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A Review on Microalgae to Achieve Maximal Carbon Dioxide (CO_2) Mitigation from Industrial Flue Gases

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Abstract - Global climate change and atmospheric CO_2 levels are increasing in the last decades mainly due to the rise in anthropogenic emissions. Point source emissions of CO_2 from power plants during industrialized process accounts much for this increase. An attractive approach for offsetting emissions is direct biofixation of CO_2 from flue gas through microalgae. Flue gas is fully utilized as resource to cultivate microalgae in order to moderate anthropogenic effect on our climate and for steer microalgal resource management towards innovative applications of microalgal biomass compounds. Treated and untreated flue gas into current discharge standard contains CO_2, NO_x, SO_x, particulate matter, halogen acids and heavy metals. All these compounds are considered to better steer and engineered flue gas-fed microalgal cultures. This review gives an overview of effect on photochemical, physiochemical and hydrodynamic process on the performance of microalgal-CO_2 fixation and biomass production. It is important to select suitable microalgae strains having a high growth rate, high CO_2 fixation ability and being easily cultivated on large scale to gain high biomass yield and valuable by-products to offset the costs of carbon mitigation.

Index Term – Industrial Flue gas; Biological carbon mitigation; CO_2 fixation; Photobioreactor; Biomass productivity.

1. INTRODUCTION

Photosynthetic microorganisms, such as microalgae and cyanobacteria, can grow fast (particularly when grown in waste waters), contain valuable compounds, and can be easily harvested (Lopez *et.al.* 2009). Microalgae and cyanobacteria species used for CO_2 mitigation include *Botryococcus braunii* (Yoo *et.al.* 2010), *Chlorella vulgaris* (Chen *et.al.* 2010; Cheng *et.al.* 2006), *Chlorella kessleri* (de Morais and Costa, 2007b), *Chlorocuccum littorale* (Ota *et.al.* 2009), *Scenedesmus sp*. (de Morais and Costa, 2007a; Ho *et.al.* 2010), *Chlamydomonas reinhardtii* (Packer, 2009) and *Spirulina sp*. (de Morais and Costa, 2007a,b,c). It is possible to increase the economics of microalgae utilization by using a two-stage process. In such a process, the CO_2 from a power generating stations or other source is first scrubbed (e.g. amine scrubber) and concentrated with a conventional process (Meldon, 2011; Rochelle, 2009).

Some microalgae species are tolerant to relatively high temperatures (close and above 30^{o}C). This type of microalgae can be cultured in conjunction with the usage of high temperature flue gases from industrial neighboring sites (Wang *et.al.* 2008). For instance, species of *Chlorella* isolated from hot springs in Japan grew at temperatures of up to 42^{o}C and in air containing more than 40% CO_2. Their tolerance to both high temperatures and high CO_2 content makes them potentially appropriate microbial cells for photobioreactors involved in CO_2 capture from flue gases (Wang *et.al.* 2008; Maeda *et.al.* 1995; Ono *et.al.* 2007; Yue and Chen, 2005). Marine algae *Chlorococcum littorale* showed exceptional tolerance to high CO_2 concentrations of up to 40% (Murakami and Ikenouchi, 1997). For *Spirulina sp*., the maximum specific growth rate and maximum productivity were 0.44d^{-1} and 0.22g/L/d respectively, with both using 6% and 12% CO_2 concentrations (v/v). The maximum cell concentration was 3.50g/L (dry basis) at both CO_2 concentrations. This indicates their great potential for CO_2 fixation from CO_2-rich streams. For *S. obliquus*, the corresponding maximum growth rate and maximum productivity were 0.22d^{-1} and 0.14g/L/d. Murakami and Ikenouchi (1997) developed an extensive screening, of more than 10 strains of microalgae with high capability of fixing CO_2. Two green algal strains, *Chlorella sp. UK001* and *Chlorococcum littorale*, showed high CO_2 fixation rates exceeding 1g CO_2/L/d.

1.1. Microalgal Species for mitigation of CO_2 emissions

Species that grow well under the natural day-night cycle are suitable for large scale outdoor cultivation systems (Stewart and Hessami, 2005), and strains that can directly use the CO_2 in power-plant flue gas are preferred (Benemann, 1993; de Morais and Costa, 2007c; Maeda et al., 1995). Industrial exhaust gases can contain 10-20% CO_2. Some strains are not inhibited by CO_2 with b50 ppm SOx, but can be inhibited by CO_2 when NOx is also present (Lee *et.al.* 2002; Negoro *et.al.* 1991; Jin *et.al.* 2006; Matsumoto *et.al.* 1997). Moreover, for instance, some strains

showed considerable CO_2 fixation ability, including *C. vulgaris* (6240 mg/L/d) (Cheng *et.al.* 2006), *Aphanothece microscopica Nageli* (5435 mg/L/d), and *Anabaena sp.* (1450 mg/L/d) (Lopez *et.al.* 2009; Chae *et.al.* 2006; Chiu *et.al.* 2008; de Morais and Costa, 2007a,b,c; Fan et al., 2008; Ho *et.al.* 2010; Jacob-Lopes *et.al.* 2009a,b; Jin *et.al.* 2006; Kurano *et.al.* 1995; Matsumoto *et.al.* 1997; Negoro *et.al.* 1991; Ryu *et.al.* 2009; Sakai *et.al.* 1995; Scragg *et.al.* 2002; Sung *et.al.* 1999; Yoo *et.al.* 2010), most with microalgal-CO_2 consumption rates of 200-600 mg/L/d; while some *Chlorella sp.* achieved CO_2 removal rates of 800-1000 mg/L/d, and could also remove sulfur dioxides, nitrogen oxides, and volatile organic compounds (Keffer and Kleinheinz, 2002). Application of such strains may minimize the costs of pre-treating of flue gas (Ono and Cuello, 2007). It should be noted that the performance of the microalgal strains mentioned above may be obtained based on different culture or experimental conditions, such as CO_2 concentration, temperature, cultural medium, light intensity, and the photobioreactor design (Cheng *et.al.* 2006; Fan *et.al.* 2008).

Biomass yield is higher in photobioreactors as compared to open raceway ponds and this is due to adequate nutritional control mechanisms and mono-specific culture growth conditions in photobioreactors (Brennan & Owende, 2010; Singh & Gu, 2010). In addition, lipid productivity is higher in photobioreactors as compared to open raceway ponds since all the growth parameters are amenable for optimization of higher lipid productivity in photobioreactors (Table 1). There is higher light utilization efficiency in photobioreactors as compared to open raceway ponds and this is mainly due to a large surface area in the open system (Campbell *et.al.* 2011). Biomass yields of 0.5-1 g/L are accepted as standard for raceway ponds. Photobioreactors are generally limited to 4 g/L for photobioreactors before the shading effect greatly limits further growth (Davis *et.al.* 2011). The theoretical maximum biomass productivity is estimated to be within the range of 77-96 g DCW m^2 day^1. This translates to 280-350 ton DCW ha^1 $ammun^1$ (Zamalloa *et.al.* 2011). This however is generally not achievable and productivities in the order of 27 to 62 g DCW m^2 day^1 (100–227 ton DCW ha^1 $ammun^1$) are regarded as reasonable targets (Schenk *et.al.* 2008; Stephens *et.al.* 2010). Based on the potential oil yield of 30–50% oil yield, the theoretical yield of 47000-08000 L ha^1 $ammun^1$ (Demirbas, 2011). The cost of biomass production is the only relevant factor for comparison between raceway ponds and photobioreactors. The cost of recovery of oil and transesterification is not affected by the type of culturing system (Chisti, 2007). Richmond (2004) reported that an average of 19-25 g DCW m^2 day^1 may be achieved in well managed ponds with peak productivities ranging from 12 to 40 g DCW m^2 day^1. Tubular reactors are able achieve cell densities ranging from 2 g/L to 6 g/L. Higher surface to volume ratios give superior productivities (Davis *et.al.* 2011). Cell densities of up to 10 g/L are possible in well-designed photobioreactors (Stephen *et.al.* 2010). The ranges of reported productivities for photobioreators are from 20 to 40 g DCW m^2 day^1 (Christenson & Sims, 2011).

