in the three sequential stages of hydrolysis, fermentation and methanogenesis. The anaerobic digestion of the algal biomass is typically carried out with the help of a different group of bacteria (Brennan and Owende, 2010; Prajapati and others, 2013):

- hydrolytic bacteria, which produces mainly exo-enzymes that disrupt the algal cell wall and break down macromolecules such as sugars, lipids and proteins to monomers and dimmers of sugars, fatty acids and amino acids;
- acidogenic bacteria, which converts monomers and dimmers to intermediate metabolites such as volatile fatty acid, alcohols, aldehydes, and ketones;
- acetogenic bacteria, which converts intermediate metabolites to acetates, ammonia, CO_2, and H_2; and
- methanogenic bacteria, which converts acetate to methane.

The limitation of this energy production process is the availability of biomass. A 500 kW bio-methane production plant requires about 10–12 thousand tonnes of biomass per year. Since microalgae grow 5-30 times faster than crop plants, it makes economic sense to use algae to produce biogas (Pires and others, 2012).

The anaerobic digestion process is appropriate for algae with a high moisture (80–90%) content, which can be useful for wet algae biomass. This is an advantage as the harvested algae do not require dewatering or further chemical extraction steps (Brennan and Owende, 2010; Prajapati and others, 2013).

The efficiency of biogas production depends on the algae species and their degradability, plus pre-treatment (Collet, 2014; Zhu and others, 2014). Biogas production yields from different microalgae are listed in Table 5. Recently, various algal biomass, including *Chlorella vulgaris, Dunaliella tertiolecta, Chlamydomonas reinhardtii, Scenedesmus obliquus, Phaeodactylum triconutum,* and *Rhizoclonium* have been tested for biogas production. A wide range of algae belonging to the genus *Chlorella, Euglena,* and *Spirulina* have much higher methane yields (>53 m^3/kg volatile solids) when compared to the methane yield of common crop biomass such as maize silage and field grass (<0.35 m^3/kg volatile solids). The highest biogas yield (0.587 m^3/kg volatile solids) was obtained from biomass of *Chlorella reinhardtii* (Prajapati and others, 2013). Nevertheless, generating biogas from algae is still at a pre-commercial stage.

Table 5 Biogas production yields from different microalgae species (Zhu and others, 2014)

Feedstock	Yield	Methane content, %
Scenedesmus obliquus	0.240 L CH_4 g^{-1} VS	–
Phaeodactylum tricornutum	0.360 L CH_4 g^{-1} VS	–
Chlorella vulgaris	0.375 L g^{-1} S	–
Blue algae from Taihu Lake, China	0.190 L g^{-1} VS	36.7
Chlamydomonas reinhardtii	0.587 L g^{-1} VS	–
Macrocystis pyrifera	0.180 L g^{-1} S	65.0
Durvillea antarctica	0.180 L g^{-1} S	65.0
Chroococcus sp.	0.401–0.487 L CH_4 g^{-1} VS	52.0–54.9%

5.1.4 Bio-ethanol

Only limited information on the production of bio-ethanol from microalgae is publically available possibly because (Lam and Lee, 2012):

- a lot of attention has been diverted to biodiesel production;
- through the nitrogen deficient cultivation method (to save energy and cost), lipid content inside the microalgae cells can be boosted by blocking carbohydrate synthesis pathways - carbohydrate is the main substrate to produce bio-ethanol; and
- biodiesel has a higher calorific value than bio-ethanol, 37.3 MJ/kg and 26.7 MJ/kg, respectively.

Nevertheless, microalgae can produce bio-ethanol because of their high contents of carbohydrates (starch dominating), cellulose and glycogen (>50% of the dry weight). Carbohydrates can be hydrolysed into sugars and then fermented to bio-ethanol by yeast. Cuellar-Bermudez and others (2014) summarise the process of ethanol production from biomass fermentation as the following steps:

- pre-treatment to release carbohydrates, in which the starch can be extracted from the cells with mechanical tools, for example, ultrasonic, explosive disintegration, mechanical shear, or by

dissolution of cell walls using enzymes. However, while the pre-treatment improves the ethanol production, energy consumption increases by 30%.

- fermentation of carbohydrates for ethanol production. The most common organism for bio-ethanol production is yeast, *Saccharomyces cerevisiae*.
- separation and purification of ethanol, in which the ethanol is drained from the tank and pumped to a holding tank to be fed to a distillation unit.

The non-fermentable slurry or residue, composed of mainly proteins, lipids, and organic acids or alkali, can be used as feedstock for methane production and for cattle-feed (Catarina Guedes and others, 2014).

Compared to woody biomass, microalgae have some properties which are beneficial to bio-ethanol fermentation (Cuellar-Bermudez and others, 2014; Zhu and others, 2014):

- microalgal cell walls are largely made up of polysaccharides with low or no percentage of lignin and hemicelluloses, which can favour the hydrolysis of cell walls into sugars. Thus, it can accelerate the bio-ethanol production process because no chemical and enzymatic pre-treatment is necessary. However, physical pre-treatment is still required to break down the cell wall to release the carbohydrates and finally convert them into sugars;
- since there are no roots, stems and leaves, microalgae have consistent components which make the pre-treatment process simpler; and
- some species, such as *Chlorella, Dunaliella, Chlamydomonas, Scenedesmus* and *Spirulina*, contain more than 50% (dry weight) of starch and glycogen, which are useful ingredients for bio-ethanol production. Bio-ethanol yields from different microalgae species are listed in Table 6.

Table 6 Bio-ethanol production yields from different microalgae species (Zhu and others, 2014)

Feedstock	Pre-treatment	Yield, g ethanol/g substrate
Kappaphycus alvarezii	Sulphuric acid	0.457
Gracilaria verrucosa	Sulphuric acid and enzymatic	0.430
Saccharomyces cerevisiae	Enzymatic	0.259
Chlorococum humicolo	Sulphuric acid	0.520
Chlorella vulgaris	Acid and enzymatic	0.400
Chlorococum sp.	Supercritical CO_2	0.383
Chlorococum infusionum	Alkaline	0.260
Gelidium amansii	Sulphuric acid	0.888
Chlamydomonas reinhardtii	Enzymatic	0.240

It is possible to simultaneously produce biodiesel and bio-ethanol from microalgae, in which lipid is extracted from microalgae prior to fermentation. This concept has been proven viable in a study in which lipid from *Chlorococum sp.* was extracted with supercritical CO_2 at 60°C and subsequently fermented by the yeast *Saccharomyces bayanus* (Harun and others, 2010). This green microalgae with pre-extracted lipids produced 60% higher ethanol concentrations than those that remained as dried intact cells without

lipid extraction This is because during the lipid extraction supercritical CO_2 can breakdown microalgae cell walls, resulting in the simultaneous release of carbohydrates ready for bio-ethanol production.

Genetic modification technologies for selected strains have also been used in an attempt to optimise microalgal bio-ethanol production. Zhu and others (2014) reported that green algae has been genetically modified to produce ethanol from sunlight and CO_2 by introducing new genes into *cyanobacterium*. Similarly, the Algenol Company (www.algenol.com) in the USA is designing and developing a strain of cyanobacteria that is capable of producing ethanol.

Bio-ethanol production from microalgae is still in the preliminary research phase, where further research about its advantages and disadvantages needs to be addressed (Zhu and others, 2014). The most successful large scale commercial production of ethanol from algae is being undertaken by Angenol. Its patented technology enables the production of ethanol for around 2.91 dollars per litre using proprietary algae, sunlight, carbon dioxide and saltwater at production levels of 74831 litres of liquid fuel per hectare per year. The company has built a pilot scale integrated biorefinery in Fort Myers, FL, USA (*see* Chapter 5).

5.1.5 Other fuel types

Microalgae can also be converted into bio-oil, bio-char, synthesis gas, bio-butanol, jet fuel, and so on. Bio-oil and bio-char production can be achieved through pyrolysis or thermochemical liquefaction. Bio-oil produced from microalgal biomass is more stable than that produced from traditional crops, although it is not as stable as fossil fuel. Such bio-oil is composed mainly of aliphatic and aromatic hydrocarbons, phenols, long-chain fatty acids, and nitrogenous compounds (Catarina Guedes and others, 2014; Zhu and others, 2014).

The pyrolysis is an anaerobic heating process carried out at high temperatures (200–750°C). Pyrolysis may take place quickly or slowly. Fast pyrolysis produces bio-oil (19–58% of the final product) and bio-char, while slow pyrolysis results in gas and bio-char, with methane and CO_2 accounting for most of the gaseous products (Catarina Guedes and others, 2014).

Thermochemical liquefaction of algae requires heating the biomass at temperatures between 200 and 500°C, under pressures above 2 MPa in the presence of a catalyst. This process leads to 9–72% bio-oil yields, together with a 6–20% gaseous mixture. Brown and others (2010) converted wet *Nannochloropsis sp.* into a crude bio-oil product via hydrothermal liquefaction processing at a temperature between 200°C to 500°C and a batch holding time of 60 minutes. A moderate temperature of 350°C led to the highest bio-oil yield of 43 wt%. Most importantly this test indicated that hydrothermal liquefaction can convert wet microalgae biomass into bio-oil without requiring any drying process. Thus it will be very energy efficient.

Synthesis gas can be obtained by the gasification of algae biomass via by reacting carbonaceous compounds with atmospheric air, steam, or oxygen at high temperature (200–700°C) in a gasifier. As a result, clean H_2 with yields from 5–56%, and CO with yields ranging from 9–52% can be achieved. Methane can be considered a byproduct since it is produced only at low levels, 2–25%. The hydrocarbon

products of gasification can be further processed to methanol; at 1000°C, methanol production is 64% (w/w), on a biomass weight basis (Catarina Guedes and others, 2014; Zhu and others, 2014).

The profile of products is mainly affected by the algae biomass composition and the processing conditions, such as temperature, pressure, residence time, and catalyst. The bio-oil yield can be 5–25% higher than the lipid content of the original microalgae, depending on the composition of other compounds such as carbohydrates. For instance, *Dunaliella tertiolecta* is mainly composed of crude protein (63.6%) and fat (20.5%) and produces a bio-oil yield of about 37% on an organic basis; on the other hand, *Spirulina sp.* (a well-known food supplement, owing to its protein content) was reported to produce a bio-oil yield of up to 54% (Catarina Guedes and others, 2014).

5.2 Non-fuel applications

As mentioned above, microalgae and cyanobacteria have a high protein and nutrient content. Therefore they have considerable biotechnological potential for commercial applications, including food, cosmetic, chemicals and pharmaceutical industries. Table 7 gives an overview of the prominent microalgae products, which are classified based on monetary value. Table 8 lists products from some common algae strains. Selected applications are discussed briefly below.

Table 7 Overview of the prominent products from microalgae (Oilgae, 2014)

High-value	Medium-high value	Low to medium value
Nutraceuticals a) Astaxanthin b) Beta carotene c) Omega-3 fatty acid (DHA and EPA) d) CoenzymeQ10 **Cosmetic** a) Anti-cellulite b) Skin anti-ageing and sensitive skin treatment – alguronic acid **Pharmaceuticals**	**Nutraceuticals** - Spirulina and Chlorella **Hydrocolloids** - Agar, Aliginate, Carrageenan **Chemicals** - Paints, dyes and colourants	**Fertiliser and animal feed** a) Aquaculture feed (shrimp feed, shellfish feed, marine fish larvae cultivation b) Animal feed c) Fertiliser **Substitutes for synthetics** a) Biopolymers and bioplastics b) Lubricants **Bioremediation** a) Wastewater treatment and nutrient credits b) CO_2 capture and carbon credits

Table 8 Products from selected algae strains (Brennan and Owende, 2010; Ho and others, 2011; Oilgae, 2014)

Microalgal species	Products
Aphanizomenon flos-aquae	Human nutrition
Arthrospira	1. β-carotene 2. Cosmetics 3. Phycobiliproteins
Chlorella	1. Health-promoting molecules 2. Food additives 3. Animal nutrition 4. Cosmetics 5. Biofuels
Crypthecodinium cohnii	DHA oil
Dunaliella salina	1. β-carotene 2. Food supplements 3. Cosmetics
Haematococcus pluvialis	1. Astaxanthin 2. Food additives 3. Pharmaceuticals
Nannochloropsis	1. Eicosapentaenoic acid (EPA) 2. Biodiesel
Spirulina	1. Pharmaceuticals 2. Phycobiliproteins 3. Human nutrition 4. Animal nutrition 5. Cosmetics

5.2.1 Human health

Microalgae biomass is marketed in tablet or powder form generally in the health food market, for example as food additives. The human consumption of microalgae biomass is restricted to very few species due to the strict food safety regulations, commercial factors, market demand and specific preparation. *Chlorella*, *Spirulina* and *Dunaliella* dominate the market, while *Chlorella* and *Spirulina* are both considered as edible algae.