Table 1. Different algae species along with their carbon dioxide removal efficiency

Strain	**Temperature (^oC)**	**Cultivation System**	**Lipid Content (%) dry weight**	**CO_2 conc. (%)**	**Growth rate P (g/l/day)**	**CO_2 removal (g/l/day)**	**Reference**
Monoruphidium minutum	25	Flask	-	13.6	1	90%	Brown, 1996; Giavarini *et.al.* 2010
Euglena gracilis	27	PBR	14-20%	10		64.8%	Chae *et.al.* 2006, Mata *et.al.*2010
Chlorococcum littorale	25	Flate Plate PBR	19.3%	20	0.4	16.7%	Iwasaki *et.al.* 1998; Hu *et.al.* 1998; Mata *et.al.* 2010
Scendesmus obliquus	30	Tubular PBR	33-35%	6	0.10	28.08%	De Morais, & Costa 2007; Janssen *et.al.* 1999
Spirulina sp.	30	Tubular PBR	4-16.6%	6	0.22	53.29%	De Morais, & Costa 2007; Mata *et.al.* 2010
Chlorella sp.	27	Sequential	10-48	15	1	85.6	Lee *et.al.* 2002; Cheng *et.al.*

		bioreactor					2013; Mata *et.al.* 2010;
Dunaliella Tertiolecta	25	Fermenter	60.6-67.8%	5	0.10	0.27	Takagi & Yoshida 2006; Sydney *et.al.* 2010
Nannochloropsis sp.	26 ± 1	Cylindrical Glass PBR	35.7%	2–15	0.17	11–47%	Rodolfi *et.al.* 2009; Chiu *et.al.* 2009b

2. CO_2 RECOVERY FROM POINT SOURCE FLUE GASES FOR BIOLOGICAL CARBON MITIGATION

The highest emissions of CO_2 are derived from the combustion of fossil fuels however cement, iron and steel production also account for large proportions of world CO_2 emissions (EPA, 2011). While these represent the high emitters of CO_2, microalgae may also be grown on flue gases emitted from many other industries which emit significant amounts of CO_2 including the production of petrochemicals, sugar, tyres, carbon black, aluminium, paper, inorganic chemicals, fertilizers, as well as in breweries and mining (EPA, 2011; Chae *et.al.* 2006). Fossil fueled power plant flue gases typically contain varying levels of CO_2, CO, NO_x, SO_x, N_2, H_2O as well as excess O_2 which was not used in combustion. CO_2 levels vary depending on the fuel being combusted. For a combined cycle gas turbine (CCGT) CO_2 concentration in flue gases is approximately 3-4% while 13-14% is common for a coal-fired power plant and up to 25% for flue gases from cement production (SEI, 2005; Alie *et.al.* 2005). High purity CO_2 gas is not required for the growth of many strains of microalgae, which reduces the cost of pre-treatment of flue gases (Olaizola *et.al.* 2004).

3. EFFECT OF SO_X

Many studies have been carried out to study the effect of toxic compounds on the growth of microalgae (Lee *et.al.* 2002; Yoshihara *et.al.* 1996). These studies have shown that the presence of SO_x greatly inhibits the growth of microalgae. For many strains of microalgae the presence of 50ppm of SO_2 stops growth (Yanagi *et.al.* 1995). Negoro *et.al.* (1991) evaluated that with CO_2 concentration of 15%, the growth of *Nannochloris sp.* and *Nannochloropsis sp.* was not affected by 50 ppm of SO_2. SO_2 leads to a reduction in pH in the medium with a concentration of 400 ppm SO_2 reducing the pH to below 4 after just 20h thus inhibiting the growth of algae (Stepan *et.al.* 2002;Matsumoto *et.al* 1997). However, with the introduction of NaOH to bring it back to pH 8, growth is not inhibited by the presence of SO_x (Matsumoto *et.al.* 1997). Hauck *et.al.* (1996) tested *C. vulgaris* and *Cyanidium caldarium* for CO_2 capture in a simulated flue gas (with NO_x and SO_x). *C. caldarium* showed to be able to grow at temperatures above 57°C and lower pH values. On the other hand, the growth of *C. vulgaris* was completely inhibited when the flue gas contained 200 ppm SO_2, 15% CO_2 and 3% O_2 in N_2 stream.

3.1. SO_2 tolerance and effects on microalgae

Sulphur dioxide has been shown to be remarkably toxic to some microalgal species (Lee *et.al.* 2000), but well tolerated by others. Both pH (Yang *et.al.* 2004) and bisulphite concentrations (Bake *et.al.* 1983) play a role in the tolerance of microalgae to SO_2. Biochemical effects of SO_2 arise from its unique ability to act as a reducing or oxidizing agent. A few mechanisms leading to toxicity have been revealed specifically for microalgae (Bake *et.al.* 1983). Yang *et.al.* (2004) found that at low concentrations (<104 mg sodium bisulphate L^{-1}) bisulphite was utilized as an S-source by *B. braunii* after oxidation of bisulphite to sulphate, but high concentrations of bisulphite (>104 mg sodium bisulphate L^{-1}) were toxic. It was suggested that in the conversion of bisulphite into sulphate, superoxide anions, hydroxyl radicals and hydrogen peroxide were formed; these highly oxidative molecular species damaged membranes and pigment, causing peroxidation of membrane lipids and bleaching of chlorophyll, thus inhibiting the growth of *B. braunii* (Giordano *et.al.* 2005). Several strategies have been tested to lower the toxicity of SO_2 sparging on microalgae. Keeping the pH above 6 to prevent formation of sulphites, for example, the addition of alkaline solutions has been successful (Lee *et.al.* 2000).

3.2. SO_2 removal by microalgae

Due to the higher solubility of SO_2 in aqueous media and due to the higher SO_2 concentrations in flue gas, the revenues from SO_2 trading are expected to be higher than those from NO_x. In the USA, an SO_2 emission trade system was introduced in 1994, with prices ranging between 48 and 152€ per kg of SO_2 (Kessels and Hennessy, 2004). Data on removal rates of SO_2 in flue gas sparge reactors is very limited. In a lab-scale microalgal bacterial flocs reactor fed with sewage and sparged with flue gas containing 572 mg N/m^3 SO_2 at a low gas flow rate of 0.0050 vm, we observed an SO_2 removal rate of 3.2±0 mg SO_2 /L/d

and an increase in the sulphate concentration of wastewater from 50.7±5.5 to 54.9±2.6 mg/L (unpublished data from experiments of Van Den Hende *et.al.* 2011a). Due to the low gas flow rate, this effluent sulphate concentration was within the severe local legislation norms for surface water of 90 to 150 mg sulphate/L (norms are for rivers where treated sewage is mostly discharged in) (Vlarem, 2010). However, this led to the pH being lower than that allowed for discharge in surface water. Therefore, at an industrial scale, legislation limits on effluent pH and sulphate concentration are more likely to set boundaries on SO_2 removal rates in flue gas-fed microalgal reactors rather than on the toxicity on microalgal species.

4. EFFECT OF NO_X

Algae can grow effectively while absorbing NO_x during the log phase of growth. However, the addition of NO and NO_2 at the early stages actually inhibited growth. *Nannochlorophsis sp.* effectively utilized NO_x at concentrations of up to 300 ppm as a nutrient and reduced its presence in the flue gas by 50% (Yoshihara *et.al.* 1996). In a similar way to SO_x, the presence of NO_x decreases pH in the media. However, its effect is much less with unaffected growth recorded in NO_x concentrations of up to 240 ppm (Stepan *et.al.* 2002). The presence of NO in flue gas is oxidized in the presence of oxygen to form NO_2 in aqueous solution which inhibits the growth of microalgae (Matsumoto *et.al.* 1997). This effect can be evaded by changing the nutrient source in the media from $NaNO_3$ to $NaNO_2$. In the case where $NaNO_2$ was used, NO_x had no hindering effects on growth; instead it was used as a nitrogen source for the algae (Matsumoto *et.al.* 1997; Brown, 1996).

4.1. NO_x tolerance and effects on microalgae

The tolerance of microalgae to NO_x depends on microalgal cell density (Yoshihara *et.al.* 1996), NO_x concentration (Doucha *et.al.* 2005), NO_x gas flow rate (Li *et.al.* 2011), reactor type (Nagase *et.al.* 1997) and species (Radmann and Costa, 2008). However, to remove NO is more difficult due to its lower solubility in the liquid phase. Considering this difficulty, Yoshihara *et.al.* (1996) cultivated the marine microalgae NOA-13, trying to eliminate NO and CO_2, simultaneously. Using a $4dm^3$ reactor column with aeration of 300ppm (v/v) NO and 15% (v/v) CO_2 in N_2 at a rate of 150 cm/min, about 40 mg of NO (half of the NO supplied) and 3.5 g of CO_2 were eliminated per day. Nagase *et.al.* (1997, 1998, 2001) investigated the potentiality of the microalga Dunaliella tertiolecta to remove NO_x from fuel flue gas; NO, the main component of NO_x in flue gases (more than 90%), was supplied with concentration ranging from 25 to 500 ppm, being removed about 65%. Santiago *et.al.* (2010) evaluated the effects of the addition of Fe(II)EDTA to microalgae Scenedesmus sp. on NO removal. The results showed that this compound enhances the NO fixation at a level higher than the one obtained with bacterial denitrification systems.

4.2. Removal of NO_x by microalgae

The rate limiting step for NO removal in bioreactor systems is the dissolution of NO into the microalgal culture medium (Jin *et.al.* 2005). The addition of a chelator greatly improves NO removal in a Scenedesmus culture (Jin *et al.,* 2008). Well known chelates able to form stable metal complexes are ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), methyliminodiacetic acid (MIDA) and dimercaptopropanesulfonic acid (DMPS). Fe(II)EDTA particularly reacts rapidly with the absorbed NO gas to form stable metal-nitrosyl complexes:

$$NO_{(g)} + Fe(II)\ EDTA \rightarrow Fe(II)\ EDTA - NO_{(aq)}$$

Flue gases and microalgal cultures contain dissolved oxygen. In the presence of dissolved oxygen, Fe(II)EDTA is easily and irreversiably oxidised to Fe(III)EDTA in bacterial systems (Jin *et.al.* 2008):

$$4Fe(II)\ EDTA^{2-} + O_2 + 4H^+ \rightarrow Fe(III)\ EDTA^- + 2H_2O$$

Since Fe(III)EDTA can no longer chelate NO (Jin *et.al.* 2008), it decreases the process efficiency. Interestingly, in a microalgal NO removal system, constant NO removal was maintained over a long duration and a certain fraction of Fe(II)EDTA remained without being oxidized to Fe(III)EDTA because of the existence of a reversible oxidation-reduction balance between Fe(II)EDTA and Fe(III)EDTA (Santiago *et.al.* 2010). So, Fe(II)EDTA can be regenerated in microalgal cultures, but this microalgal Fe(II) regeneration is species dependent. Since a long exposure to sunlight can destabilise the iron EDTA (Lockhart and Blakeley, 1975), Fe(II)EDTA addition to microalgae reactors may be too costly. Moreover, EDTA is a micropollutant. Therefore, the in situ production of iron siderophores, acting as a biochelator, seems advantageous and merits further investigation. However, NO_x removal in microalgae reactors does not lead to important revenues, since removal rates are low. For example, Van Den Hende *et.al.* (2011a) reported a removal of 0.74 g NO_x $m^{-3}_{reactor}$ day^{-1}, leading to a maximum of 0.027 €$m^{-3}_{reactor}$ $year^{-1}$ or 0.00041€kg^{-1} microalgal bacterial biomass (VSS) (applying the Dutch NO_x tariff of 0.1€ per kg NO_x; Smit, 2011).

5. EFFECT OF CO_2

Many studies have shown that elevated levels of CO_2 in the air stream increases productivity of a range of strains of microalgae (Olaizola *et.al.* 2004; Wang *et.al.* 2008; Hauck *et.al.* 1996; Yanagi *et.al.* 1995; Sawayama *et.al.* 1995). However, at high levels of CO_2 (above 20% for many strains) biomass productivity reduced and in some cases ceases though it depends greatly on the cell density of the culture as well as its pH (Chiu *et.al.* 2009). Some strains such as Nannochloropsis oculata grow much more effectively in 2% CO_2 than in air but above 5% CO_2 growth is suppressed (Hsueh *et.al.* 2009). It can be assumed that approximately 2t of CO_2 is required to produce 1t of algal biomass (Stepan *et.al.* 2002). In a study by Chiu *et.al.* (2008) Clorella sp. was shown to have higher CO_2 removal capacity but lower productivities at low CO_2 concentrations (Cheng *et.al.* 2006). At higher concentrations of CO_2 more carbon was mitigated and biomass productivity was greater, however removal efficiency was lowered due to algal cells utilizing the abundant carbon for metabolic activity rather than for making cell organelles (Chiu *et.al.* 2009). This study showed that the optimum level of carbon mitigation occurred at 1% CO_2 despite other experiments which demonstrate good growth rates at higher concentrations of CO_2 (Ramanan *et.al.* 2010).

5.1. Solubility of CO_2 in aqueous solutions

According to the two-film theory, mass transfer of CO_2 from the gas phase to the cell phase occurs through sequential stages, but is mainly determined by the gas-liquid stage (Markle, 1977). The CO_2 mass transfer rate (N_{CO2}) is approximately given by:

$$N_{CO2} = k_L\alpha\ (C_{CO2L}^{*} - C_{CO2L}) \quad \ldots\ldots\ldots\ldots\ldots\ldots 1$$

With k_L the liquid-phase mass transfer coefficient, α the specific area available for mass transfer, C_{CO2L}^{*} the CO_2 concentration in the liquor that equilibrates its actual partial pressure on the gas side, and C_{CO2L} the actual CO_2 concentration in the liquor (Markle, 1977). Several methods have been proposed for enhancing the N_{CO2} by increasing α and/or k_L, for example, microporous hollow-fibre membranes, air-lift bubble columns, stirring, gas injection methods and gas recirculation (Jacob-Lopes *et.al.* 2010). Compared to O_2, the gas-liquid transfer for CO_2 from flue gas is relatively fast, due to its relatively high solubility (1.496 g $CO_2\ L^{-1}$ in water at 25 °C and 1atm, i.e., over 100 times higher than that of O_2). CO_2 solubility is pH dependent, increases with pressure and decreases with increasing salt concentration and increasing temperature (Liu and Liu, 2013). Thus, to enhance the solubility of CO_2, the medium can be artificially cooled (Satyanrayana *et.al.* 2011).

When CO_2 dissolves in an aqueous medium, it reacts through a set of chemical equilibriums. At a pH lower than 8, the main pathway is direct hydration (Housecroft and Sharpe, 2005; Stumm and Morgan, 1981; with pK at 25°C; 1atm):

$$CO_{2(g)} \rightarrow CO_2 \quad (pK=1{:}468) \quad \ldots\ldots\ldots\ldots 2$$
$$CO_{2(aq)} + H_2O \rightarrow H_2CO_3 \quad (pK=2{:}840) \quad \ldots\ldots\ldots 3$$
$$H_2CO_3 \rightarrow HCO_3^-{}_{(aq)} + H^+ \quad (pK=6{:}352) \quad \ldots\ldots\ldots 4$$
$$HCO_3^-{}_{(aq)} \rightarrow CO_3^{2-}{}_{(aq)} + H^+ \quad (pK=10{:}329) \quad \ldots\ldots 5$$

With $H_2CO_3 = CO_{2(aq)}+H_2CO_{3(aq)}$, since these species are nearly indistinguishable.

The hydration of CO_2 (reaction 3) is slow, whereas the dissociation of carbonic acid (reactions 4 and 5) is so fast that H_2CO_3, HCO_3^- and CO_3^{2-} are in equilibrium (Dreybrodt *et.al.* 1997). At a pH above 10, the main pathway is by the attack of hydroxide ions (Housecroft and Sharpe, 2005):

$$CO_{2(aq)} + OH^-_{(aq)} \rightarrow HCO_3^-{}_{(aq)}$$
$$HCO_3^-{}_{(aq)} + OH^-{}_{(aq)} \rightarrow CO_{2(aq)} + H_2O$$

Therefore, in aqueous environments with a pH between 6.352 and 10.329 (the most common pH of microalgal cultures), bicarbonate is the dominant carbonate species.

5.2. CO_2 tolerance and effects on microalgae

Several microalgal species have shown good tolerance to sparging with gas containing 5 to 20% CO_2, i.e., concentrations as in flue gas. Even tolerance up to 40 and 100% of CO_2 has been reported (Matsumoto *et.al.* 1997; Olaizola *et.al.* 2003). By contrast, Soletto *et.al.* (2008) attributed this inhibition to an increase in osmotic pressure. Xu *et.al.* (2003) reported that high CO_2 stress inhibited the efficiency of photosystem II. Overall, the CO_2 tolerance of microalgae is dependent on cell density (Chiu *et.al.* 2008), pH (Olaizola *et.al.* 2003), nutrients, light (Soletto *et.al.* 2008), and species (Tang *et.al.* 2011). Carbon dioxide enrichment can affect the biochemical composition of algae in several ways. Reports on the effect of CO_2 on lipid content and composition are contradictory. Ota *et.al.* (2009) found that at CO_2 concentrations between 20 to 50%, the total fatty acid content of *Chlorococcum littorale* decreased. High CO_2 levels (30 to 50%) have been shown to favor the accumulation of total lipids and polyunsaturated fatty acids in certain microalgae (Chiu *et.al.* 2008; Tang *et.al.* 2011). This increase in polyunsaturated fatty acids has been explained by a relative decrease in oxygen concentration that might affect enzymatic desaturation (Vargas, 1998). Shifting

Chlorella from limiting (air 0.04%) to higher (4 to 5%) CO_2 concentrations increase the proportion of saturated fatty acids (Tsuzuki *et.al.* 1990). Desaturation of fatty acids has been seen to occur more rapidly when the CCM is induced in *Chlamydomonas reinhardtii* (Pronina *et.al.* 1998).

Xia and Gao (2005) observed that enriching the cultures of *Chlamydomonas reinhardtii* and *Chlorella pyrenoidosa* with CO_2 decreased nitrate reductase activity. They explained this by a modification of the nitrate reductase via protein phosphorylation because the phosphorylation level was higher in cells incubated in the presence of air enriched with CO_2 compared with air alone. Larsson *et.al.* (1985) found that CO_2 addition led to an increased internal N content in *Scenedesmus obtusiusculus*. Flue gas enrichment has been observed to increase the chlorophyll a: chlorophyll b ratio in *Chlorella pyrenoidosa*, but not in *Chlamydomonas reinhardtii* (Xia and Gao, 2005). An increased inorganic:organic carbon ratio also increases the chlorophyll a content of microalgal bacterial flocs (Van Den Hende *et.al.* 2011b).