Chlorella species present several health benefits when their extracts are ingested. For example, they can boost immune systems, increase hemoglobin concentrations, lower blood sugar levels and act as hypocholesterolemic and hepatoprotective agents during malnutrition and ethionine intoxication (Mata and others, 2010).

Cyanobacteria *Spriulina* is currently largely cultivated for use as a health food since it boosts the immune system, helping to prevent both viral infection and cancer. It has also been reported to increase the number of lactic acid bacteria in the gastrointestinal tract as a result of a dietary supplement for promoting a healthy hormonal balance in adults. It has also been found to produce the neurotoxin β-N-methylamino-L-alanine (BMAA) which is related to the Parkinsonism dementia complex, Lou Gehrig's disease (ALS) and Alzheimer's disease. Additionally, it has a high nutritional value due to its protein content of 55–70% of total dry weight and so has been used as a food source (Brenann and Owende, 2010; Mata and others, 2010).

Dunaliella salina is exploited for its lipids and protein contents, glycerol concentration, β-carotene content and its exceptional ability to grow under brackish conditions. These microalgae are currently being cultivated by several companies, in both Israel and Australia, as sources of these compounds and as dietary supplements and powders, containing vitamins A and C. Furthermore, it has been postulated that the carotenoids found in *Spirulina sp*. and *Dunaliella sp*. may be more potent anticancer agents than β-carotene (Brenann and Owende, 2010; Mata and others, 2010).

Microalgae also contain long chain polyunsaturated fatty acids (PUFAs), especially omega-3 and omega-6 series such as eicosapentaenoic (EPA), docosahexaenoic (DHA), and arachidonic (AA). These compounds are considered pharmacologically important for dietetic and therapeutic uses. Microalgae such as *Nannochloropsis oculata*, *Phaeodactylum tricornutum*, and *Thalassiosira pseudonana* can produce various amounts of PUFA, depending on algae species and growth phases (Mata and others, 2010). The carotenoid astaxanthin has potential applications in the nutraceuticals, cosmetics, food and feed industries. The microalgae *Haematococcus pluvialis* is a rich natural source of astaxanthin, capable of producing 1–8% astaxanthin dry wt (Brennan and Owende, 2010). *Scenedesmus sp.* could accumulate lutein which is a key carotenoid for health food-aids and essential for human eye retina health (Ho and others, 2011).

5.2.2 Animal feed and aquaculture

Although considerable efforts have been made to promote microalgae use in human food, high production costs and fear of toxicological contamination have limited their application. But microalgae culture have been more successful as a food source and feed additive in animal feed and aquaculture.

Specific algal species are suitable as a source for animal feed supplements. Algae species such as *Chlorella*, *Scenedesmus* and *Spirulina* provide beneficial aspects including improved immune response, improved fertility, better weight control, healthier skin and a lustrous coat. However, prolonged feeding at high concentrations could be detrimental, especially in relation to cyanobacteria.

Microalgae can also be used for culturing several types of zooplankton (rotifers, cladocerans, brine shrimp or copepods) used as live food in crustacean and finfish farming. *Isochrysis galbana* and *Tetraselmis suecica* are considered the best food for larval bivalves, which grow much better in unfiltered seawater to which these algae have been added. Other applications in aquaculture include colouring for farmed salmonids, stabilisation and improvement of quality of culture medium, inducement of essential biological activities in bred aquatic species, and enhancement of the immune systems of fish (Brennan and Owened, 2010; Mata and others, 2010; Pires and others, 2012).

5.2.3 Bio-fertiliser

Some conversion technologies, most notably pyrolysis, result in the formation of the solid charcoal residue biochar, that has potential agricultural applications as a bio-fertiliser (Brennan and Owende, 2010). Some types of microalgae are used to improve plant water-binding capacity and mineral composition of depleted soils (Oilgae, 2014).

5.3 Wastewater treatment

Microalgae have been used for wastewater treatment because of their ability to remove chemical and organic contaminants, heavy metals and pathogens. Microalgae can process hazardous or toxic compounds in wastewater since they produce the oxygen required by bacteria to biodegrade pollutants, such as polycyclic aromatic hydrocarbons (PAHs), phenolics and organic solvents (Brennan and Owende, 2010; Cuellar-Bermudez and others, 2014; Razzak and others, 2013).

Different studies on microalgae strains with diverse wastewater effluents have been summarised by many scientists (Brennan and Owende, 2010; Cuellar-Bermudez and others, 2014; Mata and others, 2010; Pires and others, 2012; Razzak and others, 2013). For example, *Chlorella sp*. has been tested to treat wastewater from dairy farms, municipal sources, and industrial plants. *Spirulina platensis* has been used for the biological treatment of swine wastewater and *Scenedesmus obliquus* to treat brewery effluent. All results showed that good removal efficiencies (60–80%) were achieved. *Chlorella vulgaris* can remove nitrogen and phosphorus from wastewater with an average removal efficiency of 72% for nitrogen and 28% for phosphorus. *Nannochloris, Scenedesmus obliquus, Botryococcus brauinii,* and the cyanobacterium *Phormidium bohneri* have also been investigated for nitrogen and phosphorus removal. *Chlorella vulgaris* was grown successfully in wastewater discharged from a steel plant to achieve an ammonia bioremediation rate of 0.022 g/L/d. *Spirulina sp*. can act as a biosorbent, absorbing heavy metal ions (Cr^{3+}, Cd^{2+}, and Cu^{2+}) in the wastewater. However, the biosorption properties of microalgae depend strongly on cultivation conditions.

5.4 Carbon capture and utilisation

It is undeniable that microalgae can be used for biological CO_2 fixation. Although it has the same drawbacks as conventional carbon capture and storage methods, namely large energy requirement and equipment cost, CO_2 mitigation by microalgae can be classified as carbon capture and utilisation (CCU) due to the production of value-added biomass. Microalgae capture and convert CO_2 into useful products. Thus CO_2 becomes a feedstock instead of a waste product.

Lively and others (2014) examined a number of issues related to the integration of US Algenol's Direct to Ethanol biorefinery with coal-fired power plants and compared the results with conventional CCS. The analysis first considers integration with a pulverised coal-fired power plant. The captured CO_2 is consumed within the Algenol biorefinery with the produced ethanol utilised as a liquid transportation fuel. The analysis considers the parasitic electrical load of typical liquid amine capture systems and the resulting increase in CO_2 production/power consumption as a result of the capture unit. The parasitic electrical load is assumed to be proportional to the CO_2 emission level for the different power plants, with a base assumption of 20% for pulverised coal-fired power plant. The basis for the carbon footprint calculation is: 1 MJ of net produced electricity from the pulverised coal-fired power plant with the captured CO_2 (capture efficiency = 90%) delivered to a co-located Algenol facility for conversion into biofuel. As shown in Figure 13, this yields an additional 4.6 MJ of transportation fuel energy (thermal) with an overall release of approximately 429 gCO_2, about 330 g originating from the combustion of the

ethanol (Chance and others, 2012). As a reference, in a no capture, no biofuel scenario, 1 MJ of electricity from pulverised coal and 4.6 MJ of thermal energy from gasoline would produce approximately 707 gCO_2. Furthermore, if CO_2 is captured (20% parasitic electrical load, capture efficiency = 90%) and sequestered (10% additional parasitic electrical load for compression and storage) then the overall CO_2 released will be approximately 451 gCO_2 (assuming 4.6 MJ of thermal energy from gasoline). This demonstrates that, in terms of overall carbon footprint, an Algenol biorefinery integration has major advantages over the reference case and is fully competitive with CCS.

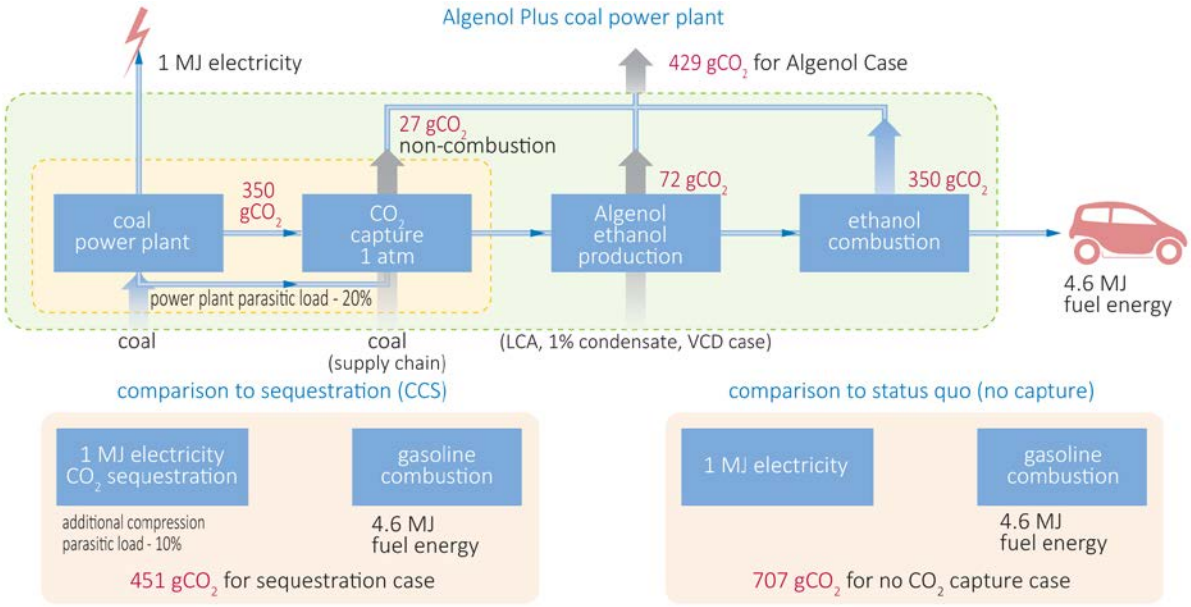

Figure 13 Comparison of CO_2 algae bio-fixation and conventional CCS (Chance and others, 2012)

Another point is that although the carbon used to grow algae biomass is still released to the atmosphere upon combustion, the overall amount of carbon has been used twice: once for energy generation in a power plant and secondly to grow algae for fuels.

The analysis is then extended to three other power plants: IGCC, supercritical coal-fired, and gas-fired. Based on Lively and others (2015) 'well-to-wheel' calculation, all scenarios yield the same conclusion that an algal ethanol biorefinery can achieve significant CO_2 reduction benefits (*see* Figure 14). The overall ordering for carbon footprint is natural gas > IGCC > supercritical > pulverised coal. This is because a pulverised coal-fired power plant releases the most CO_2 in these four scenarios.

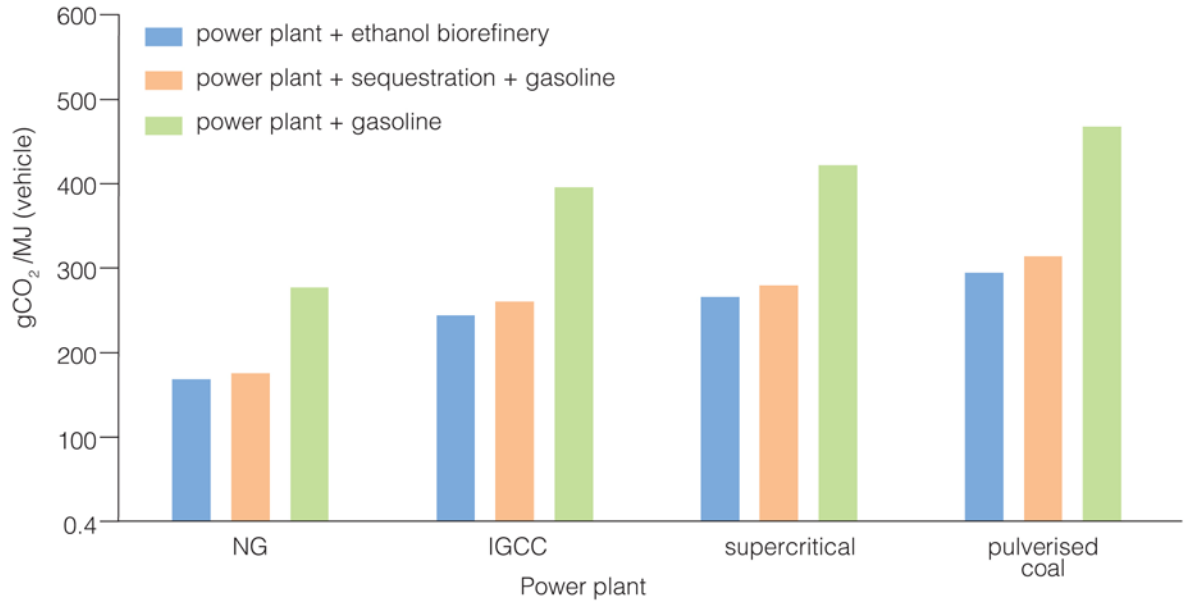

Figure 14 Well-to-wheels CO_2 emissions for an ethanol biorefinery integrated with four different power plant scenarios in comparison to CCS and no capture (Lively and others, 2015)

Two novel methods have been developed that can be used for the integration of CO_2 capture from power plants and efficient feeding to algae ponds. The first method is amine-based whilst the second is carbonate-based (Schipper and others, 2013). On a large scale, CO_2 capture is performed with an (*see* Figure 15). The solvents loaded with CO_2 are regenerated by heating, which is the most energy consuming step for the whole carbon capture chain. The amine-based method uses a conventional counter current packed bed scrubber for the absorption of CO_2 from the flue gas. Instead of heating the CO_2 loaded absorption liquid for regeneration, the liquid is fed directly into algae ponds or bioreactors (*see* Figure 16). The CO_2 in the absorption liquid is thereby brought into direct contact with the algae for it to grow. Once the absorption liquid has been regenerated, it is separated from the algae biomass through filtration and recirculated to the absorber. Thus the newly developed system has lower energy consumption since no heating is required for solvent regeneration. This can lead to a substantial decrease in costs for carbon capture. However the process is limited by the costs required for algae cultivation. Nonetheless, the algae biomass produced can also be used in commercial applications, lowering the costs. The system is also beneficial for the algae cultivation process itself. The CO_2 is chemically-bound to the absorption liquid, decreasing its release into the atmosphere compared to the release of CO_2 dissolved in water. This leads to a higher CO_2 capture efficiency as compared to, for instance, when CO_2 is bubbled through an aqueous growth medium. This is also an energy demanding procedure now avoided. Besides this, the contact efficiency of CO_2 with the liquid is higher, as is the concentration of CO_2 in the liquid. This also has the potential to increase growth rates for specific algae strains where CO_2 would otherwise be limiting.

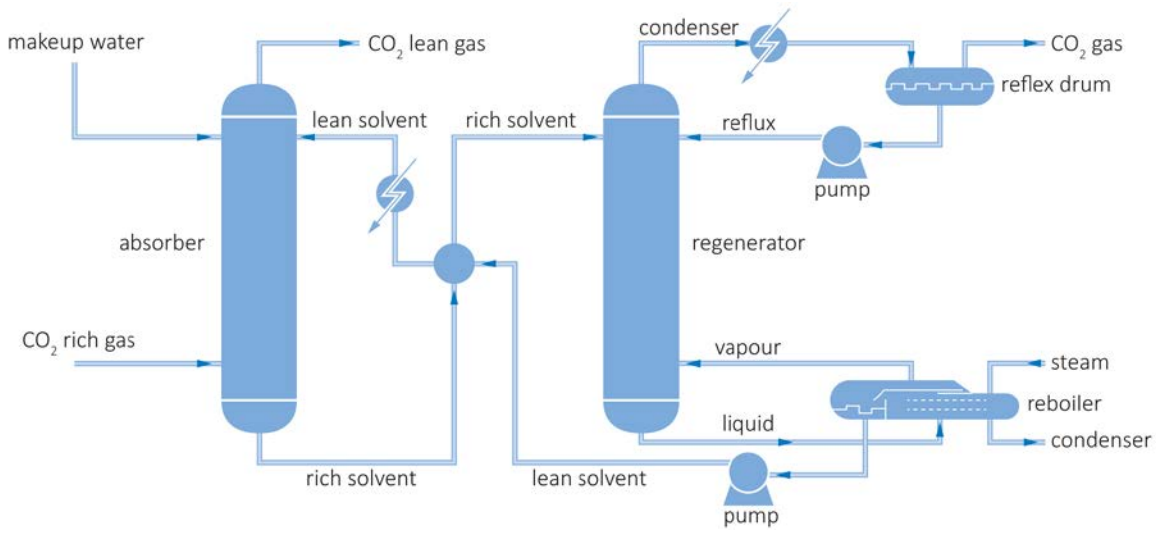

Figure 15 A conventional CO_2 capture system (Schipper and others, 2013)

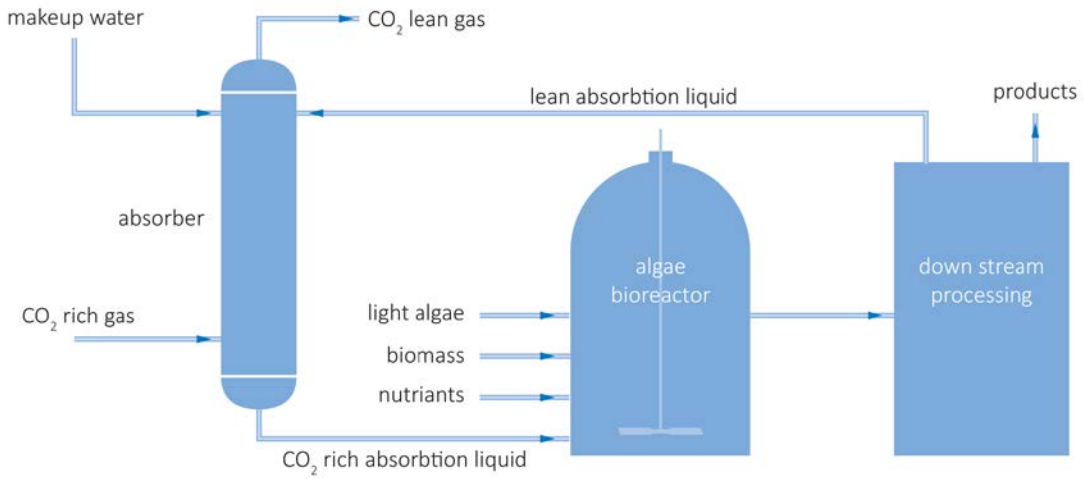

Figure 16 An alternative algae capture and utilisation system (Schipper and others, 2013)

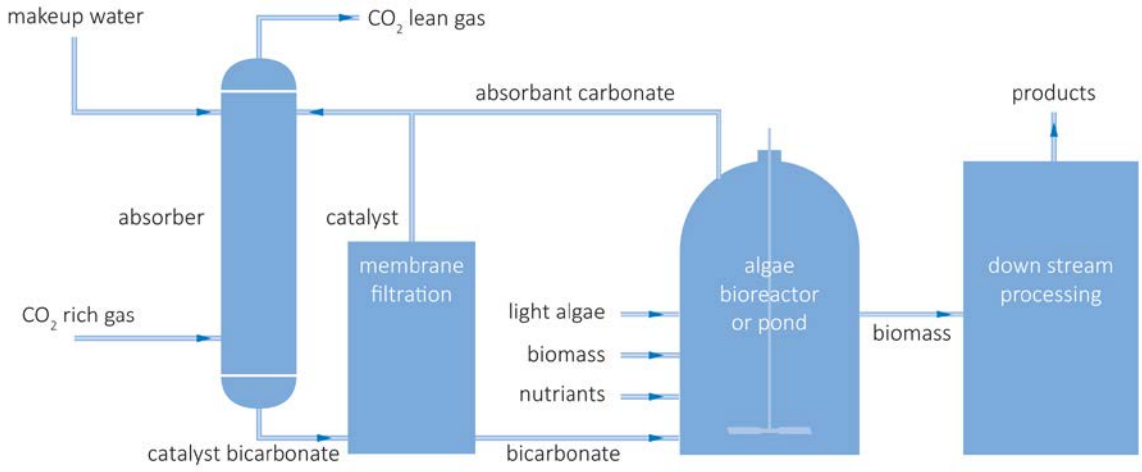

Figure 17 A carbonate-based using an enzyme integrated with algae cultivation (Schipper and others, 2013)

The second process (*see* Figure 17) uses a carbonate solution such as potassium sodium carbonate as absorption liquid for capturing CO_2. As described in the amine-based method, the CO_2 loaded solvent is

fed to algae to regenerate the absorption liquid. The uptake rate of CO_2 in carbonate solutions is too low for industrial applications, and so an enzyme, in this case carbonic anhydrase (CA), is added to enhance the rate. However, if the enzyme passes through the algae pond or bioreactor, this would lead to a substantial loss. Therefore, a step is introduced to separate the enzyme from the rich absorption liquid before its addition to the algae. Once the absorption liquid has been regenerated by the algae, it is once again mixed with the enzyme and fed into the absorber for a new cycle of CO_2 capture. Again, the primary advantage is the reduction of energy (heat) required for the regeneration of the solvent. The absorption liquid is regenerated by the algae which consume the bicarbonate. Once the majority of the bicarbonate has been removed, then the lean absorption liquid can be reused in the absorber for the next cycle of CO_2 capture. Another key advantage is the use of cheaper absorption liquids, such as potassium carbonate, compared to conventional amines-based CO_2 captures. A third advantage is that since the carbon is introduced into the algae pond in a soluble form, it directly improves the efficiency of CO_2 uptake by the algae compared to direct injection of CO_2. This not only has the potential to enhance the algae growth rate due to higher availability of CO_2, which, especially at a larger scale, can be limiting, but also reduces the energy requirement needed for the sparging of CO_2 into algae cultures.

Burgess and others (2011) compared the expected profile of CO_2 emission from Bayswater coal-fired power station in Australia against that of the solar flux at the location of the bioreactors. They concluded that solar powered photobioreactors coupled directly to a base load power station may be expected to collect not more than 25–50% of the CO_2 emitted by the power station owing to the availability of sunlight and unavailability of flue gas storage at the site. The maximum potential CO_2 capture rate is estimated at around 120 $g/m^2/d$ (annual average). Many algae are reported to experience photo inhibition or saturation at high levels in excess of 25% of maximum solar flux. This suggested a likely maximum possible capture rate of around 30 $g/m_2/d$. Assuming a mid-range saturation level of 20% full sunlight, 150 km^2 of bioreactor surface area is required to treat the flue gas output from one of the 4 x 600 MW units at the Bayswater Power Station.

5.5 Comments

Producing algae for commercial applications requires large scale cultivation and harvesting systems, which consequently requires a large land space. At a large scale, the algal growth conditions need to be carefully controlled and an optimum nurturing environment has to be provided. Reducing cost per unit is a challenge. Therefore, theoretically the integration of high value algae applications with capturing and utilising CO_2 from coal-fired power plants and wastewater treatment would reduce microalgae production costs and increase the economic viability of the whole process.

Although an Algenol biorefinery integration shows major advantages over the non-CCS case and is fully competitive with CCS in terms of carbon footprint, algae can only consume CO_2 for a fraction of the 24 hours in a day and collect only 20–25% of the CO_2 since storage of flue gas is not feasible at the flows involved. Considering the land and cost issues, algae carbon fixation can only be seen as a partial solution

for CCS. Niche applications of algae growth using power plant flue gas may however be appropriate, with commercial application aimed at the production of valuable algae products, such as bio-oil.

6 Current demonstration projects

There are many research and demonstration projects on utilising flue gas to grow algae. Some of these are well developed, for example, Algadisk supported by the Seventh Framework Program (FP7), EniTecnologie in Italy, LanzaTech in New Zealand, CO2Algaefix in Spain, Algaelink in the Netherlands, AlgaeCAT in the UK, and many more in the USA. IEA Bioenergy documented the history and the development of some algae R&D projects and is in the process of updating recent progress (IEA Bioenergy, 2010; O'Connor, 2011). This chapter only discusses projects in selected countries that are related to capturing carbon dioxide from coal-fired power plants and that have the culturing facilities close to the plant.