5.3. CO_2 fixation by microalgae

Microalgal CO_2 fixation involves photoautotrophic growth in which anthropogenically derived CO_2 may be used as a carbon source. Therefore, biomass measurements or growth rate evaluations are critical in assessing the potential of a microalgal culture system for direct CO_2 removal (Cheng *et.al.* 2006; Costa *et.al.* 2004). The effects of CO_2 concentrations in air on microalgae growth have been evaluated in several studies in photobioreactors. The goal has been to consider CO_2 capture from waste gases at high CO_2 concentrations (de Morais & Costa, 2007; Ho *et.al.* 2012; Yoshihara *et.al.* 1996). With this end, different air and CO_2 feed compositions were fed into the photobioreactor. This research has allowed the study of microalgal growth and CO_2 fixation, with this information being valuable to determine CO_2 removal efficiency. The CO_2 removal efficiency in a photobioreactor with microalgal culture can be determined as the difference of CO_2 concentration of the incoming and outgoing effluents. The removal efficiency (%) can be thus determined using the following formula (Chiu *et.al.* 2009):

(Influent of CO_2 - Effluent of CO_2)/ Influent of CO_2 x 100%

The efficiency of CO_2 removal or fixation in a closed culture system depends on (a) microalgal species, (b) CO_2 concentration, (c) photobioreactor design and (d) operating conditions (de Morais & Costa, 2007; Cheng *et.al.* 2006). Cheng *et.al.* (2006) observed in a membrane photobioreactor, a maximum CO_2 removal efficiency of 55.3% at 0.15% CO_2 with a reduction of 80 mg/L h at 1% CO_2 in a *C. vulgaris* culture. In a three serial tubular photobioreactor, 27-38% and 7-13% of CO_2 was fixed by *Spirulina sp.* and *S. obliquus*, respectively, in cultures aerated with 6% CO_2.

On the other hand, in treatments with 12% CO_2 aeration, CO_2 fixation efficiency was only 7-17% for *Spirulina sp.* and 4-9% for *S. obliquus* (de Morais & Costa, 2007). In other words, there is a species dependence on the CO_2 efficiency removal or fixation. This may be due to physiological conditions of microalgae, such as potential for cell growth and CO_2 metabolism. In studies by Yun *et.al.* (1997), the CO_2 fixation rate was determined from the carbon content of algal cells. The growth rate was established as follows:

$$R_{CO2} = C_C \mu_L * (M_{CO2}/M_C)$$

where R_{CO2} and μ_L are the fixation rate (g CO_2/m^3 h) and the volumetric growth rate (g dry weight/m^3 h), respectively, in the linear growth phase. $M_{CO2}$and M_C represented the molecular weights of CO_2, and elemental carbon, respectively. The average carbon content (C_C measured by an elemental analyzer) (CHNS932, Leco) was 0.507 g carbon/g dry cell weight. The algal growth rate was determined in the linear growth regime given that most of the algal growth occurred during this phase.

6. EFFECT OF pH

The effect pH has on growth varies with different strains of microalgae. In general a pH of 7 for freshwater algae and 8 for marine microalgae is the optimum for growth, while at pH below 4 most microalgae cease to grow (Stepan *et.al.* 2002; Matsumoto *et.al.* 1997; Huntley & Redalje, 2007; Sung *et.al.* 1999). The presence of CO_2, SO_x, NO_x all affect the pH of the media, the most significant effect on pH being associated with high concentrations of SO_x in flue gases. In general CO_2 is the main mechanism which dictates the pH of the cultivation media (Tsai *et.al.* 2012). Increasing the concentration of CO_2 in the media lowers the pH due to the effects of acidification and this has an effect on the physiology of microalgae. Moazami *et.al.* (2012) showed that cultures of S. minor and S. cylindricus grew effectively in pH ranging from 5.0 to 9.5 but with reduced productivity at pH greater than 8.5. Studies have shown that as the pH increases with biomass concentration, therefore careful management of pH in the early stages of growth are of utmost importance to ensure growth is not inhibited (Zeiler

et.al. 1995). This may be achieved by the addition of a buffer (i.e., NaOH or CO_2) to bring the pH back to the optimum level for growth of the specific strain of microalgae (Matsumoto *et.al.* 1997).

7. EFFECT OF TEMPERATURE

Since flue gases from point sources such as power plants have high temperatures (around 120^oC) the use of algae tolerant of high temperatures would achieve significant reductions in cooling costs of the gases (Ono & Cuello, 2007). Most microalgal species considered for carbon mitigation are mesophilic microalgae (optimum growth in temperatures of 13-45^oC) with high tolerance to CO_2 while there has also been some studies carried out in the production of thermophilic cyanobacteria (temperatures of 42-75^oC) to address the problem with cooling costs, however, high productivity cannot be achieved with cyanobacteria (Ono & Cuello, 2007). Another problem with cultivation of microorganisms at these high temperatures is loss of water through evaporation. Within the mesophilic range, an increase in temperature will lead to an increase in productivity up to a critical temperature limit at which growth is hindered for the specific strain of microalgae (Sung *et.al.* 1999).

8. EFFECT OF SOOT

There has been limited research carried out on the effect of soot on the growth of microalgae. A study carried out by Matsumoto *et.al.* (1997) showed that when the concentration of soot exceeded 0.2 g/l heavy metals were present in amounts (Ni=1 ppm, V=0.1 ppm) which impeded growth of microalgae. However, the concentration of soot in flue gases from power plants rarely exceeds 50 mg/m^3 and therefore it does not pose a threat to microalgae productivity (Stepan *et.al.* 2002). The main components of coal fired flue gas are Al_2O_3 SiO_2 Fe_2 O_3 accounting for 80-90% of fly ash mass. To comply with regulations of flue gas content (50 mg/N m^3) and particle size (O_2 mm) ESP with up to 99% removal efficiencies have been developed (Jaworek *et.al.* 2007).

9. EFFECT OF SALINITY

Every alga has a different optimum salinity range that can increase during hot weather conditions due to high evaporation. Salinity changes normally affect phytoplankton in three ways: (1) osmotic stress (2) ion (salt) stress; and (3) changes of the cellular ionic ratios due to the membrane selective ion permeability. The easiest way for salinity control is by adding fresh water or salt as required (Moheimani, 2005).

10. SUNLIGHT AS THE LIGHT SOURCE

The major problems associated with microalgae culture systems are the high power consumption and high operating cost of the artificial light sources. To improve the light efficiency and increase the microalgae growth rate at a lower cost would thus be a substantial step towards the development of a successful microalgae production process. Among all the light sources available, that from the sun is clearly the most abundant, as its radiation provides the highest energy flow of ca. 5.7 10^{24} J/year, which is about 10,000 times more than the total energy consumed by human beings every year (Miyake *et.al.* 1999). At mid-day, the sunlight provides the highest light intensity, at 1100 W/m^2 (Miyake *et.al.* 1999), which exceeds the intensity required for efficient production of microalgae. Most of the commercial cultivation of microalgae is carried out in open pond systems, with solar light energy being directly utilized (Pulz, 2001). However, the performance of these outdoor open pond photobioreactors is usually poor, due to the problems of it being difficult to control the culture conditions, direct exposure to UV irradiation, contamination, low light intensity and uneven distribution (Chen *et.al.* 2008), day-night cycles, diurnal variation and the need for a large area of land. Although all of these issues limit the light conversion efficiency and productivity of outdoor photobioreactors, it is the day-night cycles and diurnal variation in light intensity that are considered the major problems when using sunlight. Depending on the weather, season, solar spectrum and operation time, the length of time during which the light intensity is high enough to support microalgal growth can be very short. In the absence of light energy, the cellular metabolism mode will switch (Kitajima *et.al.* 1998), and thus both the productivity and biochemical composition of the microalgal cells are affected by the availability of the light. It has also been discovered that biomass concentration and carbohydrate content decrease during cultivation of *C. pyrenoidosa* at night (Ogbonna and Tanaka, 1998). Ong *et.al.* (2010) used an outdoor closed and vertical bubble column photobioreactor with 40 L culture volume. The CO_2 fixation rate reached 25.65 mg/min when using semi-continuous cultivation within a thermal-tolerant mutant Chlorella sp. In addition, Sato *et.al.* (2006) used a new outdoor closed type photobioreactor, and found that the productivity of *Chaetoceros calcitrans* was 37.3 g/m^2/day with the maximum cell density of 2.5 g/L. (Carlozzi, 2003) also reported the maximum photoautotrophic cyanobacterium biomass productivity of 2.7 g/L/d with a maximum biomass concentration of 6.0 g/L by using an outdoor undulated tubular reactor. (Hall *et.al.* 2003) obtained the microalga *Phaeodactylum tricornutum* productivity of 1.4 g/L/d with a maximum biomass

concentration of 3.0 g/L with an outdoor cylindrical shaped helical tubular photobioreactor. Doucha and Livansky (2009) reported that biomass productivity of the microalga *Chlorella sp.* reached 4.3 g/L/d in an outdoor open thin-layer photobioreactor. In addition, Vonshak *et.al.* (1996) successfully used outdoor tubular photobioreactors for the cultivation of *S. platensis*, while Ugwu *et.al.* (2005) reported that the biomass productivity of *Synechocystis aquatilis* achieved 9 $g/m^2/d$ in an outdoor tubular photobioreactor equipped with static mixers. Finally, Li *et.al.* (2007) demonstrated the feasibility of outdoor tubular cultivation of the marine microalga *Pavlova viridis* for photoautotrophic production of eicosapentaenoic acid (EPA).