6.1 Australia

6.1.1 Algae Tec and Bayswater Power Station

Algae Tec (algaetec.com.au) designed a high yield enclosed algae growth and harvesting system, the McConchie-Stroud, to use CO_2 from coal-fired power plants. This system is being installed at several venues in Australia and around the world. In July 2013 Algae Tec partnered with the New South Wales government owned company, Macquarie Generation, decided to site the McConchie-Stroud system alongside the Bayswater power station in the Hunter Valley, NSW. The 4 x 660 MW plant burns approximately 7.5 million tonnes of coal per year and emits about 19 million tonnes of carbon dioxide annually. Algae Tec plans to use its system to remove 270,000 tCO_2 a year, rising to 1.3 Mt once fully operational, and use it to produce around 250,000 barrels of diesel fuel a year. The project will cost about 140 million Australian dollars. Production was due to start by the end of 2014 (Algae Tec, 2013; Vorrath, 2013).

6.1.2 MBD Energy and Tarong Power Station

The Tarong power station algal synthesiser plant project in Queensland, a joint venture between MBD Energy (www.mbdenergy.com) and Stanwell Corporation, is exploring how typical power station waste streams (ash dam water and flue gas) could be utilised to intensively grow locally selected algae strains and to ascertain whether such biomass could be used in animal feed or to make fuel. The project has run for three years during which time MBD Energy has gained a significant understanding of the key elements involved in growing algae on flue gas and ash dam water from a 1400 MW power plant. Weekly harvests of biomass are being allocated to various product trials. In mid-2013, MBD Energy reduced operations at Tarong whilst working with government agencies on funding for a large scale expansion of the Tarong project (MBD, 2014).

6.2 Austria

Energie-Versorgung Niederösterreich AG (EVN) and Duernrohr Power Station

Austrian power company Energie-Versorgung Niederösterreich AG (www.evn.at) is carrying out a small scale pilot research at their Duernrohr power station in Lower Austria. They use the flue gas from the

power plant to grow Cyanobacteria in a photobioreactor (*see* Figure 18). The Cyanobacteria is then processed to produce polyhydroxybutyric for the production of bio-plastics which show a steadily increasing demand on the world market. The residual biomass is used for the generation of biogas. The results from the first three years are very promising. However, for an economically viable process, it is necessary to increase the production efficiency. At the moment, 1 tonne of converted CO_2 can generate 115 kg PHB and 320 m^3 of biogas. For the production of 1 t PHB, approximately 700m^2 of lands is needed at the power plant.

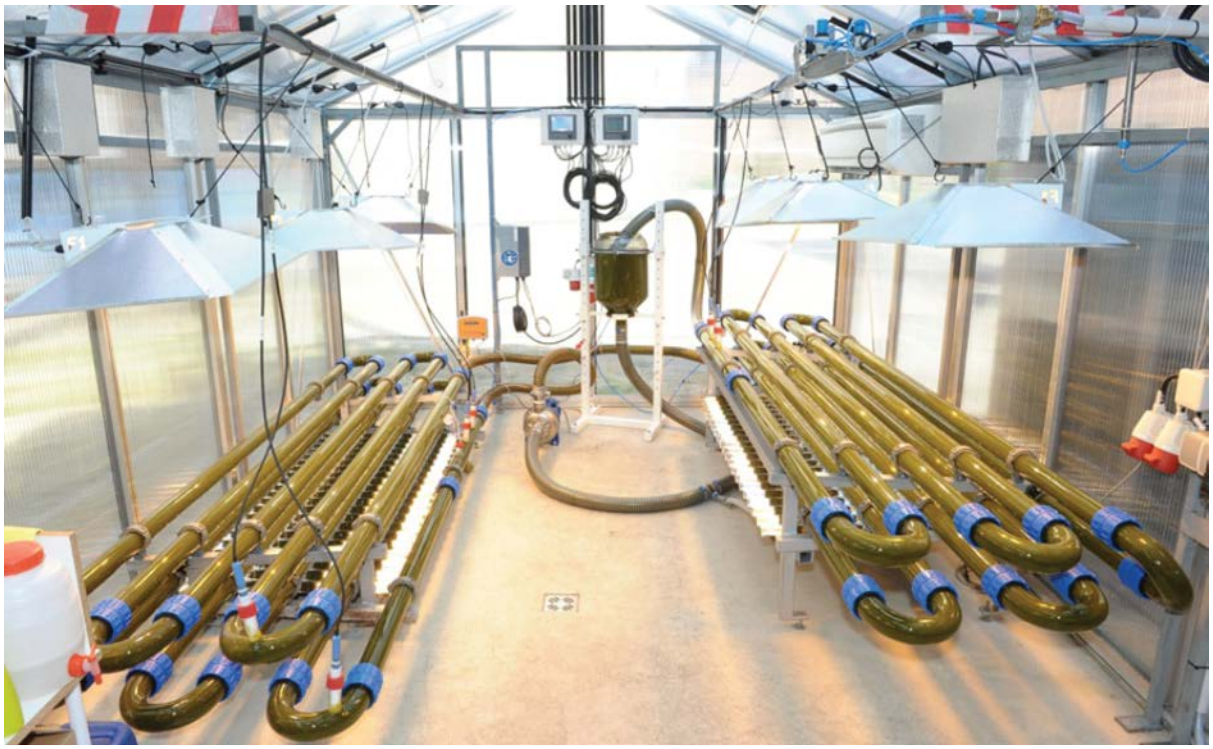

Figure 18 Photobioreactor at Duernrohr power station (Kinger, 2015)

6.3 Canada

National Research Council (NRC) and Algal Carbon Conversion Flagship

The National Research Council (NRC, www.nrc-cnrc.gc.ca) through the Algal Carbon Conversion Flagship, has invested 5 million Canadian dollars on algae biofuel projects and is working with Carbon2Algae Solutions Inc. to capture carbon emissions from facilities like coal-fired power plants and use the captured CO_2 to grow algae in northern climates. It is planned to construct a 100,000 L pilot plant with photobioreactors to demonstrate algae capturing CO_2 from a coal-fired power plant. However, the project has been delayed. The site was expected to be selected in June 2014 (Reith and others, 2014).

6.4 China and Taiwan

6.4.1 Seambiotic and Penglai Power Station's Hearol project

Registered in January 2010, Yantai Hairong Biology Technology Co. (www.hearol.com) is a joint venture between Seambiotic (*see* Section 5.6) and the Chinese companies Yantai Hairong Electricity Technology

Ltd. and Penglai Weiyuan Science &Trading Ltd., both associated with China Guodian Corporation. The project is to build a plant for the commercial cultivation of microalgae using the flue gas from the Penglai coal-fired power plant (*see* Figure 19). It is believed that the plant was running in 2012 although little information has been published. The latest report on the project is dated 24th March 2014 (Hearol, 2014; zgkjzx.com, 2014

Figure 19 Hearol project, Penglai, China (Ben-Amotz, 2011b)

6.4.2 ENN Energy Group and Daqi project

Although CO_2 is not captured from coal combustion flue gas, China ENN Energy Group Holding (www.enn.cn) has developed a microalgae carbon absorbing system to utilise the CO_2 emitted from coal-based chemical production. The technology has been shortlisted to be part of China's National High Technology R&D Program (the 863 Program). The construction of the Daqi demonstration project, which is located in Dalete Bannar, Inner Mongolia, began in May 2010 and was completed in July 2011 (*see* Figure 20). The microalgae use the CO_2 directly from coal-derived methanol and dimethylether production and are processed to biodiesel and animal feed. The system can capture 110 tonnes of CO_2 and produce 20 tonnes of biodiesel and 5 tonnes of proteins a year (ENN, 2014; MOST, 2011).

Figure 20 Daqi project at Dalete Bannar, Inner Mongolia (ENN, 2014)

Based on the Daqi field results, ENN teamed up with American Duke Energy to develop and demonstrate an economically feasible pathway for carbon dioxide utilisation with microalgae and to transform the algal biomass into a sustainable source of energy in a pilot plant. The project was started at the beginning of 2011 and will finish by 2015 (China-US Clean Energy Research Center, 2011).

6.4.3 Taipower and the Da-Lin and Lin-Kou Power Plants

Taiwan Power Company (www.taipower.com.tw) has been financing microalgae fixed carbon technology since 2010 (Taipower, 2011; 2013). The Taiwan Power Research Institute designed and built a 30 tonne photobioreactor system and an open pond system at Da-Lin coal-fired power plant to demonstrate CO_2 fixation from the flue gas (*see* Figure 21). The Da-Lin power plant has two 375 MW units and two 500 MW units and uses a seawater desulphurisation system. The flue gas from the power plant is pumped into the algae culture systems without any treatment. The photobioreactor is capable of fixing 2.234 kgCO_2 per annum. Taipower has also built an air lift photobioreactor at the 2 x 300 MW Lin-Kou power plant to capture CO_2 (13%) from the flue gas (Chen and others, 2012).

Figure 21 Microalgae culturing system at the Da-Lin and Lin-Kou power plants (Chen and Chen, 2012)

6.5 Germany

6.5.1 E.ON Hanse AG and Hamburg-Reitbrook Power Station

Together with the Institute of Environmental Technology and Energy at the Technical University Hamburg, E.ON Hanse AG (www.eon-hanse.com) is working on the 1.5 million euros project HABITAT (Hanseatic Biophotoreaktoren test center for algae cultivation and technologies). E.ON Hanse AG is supporting the project through the provision of infrastructure, consumables and technical support at its Hamburg-Reitbrook power station. In the integrated pilot plant, microalgae were grown in outdoor systems using CO_2 from conventional power plants. The Agency for Renewable Resources is funding the project. Furthermore, E.ON Hanse is supporting two independent research projects: TERM (Technology for Exploitation of the Ressource Mikroalgae) and SUBITEC (www.subitec.com) to develop microalgae cultivation systems (Brauer and others, 2013; E.ON, 2014). One of the outcomes from the TERM project is the Algae House in Hamburg (*see* Figure 7 on page 37**)**. The Algae House now uses CO_2 generated from an on-site boiler. Details about the House can be found on an IEA CCC blog (www.iea-coal.org.uk/site/2010/blog-section/blog-posts/visit-to-worlds-first-algal-house--biq-in-hamburg?).

6.5.2 RWE and Niederaussem Power Plant

RWE's (www.rwe.com) microalgae binding CO_2 system at Niederaussem power station consists of a series of V shaped 'hanging bag' photobioreactor (*see* Figure 22). The photobioreactors are located in a greenhouse to optimise growing conditions. They were erected with an area of 600 m^2, but can be extended to 1000 m^2. The system was developed by Novagreen Projekt-management GmbH. Flue gas is withdrawn from the FGD system of the lignite fired power plant and dried before being transported to the

photobioreactor. Operation started in 2008, and the system can produce up to 6,000 kg dry algae per year, fixing 12,000 kgCO_2 (RWE Power, 2009).

Figure 22 Hanging bags in the greenhouse at Niederaussem power station (RWE Power, 2009)

6.5.3 Vattenfall and Senftenberg Power Plant

Half funded by the State of Brandenburg and the European Union and the rest by Vattenfall (corporate.vattenfall.de), the Green MiSSiON (Microalgae Supported CO_2 Sequestration in Organic Chemicals and New Energy) project tested a commercial algae breeding facility at Vattenfall's Senftenberg (Brandenburg) power station from October 2011. The facility, built by the Austrian company Ecoduna, used CO_2 from the brown coal-fired power station. The project was completed in 2012. A new project 'green VISION' was launched in 2013 with the aim to identify carbon capture and storage strategies using microalgae and to investigate the feasibility of using CO_2 to produce new biomass from microalgae. The 'Hanging Gardens' algae growing system (*see* Figure 23) at Senftenberg power station has a photo-active volume of 50,000 litres and is the second largest closed algae breeding system worldwide (Algae Industry Magazine, 2011; Vattenfall, 2014).

Figure 23 Hanging Gardens at Vattenfall (Vattenfall, 2014)

6.6 India

6.6.1 National Aluminium Company Limited (NALCO) and Angul Captive Power Plant

National Aluminium Company Limited (NALCO) implemented a pilot demonstration project on bio-CCS in its captive power plant at Angul. The captive thermal power plant has a generation capacity of 1200 MW (10X120MW). Flue gas from the furnace containing about 12% CO_2 was treated and used as the major carbon source for algae growing. Nalco earmarked an area of 728 m^2 for the open pond systems (Pradhan, 2014). The construction started in 2011 and the pilot plant started operation in 2013. Current capture rate at the NALCO pilot plant is 56 tonne per hectare per year and algal biomass generation is about 37 tonne per hectare per year.

6.6.2 West Bengal Power Development Co, Sun Plant Agro and Kolaghat Power Plant

The Indian Ministry of Power promoted development of microalgae fixing CO_2 from power plant flue gas in its Working Group Report on Power for the 11th (2007-2012) and 12th (2012-2017) plans (Ministry of Power, 2007, 2012). Sudhakar and others (2011) evaluated issues related to CO_2 fixation by algae in India and concluded that the technologies could be implemented at any power plant in the country. Chattopadhyay (2011) describes a pilot project at the 1260 MW Kolaghat coal-fired power station. The project attempted to use 50% CO_2 for algal farming and the rest to produce dry ice. West Bengal Power Development Co. and Sun Plant Agro are teaming up for this project to grow algae on the wasteland near the Kolaghat power plant to produce bio-fuel. However, no updated information can be found for this project.

6.7 Israel

Seambiotic and Rutenberg Power Station

Founded in 2003, Seambiotic (www.seambiotic.com) was the first company in the world to utilise flue gas from coal burning power stations for algae cultivation. Seambiotic's pilot facility for the cultivation of marine microalgae was established in 2006 and is located at the Israel Electric Corporation's (IEC) Rutenberg coal-fired power station, close to the city of Ashkelon. The algae are cultivated in open ponds using flue gas and cooling seawater condenser effluents piped directly from the power station. The pond is about 100 to 150 m away from the stack. The total pond surface area is about 1,000 m^2. The flue gas approaching the ponds is at ambient temperature with approximately 12% CO_2 content. Seawater is supplied from the turbine condenser cooling water system of the power station's discharge channel (*see* Figure 24). According to a document on the company's website, using flue gas instead of pure food-grade CO_2 has pushed algae productivity up by 50%, possibly due to the existence of SOx, NOx and heavy metals, such as zinc, in the flue gas which act as nutrients for algae to grow. Seambiotic's final product is dry algae powder. This product is food grade and can be used in fish, animal and human food markets. The typical growth cycle of the full process at Seambiotics facility is three days at high season and seven days at low season with a production rate averaging approximately 20 g biomass/m^2/d (Seambiotic Ltd, 2010).

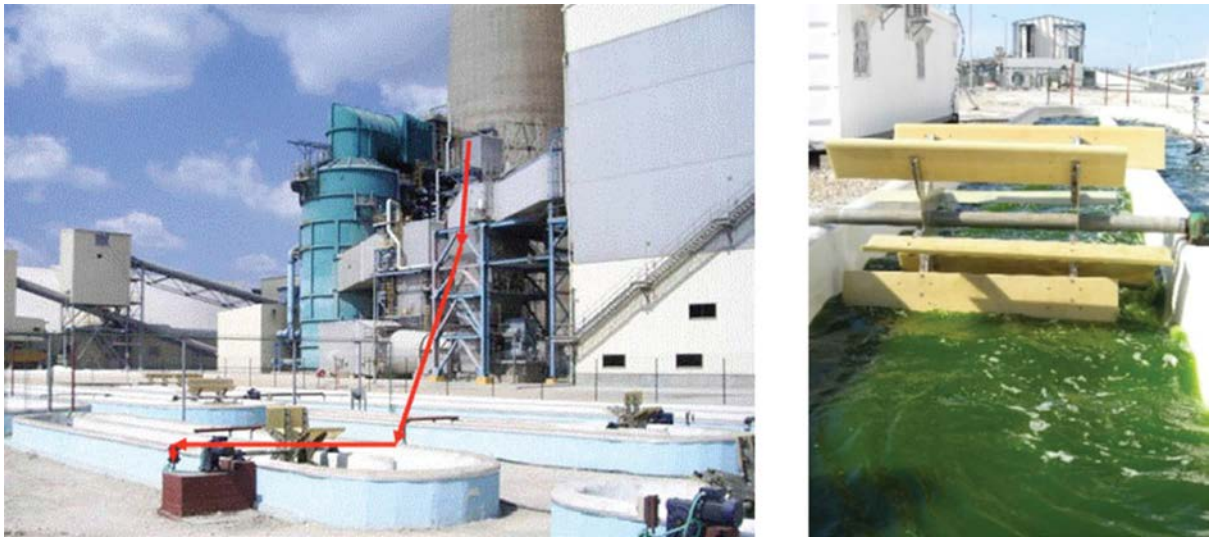

Figure 24 Flue gas from chimney to open pond at Rutenberg coal-fired power station, Israel (Ben-Amotz, 2011b)

6.8 South Africa

6.8.1 Nelson Mandela Metropolitan University and Dube Power Station

Evaluations of the use of microalgae for CO_2 capture were conducted by a number of South African research institutions and their potential was confirmed. Two pilot projects are under discussion at XSRATA and Eskom (Balmer and others, 2013). The Nelson Mandela Metropolitan University has developed a technology which mixes coal dust and algae biomass, the algae adsorbs (collects) onto the surface of the coal and binds the dust together. The result is a coal-algae composite (briquette or pellet), for which they have coined the name Coalgae™. It can be used as a substitute for coal. The university also demonstrated the cultivation of microalgae in a 20 m^3 closed photobioreactor (PRB) developed by them. Coal-fired flue gas was injected directly into the PBR system after particulate removal and SOx scrubbing. The algae product was further converted into raw bio-crude oil (Nelson Mandela Metropolitan University, 2014). The university is planning a 1 hectare technical demonstration facility (by Hatch-Goba) in one of South Africa's largest coal mining areas (Witbank) and close to Dube coal-fired power station. The construction of this facility was planned to start in early 2015. The facility will cultivate microalgae in a closed photobioreactor system using CO_2 and NOx from the power plant flue gas and a mixture of treated acid mine water and borehole water. The microalgae biomass will be used to recover and upgrade discard fine coal, which can be used for a variety of purposes, including the generation of a low emission coal through pyrolytic topping. The 1 ha facility will process between 2000 and 4000 tonnes of discard coal per annum and capture around 400 – 500 tonnes of CO_2 per annum (Zeelie, 2014).

6.8.2 MBD Energy and Khanyisa Power Station

MBD Energy is constructing a CO_2 algae bioremediation system at the 450 MW coal-fired Khanyisa power station with expectations that the system could target between 300,000 and 1,000,000 tonnes of CO_2 abatement per year by 2018 (MBD, 2014).

6.9 USA

America recognised the fuel potential of algae in the late 1950s. From the late 1970s to mid-1990s, research and demonstration projects on algae were boosted by the US Department of Energy (DOE) Aquatic Species Program (Sheehan and others, 1998). Since the end of this Program in 1996, federal funding for algal research has come from the DOE, Department of Defense, National Science Foundation, and Department of Agriculture. State funding programmes and research support from private industry also make up a significant proportion of research funding. Private investment in algal biofuels has been increasing at a dramatic rate over the last few years, significantly outpacing government funding. Today, a collection of companies are carrying out demonstration to commercial scale projects on algae production, for example, green crude oil from Sapphire Energy, high value cosmetics and nutritional products from Heliae, ethanol from Algenol, and beneficial CO_2 reuse from Duke Energy and the University of Kentucky (Algae Biomass Organization, 2013). Demonstrations on microalgae capture CO_2 from coal combustion flue gas are introduced briefly below.

6.9.1 University of Kentucky Center for Applied Energy Research (CAER) and East Bend Power Station

The Center for Applied Energy Research (CAER, www.caer.uky.edu) at the University of Kentucky has the biggest demonstration site on algae capture CO_2 in the USA. Since 2008, CAER has been working on demonstrating an algae-based system that could recycle the carbon dioxide in the coal combustion flue gas. CAER received $1.8 million funding from the Kentucky Energy and Environment Cabinet in 2013 and set up a partnership with Duke Energy to test a pilot scale system at the East Bend Station near Rabbit Hash in Northern Kentucky (University of Kentucky CAER, 2013). While the mitigation of CO_2 emissions from coal-fired power plants is the main focus of the project, the production of bio-fuels and other bio-products will also be examined in order to study the economic feasibility of using algae to capture CO_2. Duke Power's 650 MW East Bend Station is a single unit plant that burns high sulphur coal and has a wet limestone scrubber for SOx control and selective catalytic reduction (SCR) with ammonia injection for NOx control. Flue gas used in the pilot plant was obtained after the scrubber and SCR treatments. The closed loop, vertical tube photobioreactor was designed by CAER and consists of a 19,000 L feed tank, a 5700 L harvest tank and a system control enclosure. The photobioreactor was installed and started operating in December 2012 (*see* Figure 25). Summer growth studies were conducted during June and July 2013. Based on their initial work, Wilson and others (2014) concluded that CO_2 capture and recycle using microalgae is feasible from a technical standpoint. Using flue gas as the CO_2 source, algae productivity of routinely ≥30 g/m^2/d in the summer months was achieved at a significant scale (18,000\L). Moreover, an average daily productivity slightly in excess of 10 g/m^2/d was demonstrated in the month of December and 39 g/m^2/d in June and July. A protocol was developed by CARE based on flocculation and sedimentation, followed by filtration to harvest and dewater the produced algal biomass. Extraction of lipids from the harvested biomass was also demonstrated, followed by their conversion to diesel-range hydrocarbons via catalytic deoxygenation. The harvested algae biomass is characterised by an average of 42.47% C and very high volatile matter content (66.54%) with no detectable concentration

of trace elements As, Se, Cd, and Hg within the detection limit of 0.1 ppm. The absence of heavy metals is an encouraging factor for utilising the algae to high value applications. Using CAER's approach, the cost of capturing and recycling CO_2 will fall close to \$1451.5/t CO_2 (assuming an amortisation period of 10 years). The most expensive part of the process is the algae culturing stage with a high capital cost for the photobioreactor system and associated installation.

Figure 25 Photobioreactor installed at East Bend Station, KY, USA (Wilson and others, 2014)

6.9.2 Touchstone Research Laboratory

Touchstone (www.trl.com/algae) of Triadelphia, WV won an initial award in 2009 from the American Recovery and Reinvestment Act (ARRA), backed by the US DOE, to develop technologies for capturing carbon dioxide from industrial sources for storage or beneficial use. Based upon satisfactory performance in Phase 1, in 2010 Touchstone received a follow-on Phase 2 award to further demonstrate a process for capturing and reusing CO_2 generated from a small, industrial coal powered source by using algae grown in an open pond system. This project will introduce a phase change material (PCM), which was developed in Phase 1, as a layer covering the pond surface. Touchstone's DOE grant is comprised of nearly 6.8 million US dollars of ARRA funds and is matched by outside funding of almost 1.7 million US dollars (US NETL, 2014).

During Phase 1 of the project, researchers constructed a small laboratory demonstration pond to show that the use of a PCM to grow algae for CO_2 capture from an industrial source is a viable application. The results were used to help forecast the performance requirements of the PCM and gas injection components needed for the Phase 2 system. Cedar Lane Farms in Wooster, OH provides its site, existing infrastructure, and emission source for the project. Cedar Lane Farms is a commercial plant grower and has a 2.8 MW coal-fired combustor to heat its greenhouse.

During phase 2, Touchstone constructed a 2000 m^2 open pond pilot system using PCM technology and emissions from the coal-fired source. Touchstone will operate the new system over a two-year period and will gather data (PCM performance, CO_2 injection rates, water quality, algae growth, and so on) to substantiate future commercialisation efforts. The project consists of two indoor and two outdoor algae producing ponds (*see* Figure 26) with PCM covers to regulate daily temperature, control the infiltration of invasive species, and reduce water evaporation losses. The PCM absorbs infrared solar radiation during

the day as latent heat, and releases it to the water at night when temperatures drop. Approximately 7570 L of algal oil will be recovered from the process per year. Pilot-scale process development and testing of an anaerobic digestion process to convert residual algae lipids (left over after extracting oil from algae) to biofuels will be performed by the Ohio Agricultural Research and Development Center. The formal launch of Phase 2 was on the 25th July 2012. No results have been published so far (Algae Industry Magazine, 2013; US NETL, 2014).