11. EFFECTS OF HYDRODYNAMIC PROCESS

11.1. Flow and mixing

Usually, performance on microalgal-CO_2 fixation and biomass production was found to have a nonlinear relationship with aeration rate. Moreover, investigation indicates that the aeration strategy has an influence, e.g., gradual increase of CO_2 supply could enhance the growth rate and CO_2 fixation rate compared with constant CO_2 supply. This is because microalgae could adapt to the new CO_2 concentration well and enhance their CO_2 tolerance when CO_2 supply slowly increases, especially under a relatively higher concentration of CO_2 (Yun *et.al.* 1996). Currently, as a most widely used method, gas aerating (usually using bubbling) is able to provide a relatively good flow and mixing performance. It is defined as the gas volumetric flow rate per unit volumetric culture medium (vvm). For most closed cultivation, the recommended aeration rate is 0.10-1.00. The optimum aeration rate varies with microalgal species and PBR configuration, e.g., 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 PBR (Sierra *et.al.* 2008). An appropriate turbulence effect by an appropriate aeration rate is helpful to increase the microalgal performance on carbon fixation and biomass production, but extremely high aeration rate also gives rise to increase of shear stress especially in the processes of bubble generation, bubble deformation (e.g. bubble coalescence and break-up) and gas-liquid interface formation (Chalmers, 1994; Barbosa *et.al.* 2003; Dasgupta *et.al.* 2010). Moreover, the flow pattern by aeration can be improved using optimized PBR configuration, such as using horizontal and vertical baffles in flat plate airlift (Zhang *et.al.* 2001). Also, the turbulent mixing by aeration can be controlled via adequate use of baffles (Kumar *et.al.* 2010). Recently, there were preliminary investigations using a computation fluid dynamics (CFD) technique to optimize the flow and mixing in PBR (Yu *et.al.* 2009; Su *et.al.* 2010; Liu *et.al.* 2013).

11.2. Mass transfer

There is a complex mass transfer process in a Microalgal-PBR. It involves a process of three-phase mass transfer contains mass transfer between: gas (CO_2)-liquid (medium), gas (CO_2)-solid (microalgae), and liquid (medium)-solid (microalgae). In the gas aerating method, mass transfer performance and biochemical reaction rate depend on bubble size, gas hold-up, gas-liquid contact area and CO_2 concentration and gas/liquid ratio, etc. Experiments showed that a PBR could reach to higher CO_2 removal efficiency if the high-performance microalgal species were used under optimized operating conditions, e.g., for microalgae Chlorella sp. at CO_2 concentrations of 2%, 5%, 10% and 15% (v/v), the CO_2 removal efficiency was 58%, 27%, 20% and 16%, respectively (Chiu *et.al.* 2008). Other microalgal species, *S. obliquus WUST4* can adapt to the acural flue gas and reached to the CO_2 removal efficiency of 67% under 12,000-13,000 lx light intensity, 12% CO_2 concentration and 0.1 vvm aeration rate (Li *et.al.* 2011). In recent years, some new methods were used to improve mass transfer drive, including enhancing CO_2 concentration gradient (e.g., using $NaHCO_3$ as additive to generate chemical reaction), or expanding contact area (e.g., using hollow-fiber membrane PBR (Carvalho & Malcata, 2001; Carvalho *et.al.* 2006). Several novel theoretical equations have been developed to model the mass transfer between CO_2 and microalgae, e.g., linking the overall volumetric gas–liquid mass transfer coefficient with the gas holdup and the superficial aeration velocity and other principal operation variables (Sánchez Miron *et.al.* 2000), or using a nonequilibrium mathematical model of CO_2 dynamics considering the hydration of dissolved CO_2 to bicarbonate ion (HCO_3) as well as the uptake and/or cycling etc (Nedbal *et.al.* 2010).

Common biological contaminants observed include unwanted algae, mould, yeast, fungi, and bacteria. Attempts made to cultivate some microalgae species in raceway ponds failed, since cultures collapse due to predation by protozoa and contamination by other algal species.

12. KEY LIMITATION FOR BIOMASS PRODUCTIVITY IN CULTURING SYSTEM

Large scale microalgal production has a number of challenges that need to be overcome in order to make it commercially viable. These include strain selection, maintaining culture integrity, photosynthetic activity, and gaseous exchange (Brennan & Owende, 2010; Christenson & Sims, 2011; Jorquera *et.al.* 2010). Open ponds are able to culture only certain species of microalgae (Richmond, 2004). Algae that grow under extreme conditions (high pH, nutrient level, etc.)

provide a competitive advantage thus limiting contamination by other microalgae. Contamination is however inevitable and requires constant propagation of seed culture in order to keep the culture of choice as dominant (Christenson & Sims, 2011; Day *et.al.* 2012). Contamination by non-target microalgae is only regarded as problematic should the contaminating species not have a desired trait, have a negative impact on the culture or be capable of outgrowing the species of choice. Increased control of the growth environment is can effectively reduce contamination but increases the cost. Biofouling becomes a possibility if the microalgae adhere to the walls of the bioreactor. This effectively increases shading thereby reducing productivity. Biofouling can also impede culture flow, requiring more energy and thus increasing the productivity (Day *et.al.* 2012).

Supply of photosynthetically active radiation (PAR) becomes a limiting factor in dense cultures in both open and closed systems thus reducing productivity (Christenson & Sims, 2011). Supply of carbon dioxide is essential for the prevention of carbon limitation. Despite ambient air containing sufficient CO_2 for microalgae growth, CO_2 needs to be in solutions for uptake. Less than 10% of the CO_2 resources are available to the algae for uptake. Bubbling of air is not an effective delivery system for open ponds due to short residence time (Mata *et.al.* 2010). Optimisation of bubbling technology remains an engineering challenge. Removal of oxygen is imperative for the prevention photooxidative stress in photobioreactors. Oxygen above atmospheric concentration inhibits photosynthesis. This problem is usually remedied by sparging of air through the reactor or a section thereof in order to strip excess oxygen. This increases energy consumption and thus cost (Christenson & Sims, 2011).

13. LARGE SCALE BIOMASS PRODUCTION

Microalgal biomass production at large scale is almost exclusively done using open raceway ponds in the batch mode (Viswanath *et.al.* 2010; Radman *et.al.* 2007). It must be noted that currently large scale cultivation of microalgae is carried out for products other than biofuels. Cooney et.al. 2011 undertook a case study whereby they suggested that cultivation should be carried out on a continuous basis. Closed systems are more likely to be run as continuous systems due to higher efficiency and significantly lower amounts of contamination of undesirable algae and other organisms. The use of raceway ponds is however considered to be more viable for cultivation of microalgae due to a better net energy ratio when compared to closed systems (Jorquera *et.al.* 2010). Efficient open raceway pond designs typically consist of independent closed-loop systems. Artificial systems equipped with a paddle wheel are used to generate more simplified circulation by which flow is directed around bends by baffles placed in the flow channel to ensure desired mixing (Greenwell *et.al.* 2009). The main advantages of large scale biomass production using the open raceway ponds are (1) simplicity and low costs, (2) use of cheap and readily available substrate alternatives such as domestic municipal wastewater streams, (3) reduced capital costs and (4) large tracks of marginal land not suitable for agricultural purposes can be used without compromising food security (singh & Gu, 2010).

The optimization of operational parameters for large scale biomass production is technically challenging and is one of the major drawbacks of this microalgal cultivation method at this scale. Additionally, raceway pond configuration and operating procedures are extremely important for algal cultivation but have not yet been optimized for many microalgal species that have been evaluated for oil production (Rodolfi *et.al.* 2009; Greenwell *et.al.* 2009). The overall costs involved in large scale biomass production depend on prevailing economic conditions in the local market (Grima *et.al.* 2003). The design of the open raceway pond is critical for increased growth rates and consequently high biomass yield. The cascading open raceway ponds are potentially valuable since there is nutrient limitation at the end of the growth cycle and therefore increased lipid yield. The integrated use of PBRs and open raceways is an efficient method of production of large inoculums thus enabling short cultivation period by maximum efficiency to utilize light in outdoor raceways, in this manner decreasing opportunities for adverse events (Park *et.al.* 2011; Greenwell *et.al.* 2009).

14. USE OF WASTEWATER

14.1. Microalgal nutrition

The combination of CO_2 fixation from flue gas and nutrient removal from wastewater may provide a very promising alternative to current CO_2 capture strategies; it is also another important environmental benefit of these microorganisms. Microalgae contain higher nitrogen and phosphorus contents, approximately 10-11%, respectively, on a dry weight basis (Converti *et.al.* 2006; Sawayama *et.al.* 1995). Heavy metals from wastewater have been removed by microalgae even though could not compete commercially with ion exchange resins (Wilde & Benemann, 1993). The use of microalgae has also attracted attention because microalgae have the ability to remove both CO_2 and NO_x during their growth (Jin *et.al.* 2008). Chinnasamy *et.al.* (2010) cultivated native mixotrophic algal strains (*Chlamydomonas globosa*, *Chlorella minutissima* and *Scenedesmus*

bijuga) in untreated wastewater of carpet industry, using raceways, vertical reactors and polybags. In all bioreactors, a gas stream with 5–6% of CO_2 was supplied. Biomass productivity was 21.1 g/m^2 /d for polybags, 8.1 g/m^2 /d for vertical tank reactors and 5.9 g/m^2 /d for raceways. Jacob-Lopes *et.al.* (2010) evaluated the global rates of CO_2 fixation by cyanobacteria A. *microscopica Nägeli* in refinery wastewater. Wang *et.al.* (2010) concluded that green algae *Chlorella sp*. consumed two primary nitrogen nutrient i.e. ammonium or nitrate available in the wastewater samples.

Arbib *et.al.* (2012, 2013) studied the algal growth rate and nutrient removal along with carbon dioxide biofixation using *S. obliquus* and *Chlorella stigmatophor*. These species were cultivated in urban wastewater at different nitrogen and phosphorus ratios, ranging from 1:1 to 35:1. These authors found that the nitrogen to phosphorus ratios ranging between 9 and 13 (263 and 322 mg/L d respectively) are very important to achieve optimum batch biomass productivity. Renuka *et.al.* (2013) worked with different microalgae groups. Their findings showed highest dry cell weight (0.97 mg/L) using *Calthrix sp.* with 57–58% NO_3-N, 44-91% PO_4-P removal from sewage wastewater.

A recent study characterized a Chlorella species called *Chlorella minutissima* which was identified in wastewater treatment oxidation ponds in India (Bhatnagar *et.al.* 2010). *C. minutissima* was able to grow well in high concentrations of raw sewage and dominated the subsequent pond stages in the oxidation pond system. Analysis has found that this species can grow heterotrophically in the dark, and mixotrophically in the light utilizing a variety of organic carbon substrates, over a wide pH range. Furthermore, *C. minutissima* can utilize either ammonia or nitrate as an N source. The growth of these algae was shown to be highest under mixotrophic (photoheterotrophic) conditions with biomass productivity of 379 mg/L after 10 days of growth compared to biomass of 73.03 mg/L under photoautotrophic conditions (Wang *et.al.* 2010). *C. minutissima* could, therefore, be a good candidate for high biomass productivity in a wastewater high-rate pond system.

15. PROCESS IMPROVEMENT AND APPLICATION

Over the past two decades, microalgae-based CO_2 fixation, biomass production and its energy utilization have made great progress in both bench-scale scientific research and pilot-scale application (Chisti & Yan, 2011; Chisti, 2010). Currently, more than 50 institutions in the world are committing to commercialization of microalgal technology and products. Details of the startup companies are available in Ref. (Chisti *et.al* 2013; Bahadar & Khan, 2013). They are distributed in the America (66%), Europe (14%), Asia (16%) and others (4%). Volumes and sizes of some photobioreactors (PBRs) for laboratory-scale microalgal-CO_2 fixation and biomass production. The features (pros and cons) of PBRs for large-scale industrial application were summarized and compared according to their structure and technical-economic performance (Kunjapur & Eldridge, 2010; Bahadar & Khan, 2013; Ho *et.al.* 2011). Usually, the open microalgal cultivation includes shallow, mixed and raceway ponds. They have the advantages of extremely simple construction, low-cost operation and easy maintenance. The open ponds are designed as 0.25 m in width and 0.2-0.5 ha in area for commercial microalgae production (Slade & Bauen, 2013; Leite *et.al.* 2013). However, due to the limitation of light penetration they are unable to be designed with large depth, usually 0.15-0.35 m and maximum 0.4 m in depth in order to ensure the light exposure to microalgal cells.

Another kind of high rate pilot-scale microalgae production is closed cultivation, including cultivation using tubular, bubble column and air-lift, and flat plate PBRs. No matter what kind of design, the improvements of process parameter for CO_2 fixation and biomass production are mainly focused on physicochemical parameters, e.g., light exposure and nutrition conditions, and hydrodynamic parameters including mixing and mass transfer by increasing the gas-liquid contact area and retention time, although there is still controversies in the economy and practicality when they are scaled up for commercial use (Mirón *et.al.* 1997). Specifically, for the tubular PBRs, the diameter was designed to be about 5 cm for small scale and 10-20 cm for large scale. As expected, decreased diameter and right position (e.g., horizontal or vertical position) help improve the light exposure (Molina *et.al.* 2001). For the purpose of high concentration culture, tubular PBRs need to be scaled-up by means of increasing the tube length and diameter. However, increase of length may give rise to the nonuniformity of CO_2 mass transfer and accumulation of dissolved oxygen, and increase of diameter results in an adverse effect on the light characteristics (Tababa *et.al.* 2012). In comparison, using multiple parallel-tube configurations and increasing the tube unit number without increasing diameter may be more acceptable measures to improve light exposure and mass transfer. Compared with tubular PBRs, PBRs using bubble column design were considered to be competitive in technical economic performance. Bubble column PBRs can be designed as more than 2-5 m in height and 50 cm in sectional dimension with rounded or rectangular

cross-sections. A vertical orientation is helpful to save land area and reduce energy consumption, making it easy to scale-up. Additionally, it has a wide adaptability to light intensity and superficial gas velocity, making it easy to operate. Given the physicochemical parameters, improvement of key operating parameters including appropriate increase of gas hold-up and decrease of bubble diameter, are in favor of enhancing their turbulence and mass transfer performance in gas (CO_2)-liquid (culture medium)-solid (microalgae cell). In practice, bubble columns can also be designed as multistage or series connection to obtain high CO_2 fixation and biomass productivity. As other vertical PBRs, air-lift PBRs are also considered to have an improvement on gas–liquid mixture and light/dark cycle. However, the potential risk in microalgal cell damage due to high shear effect should be avoided. Flat panel was considered as another kind of closed microalgae cultivation system for large scale application. They are usually featured with large surface area and vertically suspended orientation, which effectively increase the surface area illuminated by both direct and diffuse light and provide structural support and even temperature control to optimize microalgal growth (Tredici & Zittelli, 1998; Zhang *et.al.* 2001; Barbosa *et.al.* 2005; Janssen *et.al.* 2003). CO_2 fixation and biomass production can be improved using high aeration rate to accomplish turbulence mixing, CO_2 mass transfer and removal of excess oxygen in the culture medium (Sierra *et.al.* 2008). However, this configuration still would be challenging due to the high stress to microalgal cell and high operating cost. In addition, some other else special PBRs were also used in practice, e.g., a tower PBR is able to achieve CO_2 fixation and biomass production from combustion flue gas (Yang *et.al.* 2012). This structure increases the gas-liquid contact area and retention time using multi-layer design and keeps constant light intensity using a built-in light source.

Conclusion

Phototrophic carbon dioxide (CO_2) fixation along microalgae fast growing strains is very promising alternative to conventional carbon sequestration approach because it convert CO2 into microalgal biomass. The concept of coupling algae form with coal fired power plant offers a sophisticated approach for CO_2 recycling from coal combustion into renewable biofuel. An additional economic incentives can be gained by combining microalgae carbon fixation ability with wastewater treatment. As nitrogen, phosphorous and metal from waste water are utilized as nutrients for algal biomass production, without using freshwater. Further detailed studies are need to be conducted for see the behavior of metals from flue gas after introducing it into the culture media. For researcher, still lots of application niches need to be explored such as enhanced removal of carbon and sulphur compounds, production of catalysts for environmental technology, enhanced (bio) gas production, enhanced biomass composition and availability and culture of extremophiles.

REFERENCES

[1]. Alie, C.; Backham, L.; Croiset, E.; Douglas, P. L. (2005): Simulation of CO_2 capture using MEA scrubbing: a flowsheet decomposition method. *Energy conversion and management*, **46**(3), pp. 475-487.

[2]. Arbib, Z.; Ruiz, J.; Alvarez, P.; Garrido, C.; Barragan, J.; Perales, J. A. (2012): Chlorella stigmatophora for urban wastewater nutrient removal and CO_2 abatement. *International journal of phytoremediation*, **14**(7), pp. 714-725.

[3]. Arbib, Z.; Ruiz, J.; Álvarez-Díaz, P.; Garrido-Pérez, C.; Barragan, J.; Perales, J. A. (2013): Photobiotreatment: influence of nitrogen and phosphorus ratio in wastewater on growth kinetics of Scenedesmus obliquus. *International journal of phytoremediation*, **15**(8), pp. 774-788.

[4]. Bahadar, A.; Khan, M. B. (2013): Progress in energy from microalgae: a review. *Renewable and Sustainable Energy Reviews*, **27**, pp. 128-148.

[5]. Barbosa, M. J. G. V. (2003): Microalgal photobioreactors: Scale-up and optimization. *The Netherlands: Wageningen University*, *168*.

[6]. Barbosa, M. J.; Zijffers, J. W.; Nisworo, A.; Vaes, W.; van Schoonhoven, J.; Wijffels, R. H. (2005): Optimization of biomass, vitamins, and carotenoid yield on light energy in a flat-panel reactor using the A-stat technique. *Biotechnology and bioengineering*, **89**(2), pp. 233-242.

[7]. Benemann, J. R. (1993): Utilization of carbon dioxide from fossil fuel-burning power plants with biological systems. *Energy conversion and management*, **34**(9), pp. 999-1004.

[8]. Bhatnagar, A.; Bhatnagar, M.; Chinnasamy, S.; Das, K. C. (2010): Chlorella minutissima—a promising fuel alga for cultivation in municipal wastewaters. *Applied biochemistry and biotechnology*, **161**(1-8), pp. 523-536.