Figure 26 The pilot-scale production ponds at Cedar Lane Farms, Wooster, OH, USA (Touchstone Research Laboratory **www.trl.com/algae**)

6.9.3 Agcore Technologies' COPAS™, system

Agcore Technologies (www.agcoretech.com), has developed a '1 Ton' continuous carbon capture and algae production platform, COPAS™, an assembly line of processes where waste emissions enter on one side and dry algae exits on the opposite side. The platform's pilot version is operating at Agcore's 2973 m^2 algae farm in Cranston. The COPAS™ system can separate carbon dioxide from flue gases produced by power plants, fermentation plants, or cement plants. Both combusted and simulated emissions have been tested with CO_2 contents ranging from 6% to 19%, ranges representative of commonly combusted fuels such as natural gas and coal. The carbon dioxide can be purified and pressurised for commercial gas use or sent in gaseous form for agriculture use. COPAS™ is available in modular systems and is also being designed in scrubber style. A commercial mobile unit is expected to be available in the near future (Agcore Technologies, 2014; Algae Industry Magazine, 2013)

6.9.4 GreenFuel Technologies Corporation and its projects

GreenFuel Technologies Corporation was a start-up that developed a process, Emissions-to-Biofuels, growing algae using emissions from fossil fuel, mainly to produce biofuel from algae. It was based in Cambridge, MA. A beta emission reduction system was installed at an MIT cogeneration facility in 2004,

and after performing beyond expectations, was moved to a larger power plant in Autumn 2005. Pilot units were tested at power plants in Arizona, Massachusetts and New York. It was reported in December 2006 that Arizona Public Service Company and GreenFuel Technologies Corporation had successfully recycled CO_2 from the 1,040 MW Redhawk power plant in Arlington, AZ (Green Car Congress, 2006). Arizona Public Service Co. received a $70.5 million US DOE grant in September 2009 to feed algae with the carbon dioxide coming from its Cholla coal-fired power plant. In April 2007, NRG Energy, Inc. and GreenFuel Technologies Corporation announced the commencement of field testing GreenFuel's Emissions-to-Biofuels technology at NRG's Big Cajun II, a 1,489 MW coal-fired power plant in New Roads, LA (Renewableenergyworld.com, 2007). However, due to financial difficulties, GreenFuel Technologies shut down in May 2009 (Kanellos, 2009; LaMonican, 2009). Further information about these projects after 2009 could not be found.

6.10 Comments

There are a number of companies culturing algae at a commercial scale for its valuable applications. Although the idea of using CO_2 from flue gas for algae growth has been around for 50 years or more, only Seambiotic in Israel is commercially producing significant quantities of algae using the flue gas from a coal-fired power plant. Apart from Seambiotic, the United States is ahead of the rest of the world in research and development in the field of utilising flue gas to culture microalgae.

7 Discussion and conclusions

Theoretically, using fast-growing microalgae to fix carbon dioxide from a coal-fired power plant is a promising alternative to conventional CO_2 capture and storage approaches, as CO_2 is converted to microalgal biomass, which could be utilised to produce commercially valuable products. Compared to current chemical/physical CO_2 removal processes, microalgae mitigation of CO_2 is more environmentally friendly and sustainable and it does not reduce the thermal efficiency of the power plant.

Microlagal CO_2 fixation is a complex process, especially in flue gas environments. The process is influenced by culture parameters, including physicochemical parameters (such as CO_2 concentration, pollutants in the flue gas, initial inoculation density, culture temperature, light, nutrients and pH) and hydrodynamic parameters (for example, flow, mixing and mass transfer). These parameters are related and interact with each other. It is crucial to comprehensively consider the effects of all the process factors in order to improve microalgal growth and its tolerance to the environment.

Beside the culture conditions, the choice of microalgal species is important as they directly influence the photosynthesis efficiency, and hence, the performance of carbon fixation and biomass production. The desirable attributes of microalgal species for capturing CO_2 include fast growth rate, high photosynthetic rate, strong environmental tolerance/adaptability of trace constituents of flue gas, high temperature tolerance, the possibility of producing high value products, and ease of harvesting and processing.

Microalgae cultivation can be carried out in open pond or closed photobioreactor systems. Open culture systems are normally less expensive to build and operate, more durable and with a large production capacity compared to large closed reactors. However, open ponds are more susceptive to weather conditions, and do not allow the control of culture medium temperature, water evaporation and light. Potential contamination is also a serious threat to the operational success of outdoor open ponds or raceways. Most importantly, they require an extensive land area and consume large amounts of water. In contrast, closed system photobioreactors can overcome the disadvantages of the open pond systems and have the advantages of better operational stability and condition control. However, the high capital and operation costs of closed photobioreactors are still barriers impeding the mass cultivation of microalgae. The key to promoting the use of microalgae to capture CO_2 is to make the photobioreactors cheaper.

Technologies are available to harvest, process and produce valuable products from microalgae. However, most of the existing technologies are adapted from technologies already in use in the food, biopharmaceutical and wastewater treatment sectors. They are not developed specifically for algae production. Therefore, they are inefficient and require a large amount of energy. These are the areas that need to be investigated in order to improve the economics of algae carbon fixation. In addition, the economics of CO_2 capture can be significantly improved if the algae products can be sold. Therefore, selecting energy efficient harvesting and processing methods and high value strains to produce commercially sound applications is also a key to promoting microalgae capture of CO_2. Nevertheless, the markets for algae are still in their infancy.

CO_2 or flue gas transportation is another issue. Apart from the constraints identified above, keeping algae cultivation systems close to the carbon dioxide source is the optimal solution to avoid the cost of building long pipelines for transportation. However, microalgae cultivation requires a large land area. For new power plants to use microalgae bio-fixation as a CCS approach, it is necessary to select a site with available land for large scale cultivation. Available land might be a problem for existing power plant.

Although the idea of using CO_2 from flue gas for algae growth has been around for 50 years, only Seambiotic in Israel has commercially produced significant quantities of algae from open pond systems using the flue gas from a coal-fired power plant. Other projects are still at the planning, construction or pilot stages. America is leading the way in terms of research and development.

Algae companies are almost ready to bring their bio-carbon capture and utilisation efforts to the marketplace as a viable alternative to conventional CCS. They need a large, constant amount of CO_2 for the technology to work. However, those strains which can thrive under flue gas conditions do not often have a high commercial value. If algae companies have to pay the power companies to reuse the flue gas, they may not have the motivation to produce low value algae biomass just for the purpose of endorsing CCS. The CO_2 fixation rate of microalgae tends to be too low to compete with conventional CCS methods. Using flue gas to culture algae is more applicable to the production of high value products than CO_2 fixation. Power companies will only be willing to invest large amounts of capital, land and water if the microalgae products can be sold at a good price. Therefore, it is very important for algae companies and power companies to form a win-win partnership to share the costs and profits.

Another potential advantage of the bio-CCS approach is the combination of CO_2 fixation, biomass production and wastewater treatment. The nitrogen and phosphorous compounds in wastewater can be used by some algae strains.

It is clear that microalgae capturing of CO_2 is technically feasible and has economic potential. But before cheap, efficient photobioreactors become available, algal capture CO_2 is better viewed as a means of providing high value end products rather than as a direct competitor to conventional CCS technology.

8 References

Algae Biomass Organization (2013) *Algae industry project book 2013*. Available at: www.algaebiomass.org/wp-content/uploads/2010/06/ABO_project_book_lo-res_July2013.pdf, 16 pp (Jul 2013)

Algae Tec (2013) *Algae Tec signs carbon capture biofuels deal with Australia's largest coal-fired power company*. Available at: algaetec.com.au/2013/07/algae-tec-signs-carbon-capture-biofuels-deal-with-australias-largest-coal-fired-power-station, 1 pp (2 July 2013, retrieved on 16 Sep 2014)

AlgaeIndustryMagazine.com (2011) *Vattenfall launches microalgae production*. Available at: www.algaeindustrymagazine.com/vattenfall-launches-microalgae-production, 1 pp (4 Nov 2011, retrieved on 20 Sep 2014)

AlgaeIndustryMagazine.com (2013) *Touchstone testing new algae technologies in Ohio*. Available at: www.algaeindustrymagazine.com/touchstone-testing-new-algae-technologies-in-ohio, 1 pp (25 Jan 2013, retrieved on 14 Sep 2014)

AlgaeIndustryMagazine.com (2013) *Captured carbon to algae with Agcore's COPAS™ system*. Available at: www.algaeindustrymagazine.com/captured-carbon-to-algae-with-agcores-copas-system, 1 pp (29 Jul 2013, retrieved on 14 Sep 2014)

Balmer M, Surridge-Talbot K, van der Merwe A (2013) *State of algal energy research specific to bio-energy application in South Africa*. Deutsche Gesellschaft für Internationale, Zusammenarbeit (GTZ) GmbH, South African – German Energy Programme (SAGEN), Pretoria, South Africa. 79 pp (Mar 2013)

Becker E W, Vemkataramm L V (1982) *Biotechnology and exploitation of Algae: the Indian approach: a comprehensive report on the cultivation and utilization*. German Agency for Technical Cooperation, Eschborn, Germany, 216 pp (1982)

Ben-Amotz A (2008) Bio-fuel and CO_2 Capture by Algae. In: *11th International Conference on Allied Phycology*; Galway, Ireland, 24 Jun 2008; 86 pp (Jun 2008)

Ben-Amotz A (2011a) Algae applications for power generation and CO_2 recycling. In: *Israel Sustainable Energy Society Annual Meeting 2011*, Tel Aviv, Isreal, 5 Oct 2011; 12 pp (Oct 2011)

Ben-Amotz A (2011b) Biotechnology of the algae Dunaliella and Nannochloropsis for production of commercial products and biofuel. In *The 1st international Conference on algal biomass, biofuels and bioproducts*; St. Louis, MI, USA, 17-20 Jul 2011; pp 17-20 (Jul 2011)

Bhatti S, MacPherson M J, Kozera C, McGinn P J, O'Leary S J B (2014) Microalgae conversion of industrial carbon dioxide emissions to value-added biomass and biofuels: sampling, isolation and screening of microalgal strains for industrial deployment in Canada. In: *4th international conference on algal biomass, biofuels and bioproducts*, Santa Fe, NM, USA, 16-18 Jun 2014. v pp (2014)

Brauer T, Kuchta K, Wieczorek N, Pell L (2013) *Cultivation of microalgae for biomass and biogas production by exploiting combustion exhaust*. Slides provided by Dr Thomas Brauer, 25 pp (2013)

Brennan L, Owende P (2010) Biofuels from microalgae - a review of technologies for production, processing, and extractions of biofuels and co-products. *Renewable and Sustainable Energy Reviews*; **14**(2); 557-577 (Feb 2010)

Brown T. M, Duan P, Savage P E (2010) Hydrothermal liquefaction and gasification of Nannochloropsis sp. *Energy and Fuels*; **24**(6); 3639-3646 (2010)

Burgess J, Jeffery L, Lowe A, Schuck S, Flentje W (2011) *Novel CO_2 capture task force report*. Available at: www.anlecrd.com.au/projects/novel-co-sub-2-sub-capture-storage-task-force, 174 pp (Dec 2011)

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 (Nov-Dec 2006)

Catarina Guedes A, Amaro H M, Sousa-Pinto I, Xavier Malcata F (2014) Chapter 10 – application of spent biomass. In *Biofuels from Algae*, Elsevier B V, pp 205-233 (2014)

Chance R, Sharma P, McCool B, Thomas V, Realff M (2012) Life cycle analysis of a cyanobacteria-based process for the production of ethanol. In: *Bundesalgenstammtisch 5th Federal Algae Roundtable Meeting*, 26 Mar 2012. Available at: events.dechema.de/events_media/14_ChanceRoundtable2012-p-3986.pdf, 11 pp (Mar 2012)