[9]. Bhatnagar, M.; Bhatnagar, A. (2000): Algal and cyanobacterial responses to fluoride. *Fluoride*, **33**(2), pp. 55-65.

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

[11]. Brown, L. M. (1996): Uptake of carbon dioxide from flue gas by microalgae. *Energy Conversion and Management*, **37**(6), pp. 1363-1367.

[12]. Campbell, P. K.; Beer, T., Batten, D. (2011): Life cycle assessment of biodiesel production from microalgae in ponds. *Bioresource technology*, **102**(1), pp. 50-56.

[13]. Carlozzi, P. (2003): Dilution of solar radiation through "culture" lamination in photobioreactor rows facing south–north: a way to improve the efficiency of light utilization by cyanobacteria (Arthrospira platensis). *Biotechnology and bioengineering*, **81**(3), pp. 305-315.

[14]. Carvalho, A. P.; Malcata, F. X. (2001): Transfer of Carbon Dioxide within Cultures of Microalgae: Plain Bubbling versus Hollow-Fiber Modules. *Biotechnology progress*, **17**(2), pp. 265-272.

[15]. Carvalho, A. P.; Meireles, L. A.; Malcata, F. X. (2006): Microalgal reactors: a review of enclosed system designs and performances. *Biotechnology progress*, **22**(6), pp. 1490-1506.

[16]. Chae, S. R.; Hwang, E. J.; Shin, H. S. (2006): Single cell protein production of Euglena gracilis and carbon dioxide fixation in an innovative photo-bioreactor. *Bioresource technology*, **97**(2), pp. 322-329.

[17]. Chalmers, J. J. (1994): Cells and bubbles in sparged bioreactors. *Cytotechnology*, **15**(1-3), pp. 311-320.

[18]. Chen, C. Y.; Saratale, G. D.; Lee, C. M.; Chen, P. C.; Chang, J. S. (2008): Phototrophic hydrogen production in photobioreactors coupled with solar-energy-excited optical fibers. *International Journal of Hydrogen Energy*, **33**(23), pp. 6886-6895.

[19]. Chen, C. Y.; Yeh, K. L.; Su, H. M.; Lo, Y. C.; Chen, W. M.; Chang, J. S. (2010): vulgaris isolate. *Biotechnology progress*, **26**(3), pp. 679-686.

[20]. 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), pp. 324-329.

[21]. Chinnasamy, S.; Bhatnagar, A.; Claxton, R.; Das, K. C. (2010): Biomass and bioenergy production potential of microalgae consortium in open and closed bioreactors using untreated carpet industry effluent as growth medium. *Bioresource technology*, **101**(17), pp. 6751-6760.

[22]. Chisti, Y. (2007): Biodiesel from microalgae. *Biotechnology advances*, **25**(3), pp. 294-306.

[23]. Chisti, Y. (2010): Fuels from microalgae. *Biofuels*, **1**(2), pp. 233-235.

[24]. Chisti, Y.; Yan, J. (2011): Energy from algae: Current status and future trends: Algal biofuels–A status report. *Applied Energy*, **88**(10), pp. 3277-3279.

[25]. 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), pp. 3389-3396.

[26]. Chiu, S. Y.; Kao, C. Y.; Tsai, M. T.; Ong, S. C.; Chen, C. H.; Lin, C. S. (2009): Lipid accumulation and CO 2 utilization of Nannochloropsis oculata in response to CO 2 aeration. *Bioresource technology*, **100**(2), pp. 833-838.

[27]. Christenson, L.; Sims, R. (2011): Production and harvesting of microalgae for wastewater treatment, biofuels, and bioproducts. *Biotechnology advances*, **29**(6), pp. 686-702.

[28]. Converti, A.; Lodi, A.; Del Borghi, A.; Solisio, C. (2006): Cultivation of Spirulina platensis in a combined airlift-tubular reactor system. *Biochemical Engineering Journal*, **32**(1), pp. 13-18.

[29]. Cooney, M. J.; Young, G.; Pate, R. (2011): Bio-oil from photosynthetic microalgae: case study. *Bioresource technology*, **102**(1), pp. 166-177.

[30]. Costa, J. A. V.; Colla, L. M.; Duarte Filho, P. F. (2004): Improving Spirulina platensis biomass yield using a fed-batch process. *Bioresource Technology*, **92**(3), pp. 237-241.

[31]. Dasgupta, C. N.; Gilbert, J. J.; Lindblad, P.; Heidorn, T.; Borgvang, S. A.; Skjanes, K.; Das, D. (2010): Recent trends on the development of photobiological processes and photobioreactors for the improvement of hydrogen production. *International journal of hydrogen energy*, **35**(19), pp. 10218-10238.

[32]. Davis, R.; Aden, A.; Pienkos, P. T. (2011): Techno-economic analysis of autotrophic microalgae for fuel production. *Applied Energy*, **88**(10), pp. 3524-3531.

[33]. Day, J. G.; Slocombe, S. P.; Stanley, M. S. (2012): Overcoming biological constraints to enable the exploitation of microalgae for biofuels. *Bioresource Technology*, **109**, pp. 245-251.

[34]. De Castro, M. L.; Garcıa-Ayuso, L. E. (1998): Soxhlet extraction of solid materials: an outdated technique with a promising innovative future. *Analytica chimica acta*, **369**(1), pp. 1-10.

[35]. De Morais, M. G.; Costa, J. A. V. (2007a): Biofixation of carbon dioxide by Spirulina sp. and Scenedesmus obliquus cultivated in a three-stage serial tubular photobioreactor. *Journal of Biotechnology*, **129**(3), pp. 439-445.

[36]. De Morais, M. G.; Costa, J. A. V. (2007b): Carbon dioxide fixation by Chlorella kessleri, C. vulgaris, Scenedesmus obliquus and Spirulina sp. cultivated in flasks and vertical tubular photobioreactors. *Biotechnology letters*, **29**(9), pp. 1349-1352.

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

[38]. Demirbas, A. (2011): Competitive liquid biofuels from biomass. *Applied Energy*, **88**(1), pp. 17-28.

[39]. Doucha, J.; Lívanský, K. (2009): Outdoor open thin-layer microalgal photobioreactor: potential productivity. *Journal of applied phycology*, **21**(1), pp. 111-117.

[40]. Doucha, J.; Straka, F.; Lívanský, 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), pp. 403-412.

[41]. Dreybrodt, W.; Eisenlohr, L.; Madry, B., Ringer, S. (1997): Precipitation kinetics of calcite in the system $CaCO_3$ H_2O $C0_2$: The conversion to CO_2 by the slow process H++ HCO_3−⟶ CO_2+ H_2O as a rate limiting step. *Geochimica et Cosmochimica Acta*, **61**(18), pp. 3897-3904.

[42]. EPA (2011): Inventory of U.S. greenhouse gas emissions and sinks 1990–2009, U.S. Environmental Protection Agency.

[43]. EPA (1999): Nitrogen oxides (NO_x), why and how they are controlled. North Carolina: United States Environmental Protection Agency, Clean Air Technology Center [Nov. , Report No: EPA-456/F-99-006a].

[44]. Fan, L. H.; Zhang, Y. T.; Zhang, L.; Chen, H. L. (2008): Evaluation of a membrane-sparged helical tubular photobioreactor for carbon dioxide biofixation by Chlorella vulgaris. *Journal of Membrane Science*, **325**(1), pp. 336-345.

[45]. Giavarini, C.; Maccioni, F.; Santarelli, M. L. (2010): CO2 sequestration from coal fired power plants. *Fuel*, **89**(3), pp. 623-628.

[46]. Giordano, M.; Beardall, J.; Raven, J. A. (2005): CO2 concentrating mechanisms in algae: mechanisms, environmental modulation, and evolution. *Annu. Rev. Plant Biol.*, **56**, pp. 99-131.

[47]. Gouveia, L.; Marques, A. E.; da Silva, T. L.; Reis, A. (2009): Neochloris oleabundans UTEX# 1185: a suitable renewable lipid source for biofuel production. *Journal of industrial microbiology & biotechnology*, **36**(6), pp. 821-826.

[48]. Greenwell, H. C.; Laurens, L. M. L.; Shields, R. J.; Lovitt, R. W.; Flynn, K. J. (2009): Placing microalgae on the biofuels priority list: a review of the technological challenges. *Journal of the Royal Society Interface*, rsif20090322.

[49]. Grima, E. M.; Belarbi, E. H.; Fernández, F. A.; Medina, A. R.; Chisti, Y. (2003): Recovery of microalgal biomass and metabolites: process options and economics. *Biotechnology advances*, **20**(7), pp. 491-515.

[50]. Hall, D. O.; Acién Fernández, F. G.; Guerrero, E. C.; Rao, K. K.; Grima, E. M. (2003): Outdoor helical tubular photobioreactors for microalgal production: Modeling of fluid-dynamics and mass transfer and assessment of biomass productivity. *Biotechnology and bioengineering*, **82**(1), pp. 62-73.

[51]. Hauck, J. T.; Scierka, S. J.; Perry, M. B. (1996): Effects of simulated flue gas on growth of microalgae. *Preprints of Papers, American Chemical Society, Division of Fuel Chemistry*, *41*(CONF-960807--).