Chattopadhyay T (2011) Reduction CO_2 in thermal power plant by algae based carbon capture technology. In: *International workshop on use of algae technology, hydrogen production, and use of algae biomass*, 17-18 Oct 2011, Kolkata, India, 28 pp (2011)

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**(1), 71-81 (Jan 2011)

Chen H-W, Yang, T-S, Chen M-J, and others (2012) Application of power plant flue gas in a photobioreactor to grow Spirulina algae, and a bioactivity analysis of the algal water-soluble polysaccharides. *Bioresource Technology*, **120**, 256-263 (Sep 2012)

Chen M-J, Chen H-W (2012) Microalgae based CO_2 capture from TPC thermal power plant. In: *2012 Taiwan Symposium on Carbon Capture, Storage and Utilization*, Taipei, Taiwan, 25-27 Nov 2012. Available at: www.2012ccsu.org.tw, 29 pp (Nov 2012)

Cheng L, Zhang L, Chen H, Gao C (2006) Carbon dioxide removal from air by microalgae cultured in a membrane-photobioreactor. *Separation and purification technology*; **50**(3); 324-329 (Jul 2006)

China-US Clean Energy Research Center (2011) *Task7: carbon dioxide utilization with microalgae*. Available at: cerc-actc.hust.edu.cn/upfiles/20115/905Task%207.pdf, 10 pp (May 2011)

Chiu S Y, Kao C Y, Chen C H, Kuan T C, Ong S C, Lin C S (2008) Reduction of CO_2 by a high-density culture of Chlorella sp. in a semicontinuous photobioreactor. *Bioresource Technology;* **99** (9); 3389-3396. (Jun 2008)

Chisti Y (2007) Biodiesel from microalgae. *Biotechnology Advances*; **25**(3); 294-306 (May-Jun 2007)

Collet P, Spinelli D, Lardon L, Hélias A, Steyer J-P, Bernard O (2014) Chapter 13 –Life-cycle assessment of microalgal based biofuels. In *Biofuels from Algae*, Elsevier B V, pp 287-312 (2014)

Colt (2014) *Product overview solarleaf bioreactor façade*. Available at: www.colt-info.de/solarleaf.html, 1 pp (Retrieved on 30 Jul 2014)

Costa J A V, Linde G A, Atala D I P, Mibielli G M, Krüger R T (2000) Modelling of growth conditions for cyanobacterium Spirulina platensis in microcosms. *World Journal of Microbiology and Biotechnology*; **16**(1); 15-18 (Feb 2000)

Cuellar-Bermudez S P, Garcia-Perez, J S, Rittmann B E, Parra-Saldivar R (2014) Photosynthetic bioenergy utilizing CO_2: an approach on flue gases utilization for third generation biofuels. *Journal of Cleaner Production*; in press, 1-13 (available online 20 Mar 2014)

Davidson R M (2007) *Post-combustion carbon capture from coal-fired plants - solvent scrubbing*. Report CCC/125, London, UK, IEA Clean Coal Centre, 58 pp (Jul 2007)

Davidson R M (2009) *Post-combustion carbon capture – solid sorbents and membranes*. CCC/144, London, UK, IEA Clean Coal Centre, 64 pp (Jan 2009)

Davidson R M (2011) *Pre-combustion capture of CO_2 in IGCC plants*. CCC/191, London, UK, IEA Clean Coal Centre, 98 pp (Dec 2011)

Davidson R M (2012) *Hybrid carbon capture systems*. CCC/204, London, UK, IEA Clean Coal Centre, 25 pp (Sep 2012)

Davidson R M, Santos S O (2010) *Oxyfuel combustion of pulverised coal*. CCC/168, London, UK, IEA Clean Coal Centre, 63 pp (Jun 2010)

Dawson J, Wilson M (2014) A survey of freshwater algae for potential use in carbon sequestration of cooled flue gas from coal fired power plants. In: *4th international conference on algal biomass, biofuels and bioproducts*, Santa Fe, NM, USA, 16-18 Jun 2014. v pp (2014)

De Morais M G, Costa J A V (2007) Isolation and selection of microalgae from coal fired thermoelectric power plant for biofixation of carbon dioxide. *Energy Conversion and Management*; **48** (7); 2169-2173 (Jul 2007)

Doucha J, Straka F, Livansky K (2005) Utilization of flue gas for cultivation of microalgae (Chlorella sp.) in an outdoor open thin-layer photobioreactor. *Journal of Applied Phycology*; **17** (5); 403-412 (Oct 2005)

Douskova J, Doucha J, Livansky K, Machat J (2009) Simultaneous flue gas bioremediation and reduction of microalgal biomass production costs. *Apply Microbiology Biotechnology*; 82;179–185 (2009)

ENN (2014) *Microalgae Carbon Sequestration Technology*. Available at: www.enn.cn, (retrieved on 18 Sep 2014)

E.ON (2014) *Microalgae*. Available at: www.eon-hanse.com/cps/rde/xchg/eon-hanse/hs.xsl/137.htm, (retrieved on 24 Sep 2014)

Fernandes B D, Dragone G M, Teixeira J A, Vicente A A (2010) Light regime characterization in an airlift photobioreactor for production of microalgae with high starch content. *Applied Biochemistry and Biotechnology*; **161** (1-8); 218-226 (May 2010)

Fidalgo J. P, Cid A, Torres E, Sukenik A, Herrero C (1998) Effects of nitrogen source and growth phase on proximate biochemical composition, lipid classes and fatty acid profile of the marine microalga Isochrysis galbana. *Aquaculture*, **166**(1-2), 105-116 (Jul 1998)

Green Car Congress (2006) Arizona Public Service and GreenFuel Technologies recycle power plant flue gases into transportation-grade biodiesel and ethanol. Available at: www.greencarcongress.com/2006/12/arizona_public_.html, (1 Dec 2006)

Ghorbani A, Rahimpour H R, Ghasemi Y, Zoughi S, Rahimpour M R (2014) A review of carbon capture and sequestration in Iran: microalgal biofixation potential in Iran. *Renewable and Sustainable Energy Reviews*; **35**; 73–100 (Jul 2014)

Gonçalves A L, Simões M, Pires J C M (2014) The effect of light supply on microalgal growth, CO_2 uptake and nutrient removal from wastewater. *Energy Conversion and Management*; **85**; 530-536 (Sep 2014)

Grobbelaar J U (1994) Turbulence in mass algal cultures and the role of light/dark fluctuations. *Journal of Applied Phycology*; **6**(3); 331-335 (1994)

Hanagata N, Takeuchi T, Fukuju Y, Barnes D J, Karube I (1992) Tolerance of microalgae to high CO_2 and high temperature. *Phytochemistry*; **31** (10), 3345–3348 (Oct 1992)

Halim R, Gladman B, Danquah M K., Webley P A (2011) Oil extraction from microalgae for biodiesel production. *Bioresource Technology*, **102**(1), 178-185 (Jan 2011)

Hearol (2014) www.hearol.com, (accessed on 19 Sep 2014)

Harun R, Danquah M K, Forde G M (2010) Microalgal biomass as a fermentation feedstock for bioethanol production. *Journal of Chemical Technology and Biotechnology*; **85**(2); 199-203 (Feb 2010)

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** (2); 189-198 (Apr 2011)

Huo S, Dong R, Wang Z, Pang C, Yuan Z, Zhu S, Chen L (2011). Available resources for algal biofuel development in China. *Energies*; **4**(9); 1321-1335 (Aug 2011)

IEA Bioenergy (2010) *Algae – the future for bioenergy? Summary and conclusions from the IEA Bioenergy ExCo 64 workshop*. Available at: www.bioenergy.com, 15 pp (2010)

Jiang Y, Zhang W, Wang J, Chen Y, Shen S, Liu T (2013) Utilization of simulated flue gas for cultivation of Scenedesmus dimorphus. *Bioresource Technology*; **128**; 359-364 (Jan 2013)

Kao, C-Y, Chen, T-Y, Chang, Y-B, Chiu, T-W, Lin, H-Y, Chen, C-D, Chang, J-S., Lin, C-S (2014) Utilization of Carbon Dioxide in Industrial Flue Gases for the Cultivation of Microalgal Chlorella sp. *Bioresource Technology*; **166**; 485-493 (Aug 2014)

Kadam K L (1997) Power plant flue gas as a source of CO_2 for microalgae cultivation: economic impact of different process options. In: *Proceedings of the 3rd International Conference on Carbon Dioxide Removal* (Herzog H J ed.), Cambridge, MA, USA, 9–11 September 1996. *Energy Conversion and Management*; **38**; S505-S510 (1997)

Kanellos M (2009) *GreenFuel Technologies closing down*. Available at: www.greentechmedia.com/articles/read/greenfuel-technologies-closing-down-4670, (13 May 2009, retrieved on 15 Sep 2014)

Kinger G (2015) Personal communication. Email: gerald.kinger@evn.at

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 (Jul 2010)

Kumar K, Dasgupta C N, Nayak B, Lindblad P, Das D (2011) Development of suitable photobioreactors for CO_2 sequestration addressing global warming using green algae and cyanobacteria. *Bioresource Technology*; **102** (8); 4945-4953 (Apr 2011)

Kumar K, Banerjee D, Das D (2014) Carbon dioxide sequestration from industrial flue gas by Chlorella sorokiniana. *Bioresource Technology*; **152**; 225-233 (Jan 2014)

Kvamsdal H M, Haugen G, Svendsen, H F (2011) Flue-gas cooling in post-combustion capture plants. *Chemical Engineering Research and Design*; **89**(9); 1544-1552 (2011)

Lam M K, Lee K T (2012) Microalgae biofuels: a critical review of issues, problems and the way forward. *Biotechnology Advances*; **30** (3); 673-690 (May-Jun 2012)

Lam M K, Lee K T, Mohamed A R (2012) Current status and challenges on microalgae-based carbon capture. *International Journal of Greenhouse Gas Control*; **10**; 456-469 (Sep 2012)

LaMonican M (2009) *Algae front-runner GreenFuel shuts down*. Available at: www.cnet.com/news/algae-front-runner-greenfuel-shuts-down, (13 May 2009, retrieved on 15 Sep 2014)

Lee J S, Kim D K, Lee J P, Park S C, Koh J H, Cho H S, Kim S W (2002) Effects of SO_2 and NO on growth of Chlorella sp. KR-1. *Bioresource Technology*; **82**(1); 1-4 (Mar 2002)

Li F, Yang Z, Zeng R, Yang G, Chang X, Yang J, Hou Y (2011) Microalgae capture of CO_2 from actual flue gas discharged from a combustion chamber, *Industrial and Engineering Chemistry Research*; **50** (10); 6496-6502 (Apr 2011)

Maeda, K, Owada, M, Kimura, N, Omata, K, Karube, I (1995) CO_2 fixation from flue gas on coal fired thermal power plant by microalgae. *Energy Conversion and Management*; **36** (6-9), 717-720 (Jun-Sep 1995)

Mata T M, Martins A A, Caetano N S (2010) Microalgae for biodiesel production and other applications: a review. *Renewable and Sustainable Energy Reviews*; **14** (1); 217-232 (Jan 2010)

MBD (2014) *Emissions abatement*. Available at: www.mbdenergy.com/about_emissions_solutions.php, 1 pp (2014, retrieved on 16 Sep 2014)

MBD (2014) *Construction update*. Available at: www.mbdenergy.com/home_construction.php, 1 pp (2014, retrieved on 25 Sep 2014)

Ministry of Power (2007) *Report of the Working Group on Power for twelfth plan (2007-12)*. Available at: http://planningcommission.nic.in/aboutus/committee/wrkgrp11/wg11_power.pdf, New Delhi, India, Planning Commission, 480 pp (Feb 2007)

Ministry of Power (2012) *Report of The Working Group on Power for twelfth plan (2012-17)*. Available at: http://planningcommission.gov.in/aboutus/committee/wrkgrp12/wg_power1904.pdf, New Delhi, India, Planning Commission, 466 pp (Jan 2012)

MOST (2011) *Carbon capture utilization and storage technology development in China*. Available at: www.acca21.org.cn/gest/etc/CCUS_en.pdf, 61 pp (Sep 2011)

Murakami M, Ikenouchi M (1997) The biological CO_2 fixation and utilization project by rite (2) – Screening and breeding of microalgae with high capability in fixing CO_2. *Energy Conversion and Management*; **38**; S493-S497

Molina Grima E, Belarbi E H, Acién Fernández F G, Robles Medina A, Chisti Y (2003) Recovery of microalgal biomass and metabolites: process options and economics. *Biotechnology Advances*, **20**(7-8), 491-515 (Jan 2003)

Nagase H, Yoshihara K, Eguchi K, Okamoto Y, Murasaki S, Yamashita R, Hirata K, Miyamoto K (2001) Uptake pathway and continuous removal of nitric oxide from flue gas using microalgae. *Biochemical Engineering Journal*; **7** (3); 241-246 (May 2001)

Negoro M, Shioji N, Miyamoto K, Miura Y (1992) Growth of microalgae in high CO_2 gas and effects of SOx and NOx. *Applied Biochemistry and Biotechnology*; **28–29**; 877–886 (Spring 1991)

Nelson Mandela Metropolitan University (2014) *First public showcasing of cutting-edge algae-to-energy technology*. Available at: news.nmmu.ac.za/News/First-public-showcasing-of-cutting-edge-algae-to-e, (21 Jan 2014, retrieved on 25 Sep 2014)

O'Connor D (2011) *Algae as a feedstock for biofuels - an assessment of the current status and potential for algal biofuels production*. Available at: www.ieabioenergy.com/publications/algae-as-a-feedstock-for-biofuels, 23 pp (Sep 2011)

Ogbonna, J C, Tanaka, H (2000) Light requirement and photosynthetic cell cultivation - development of processes for efficient light utilization in photobioreactors. *Journal of Applied Phycology*; **12** (3-5); 207-218 (Oct 2000)

Oilgae (2014) *Capture of CO_2 emissions using algae*. Available at: www.oilgae.com/ref/downloads/Analysis_of_CO2_Capture_Using_Algae.pdf, 24 pp (retrieved on 21 Mar 2014)

Oilgae (2014) *Emerging algae product and business opportunities*. Available at: www.oilgae.com/ref/wp/downloads/emerging-algae-products-and-business-opportunities.pdf, 15 pp (Retrieved on 8 Sep 2014)

Oswald W J, Golueke C G (1968) Harvesting and processing of waste-grown microalgae. In *Algae, Man and Environment, Proceedings of an International Symposium.* Syracuse, NY, USA, 18-20 June 1967. Syracuse University Press, Syracuse, NY, USA, 371-390 (1968)

Pires J C M, Alvim-Ferraz M C M, Martins F G, Simões M (2012) Carbon dioxide capture from flue gases using microalgae: engineering aspects and biorefinery concept. *Renewable and Sustainable Energy Reviews*; **16** (5); 3043-3053 (Jun 2012)

Pradhan R R (2014) CCS by microalgae - A pilot project in the thermal power plant of NALCO, India. In: *International Workshop on Public Education, Training, and Community Outreach for Carbon Capture, Utilization, and Storage*, 30-31 Jul 2014, Decatur, IL, USA, 23 pp (Jul 2014)

Prajapati S K, Kaushik P, Malik A, Vijay V K (2013) Phycoremediation coupled production of algal biomass, harvesting and anaerobic digestion: Possibilities and challenges. *Biotechnology Advances*; **31** (8); 1408-1425 (Dec 2013)

Pulz O (2001) Photobioreactors: production systems for phototrophic microorganisms. *Applied Microbiology and Biotechnology*; **57**(3); 287-293 (Oct 2001)

Rachlin, J W, Grosso, A (1991) The effects of pH on the growth of Chlorella vulgaris and its interactions with cadmium toxicity. *Archives of Environmental Contamination and Toxicology*; **20** (4); 505-508 (1991)

Razzak S A, Hossain M M, Lucky R A, Bassi A S, and de Lasa H (2013) Integrated CO_2 capture, wastewater treatment and biofuel production by microalgae culturing a review. *Renewable and Sustainable Energy Reviews*; **27** (C); 622-653 (2013)

Reith M, O'leary S J, Patrzykat A (2014) The NRC carbon conversion flagship: research activities in support of commercial algae cultivation in northern climates. In: *4th international conference on algal biomass, biofuels and bioproducts*, Santa Fe, NM, USA, 16-18 Jun 2014. v pp (2014)

RenewableEnergyWorld.com (2007) *NRG Energy testing GreenFuel Technologies' algae bioreactor system*. Available at: www.renewableenergyworld.com/rea/news/article/2007/04/nrg-energy-testing-greenfuel-technologies-algae-bioreactor-system-48172, (18 Apr 2007, retrieved on 15 Sep 2014)

Richmond A (ed.) (2008) *Handbook of microalgal culture: biotechnology and applied phycology*. John Wiley & Sons, Hoboken, NJ, USA (2008)

Rickman M, Pellegrino J, Hock J, Shaw S, Freeman B (2013) Life-cycle and techno-economic analysis of utility-connected algae systems. *Algal Research*; **2**(1); 59-65 (Jan 2013)

RWE Power (2009) *RWE's algae project in Bergheim-Niederaussem*. Available at: www.rwe.com/web/cms/mediablob/en/247480/data/235578/1/rwe-power-ag/lignite/blob.pdf, 9 pp (2009)

Schipper K, van der Gijp S, van der Stel R, Goetheer E (2013) New methodologies for the integration of power plants with algae ponds. *Energy Procedia*; **37**; 6687-6695 (2013)

Seambiotic Ltd (2010) *Algae Pilot Plant.* Available at: www.seambiotic.com/News/scientific-white-papers, 9 pp (Aug 2010)

Sheehan J, Dunahay T, Benemann J, Roessler P (1998) *A look back at the US Department of Energy's aquatic species program – biodiesel from algae*. Report no. NREL/TP-580-24190, Golden, CO, USA, National Renewable Energy Laboratory, 328 pp (Jul 1998)

Show K Y, Lee D J, Chang J. S (2013) Algal biomass dehydration. *Bioresource Technology*, **135**, 720-729 (May 2013)

Show K-Y, Lee D-J (2014) Chapter 5 – algal biomass harvesting. In *Biofuels from Algae*, Elsevier B V, pp 85-110 (2014)

Singh R N, Sharma S (2012) Development of suitable photobioreactor for algae production – a review. *Renewable and Sustainable Energy Reviews*; **16**(4); 2347-2353 (May 2012)

Solovchenko A, Khozin-Goldberg I (2013) High-CO_2 tolerance in microalgae: possible mechanisms and implications for biotechnology and bioremediation. *Biotechnology letters*; **35**(11); 1745-1752 (2013)

Sternberg K (2014) *Report on the state of algae related research and industrial activities in Germany*. Public Output report of the EnAlgae project, Swansea, UK, 18 pp (Jun 2014)

Sung K D, Lee J S, Shin C S, Park S C (1998) Isolation of a new highly CO_2 tolerant fresh water Microalgae Chlorella sp. KR-1. *Korean Journal of Chemical Engineering*; **15** (4); 449-450 (Jul 1998)

Sudhakar K, Suresh S, Premalatha M (2011) An overview of CO_2 mitigation using algae cultivation technology. *International Journal of Chemical Research*; **3**(3); 110-117 (2011)

Taipower (2011) *Taiwan Power Company sustainability report 2013*. Available at:www.taipower.com.tw/TaipowerWeb//upload/files/4/2011e-13.pdf, 99 pp (2011)

Taipower (2013) *Taiwan Power Company sustainability report 2013*. Available at: www.taipower.com.tw/UpFile/CompanyENFile/2013Taipower_English_EBook.pdf, 96 pp (2013)

Uduman N, Qi Y, Danquah M K, Forde G M, Hoadley A (2010) Dewatering of microalgal cultures: a major bottleneck to algae-based fuels. *Journal of Renewable and Sustainable Energy*; **2**(1); 12701-12715 (2010)

University of Kentucky CAER (2013) *Project facts: demonstration of an algae-based system for CO_2 mitigation from coal-fired power plants*. Available at: www.caer.uky.edu/factsheets/biofuels_Crocker_Algae-Demo-Project_EastBend-1-07-13.pdf, 1 pp (retrieved on 14 Sep 2014)

US DOE (2010) *National algal biofuels technology roadmap*. US Department of Energy, Office of Energy Efficiency and Renewable Energy, Biomass Program, Washington, DC, USA. Available at: www1.eere.energy.gov/bioenergy/pdfs/algal_biofuels_roadmap.pdf, 140 pp (2010)

US NETL (2014) *ICCS (Research) -Recovery Act: re-utilization of industrial CO_2 for algae production using a phase change material*. Available at: www.netl.doe.gov/research/factsheet-print?k=FE0002546, 1 pp (retrieved on 14 Sep 2014)

Van Den Hende S, Vervaeren H, Boon N (2012) Flue gas compounds and microalgae: (bio-) chemical interactions leading to biotechnological opportunities. *Biotechnology Advances*; **30** (6); 1405-1424 (Nov-Dec 2012)

Vandamme D, Pontes, S C V, Goiris K, Foubert I, Pinoy, L J J, Muylaert K (2011) Evaluation of electro-coagulation-flocculation for harvesting marine and freshwater microalgae. *Biotechnology and Bioengineering*; **108**(10); 2320-2329 (Oct 2011)

Vattenfall (2014) *Vattenfall und die GMB GmbH erforschen den Nutzen von Mikroalgen bei der Umwandlung von CO_2 in Biomasse*, Available at: corporate.vattenfall.de/nachhaltigkeit/energie-der-zukunft/nachhaltige-energielosungen/energie-aus-algen; (retrieved on 24 Sep 2014)

Vorrath S (2013) *Algae Tec in deal to convert NSW coal plant CO_2 into biofuel*. Available at: reneweconomy.com.au/2013/algae-tec-in-deal-to-convert-nsw-coal-plant-co2-into-biofuel-66718, 1 pp (2 July 2013, retrieved on 16 Sep 2014)

Williams, P J L B; Laurens, L M (2010) Microalgae as biodiesel and biomass feedstocks: review and analysis of the biochemistry, energetics and economics. *Energy and Environmental Science*; **3**(5); 554-590 (Mar 2010)

Wilson M. H, Groppo J, Placido, A, Graham S, Morton III S A, Santillan-Jimenez E, Andrews R (2014) CO_2 recycling using microalgae for the production of fuels. *Applied Petrochemical Research*; **4**(1); 41-53 (May 2014)

Yamasaki A (2003) An overview of CO_2 mitigation options for global warming - emphasizing CO_2 sequestration options**.** *Journal of Chemical Engineering of Japan*; **34**; pp 361–375 (2003)

Yen H-W, Hu I-C, Chen C-Y, Chang J-S (2014) Chapter 2 – design of photobioreactors for algal cultivation. In *Biofuels from Algae*, Elsevier B V, pp 23-45 (2014)

Yoo C, Jun S Y, Lee J Y, Ahn C Y, Oh H M (2010) Selection of microalgae for lipid production under high levels carbon dioxide. *Bioresource Technology*; **101** (1); supplement; S71-S74 (Jan 2010)

Yun Y-S, Lee S B, Park J M, Lee C-I, Yang J-W (1997) Carbon dioxide fixation by algal cultivation using wastewater nutrients. *Journal of Chemical Technology and Biotechnology*; **69**: 451-455 (1997)

Zeelie B (2014) Personal email communication. (26 Sep 2014)

zgkjzx.com (2014) *Analyst of existing China and Israel science and technology cooperation*. Available at: www.zgkjzx.com/html/cytz2/other/2014/0324/126763.html, in Chinese (24 March 2014, retrieved on 18 Sep 2014)

Zhang K, Miyachi S, Kurano N (2001) Evaluation of a vertical flat-plate photobioreactor for outdoor biomass production and carbon dioxide bio-fixation: effects of reactor dimensions, irradiation and cell concentration on the biomass productivity and irradiation utilization efficiency. *Applied Microbiology and Biotechnology*; **55**(4); 428-433 (May 2001)

Zhao B, Su Y (2014) Process effect of microalgal-carbon dioxide fixation and biomass production: a review. *Renewable and Sustainable Energy Reviews*; **31**(1); 121-132 (Jan 2014)

Zhu L D, Hiltunen E, Antila E, Zhong J J, Yuan Z H, Wang Z M (2014) Microalgal biofuels: flexible bioenergies for sustainable development. *Renewable and Sustainable Energy Reviews*; **30**; 1035-1046 (Feb 2014)