[52]. Ho, S. H.; Chen, C. Y.; Chang, J. S. (2012): Effect of light intensity and nitrogen starvation on CO2 fixation and lipid/carbohydrate production of an indigenous microalga Scenedesmus obliquus CNW-N. *Bioresource technology*, **113**, pp. 244-252.

[53]. 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), pp. 189-198.

[54]. Ho, S. H.; Chen, W. M.; Chang, J. S. (2010): Scenedesmus obliquus CNW-N as a potential candidate for CO 2 mitigation and biodiesel production. *Bioresource Technology*, **101**(22), pp. 8725-8730.

[55]. Housecroft, C.E.; Sharpe, A.G. (2005): Inorganic chemistry. 2nd Edition. Essex (Egland): Pearson Education Limited.

[56]. Hsueh, H. T.; Chu, H.; Yu, S. T. (2007): A batch study on the bio-fixation of carbon dioxide in the absorbed solution from a chemical wet scrubber by hot spring and marine algae. *Chemosphere*, **66**(5), pp. 878-886.

[57]. Hu, Q.; Kurano, N.; Kawachi, M.; Iwasaki, I.; Miyachi, S. (1998): Ultrahigh-cell-density culture of a marine green alga Chlorococcum littorale in a flat-plate photobioreactor. *Applied Microbiology and Biotechnology*, **49**(6), pp. 655-662.

[58]. Huntley, M. E.; Redalje, D. G. (2007): CO2 mitigation and renewable oil from photosynthetic microbes: a new appraisal. *Mitigation and adaptation strategies for global change*, **12**(4), pp. 573-608.

[59]. Illman, A. M.; Scragg, A. H.; Shales, S. W. (2000): Increase in Chlorella strains calorific values when grown in low nitrogen medium. *Enzyme and microbial technology*, **27**(8), pp. 631-635.

[60]. Iwasaki, I.; Hu, Q.; Kurano, N.; Miyachi, S. (1998): Effect of extremely high-CO 2 stress on energy distribution between photosystem I and photosystem II in a 'high-CO 2'tolerant green alga, Chlorococcum littorale and the intolerant green alga Stichococcus bacillaris. *Journal of Photochemistry and Photobiology B: Biology*, **44**(3), pp. 184-190.

[61]. Jacob-Lopes, E.; Revah, S.; Hernández, S.; Shirai, K.; Franco, T. T. (2009a): Development of operational strategies to remove carbon dioxide in photobioreactors. *Chemical Engineering Journal*, **153**(1), pp. 120-126.

[62]. Jacob-Lopes, E.; Scoparo, C. H. G.; Queiroz, M. I.; Franco, T. T. (2010): Biotransformations of carbon dioxide in photobioreactors. *Energy Conversion and Management*, **51**(5), pp. 894-900.

[63]. Janssen, A. E.; Sjursnes, B. J.; Vakurov, A. V.; Halling, P. J. (1999): Kinetics of lipase-catalyzed esterification in organic media: correct model and solvent effects on parameters. *Enzyme and microbial technology*, **24**(8), pp. 463-470.

[64]. Jaworek, A.; Krupa, A.; Czech, T. (2007): Modern electrostatic devices and methods for exhaust gas cleaning: A brief review. *Journal of Electrostatics*, **65**(3), pp. 133-155.

[65]. Jin, H. F.; Lim, B. R.; Lee, K. (2006): Influence of nitrate feeding on carbon dioxide fixation by microalgae. *Journal of Environmental Science and Health Part A*, **41**(12), pp. 2813-2824.

[66]. Jin, H. F.; Santiago, D. E.; Park, J.; Lee, K. (2008): Enhancement of nitric oxide solubility using Fe (II) EDTA and its removal by green algae Scenedesmus sp. *Biotechnology and Bioprocess Engineering*, **13**(1), pp. 48-52.

[67]. Jin, Y.; Veiga, M. C.; Kennes, C. (2005): Bioprocesses for the removal of nitrogen oxides from polluted air. *Journal of chemical technology and biotechnology*, **80**(5), pp. 483-494.

[68]. Jorquera, O.; Kiperstok, A.; Sales, E. A.; Embiruçu, M.; Ghirardi, M. L. (2010): Comparative energy life-cycle analyses of microalgal biomass production in open ponds and photobioreactors. *Bioresource technology*, **101**(4), pp. 1406-1413.

[69]. Keffer, J. E.; Kleinheinz, G. T. (2002): Use of Chlorella vulgaris for CO2 mitigation in a photobioreactor. *Journal of Industrial Microbiology and Biotechnology*, **29**(5), pp. 275-280.

[70]. Kessels, J.; Hennessy, W. (2004): The impact of emissions trading on the coal industry. *New Zealand: CRL Energy International Energy Agency, Clean Coal Centre*.

[71]. Kitajima, Y.; El-Shishtawy, R. M.; Ueno, Y.; Otsuka, S.; Miyake, J.; Morimoto, M. (1998): Analysis of compensation point of light using plane-type photosynthetic bioreactor. In *BioHydrogen* (pp. 359-367). Springer Us.

[72]. Kumar, A.; Ergas, S.; Yuan, X.; Sahu, A.; Zhang, Q.; Dewulf, J.; ... Van Langenhove, H. (2010): Enhanced CO 2 fixation and biofuel production via microalgae: recent developments and future directions. *Trends in biotechnology*, **28**(7), pp. 371-380.

[73]. Kunjapur, A. M.; Eldridge, R. B. (2010): Photobioreactor design for commercial biofuel production from microalgae. *Industrial & engineering chemistry research*, **49**(8), pp. 3516-3526.

[74]. Kurano, N.; Ikemoto, H.; Miyashita, H.; Hasegawa, T.; Hata, H.; Miyachi, S. (1995): Fixation and utilization of carbon dioxide by microalgal photosynthesis. *Energy Conversion and Management*, **36**(6), pp. 689-692.

[75]. Larsson, M.; Larsson, C. M.; Guerrero, M. G. (1985): Photosynthetic nitrogen metabolism in high CO_2 and low CO_2 adapted Scenedesmus. *Journal of experimental botany*, **36**(9), pp. 1373-1386.

[76]. Lee, J. H.; Lee, J. S.; Shin, C. S.; Park, S. C.; Kim, S. W. (2000): Effects of NO and SO2 on growth of highly-CO2-tolerant microalgae. *Journal of microbiology and biotechnology*, **10**(3), pp. 338-343.

[77]. 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), pp. 1-4.

[78]. Leite, G. B.; Abdelaziz, A. E.; Hallenbeck, P. C. (2013): Algal biofuels: challenges and opportunities. *Bioresource technology*, **145**, pp. 134-141.

[79]. Li, F. F.; Yang, Z. H.; Zeng, R.; Yang, G.; Chang, X.; Yan, J. B.; Hou, Y. L. (2011): Microalgae capture of CO2 from actual flue gas discharged from a combustion chamber. *Industrial & Engineering Chemistry Research*, **50**(10), pp. 6496-6502.

[80]. Li, M.; Hu, C.; Zhu, Q.; Kong, Z.; Liu, Z. (2007): Outdoor mass culture of the marine microalga Pavlova viridis (Prymnesiophyceae) for production of eicosapentaenoic acid (EPA). *Cryptogamie. Algologie*, **28**(4), pp. 397-410.

[81]. Liu, Q.; Liu, Z. (2013): Carbon supported vanadia for multi-pollutants removal from flue gas. *Fuel*, **108**, pp. 149-158.

[82]. Liu, R.; Liu, Y.; Liu, C. Z. (2013): Development of an efficient CFD-simulation method to optimize the structure parameters of an airlift sonobioreactor. *Chemical Engineering Research and Design*, **91**(2), pp. 211-220.

[83]. Lockhart, H. B.; Blakeley, R. V. (1975): Aerobic photodegradation of iron (III)-(ethylenedinitrilo) tetraacetate (ferric EDTA). Implications for natural waters. *Environmental Science & Technology*, **9**(12), pp. 1035-1038.

[84]. López, C. G.; Fernández, F. A.; Sevilla, J. F.; Fernández, J. S.; García, M. C.; Grima, E. M. (2009): Utilization of the cyanobacteria Anabaena sp. ATCC 33047 in CO 2 removal processes. *Bioresource technology*, **100**(23), pp. 5904-5910.

[85]. Maeda, K.; Owada, M.; Kimura, N.; Omata, K.; Karube, I. (1995): CO 2 fixation from the flue gas on coal-fired thermal power plant by microalgae. *Energy Conversion and Management*, **36**(6), pp. 717-720.

[86]. Markl, H. (1977): CO2 transport and photosynthetic productivity of a continuous culture of algae. *Biotechnology and Bioengineering*, **19**(12), pp. 1851-1862.

[87]. 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), pp. 217-232.

[88]. Matsumoto, H.; Hamasaki, A.; Sioji, N.; Ikuta, Y. (1997): Influence of CO2, SO2 and NO in Flue Gas on Microalgae Productivity. *Journal of chemical engineering of Japan*, **30**(4), pp. 620-624.

[89]. Meldon, J. H. (2011): Amine screening for flue gas CO2 capture at coal-fired power plants: Should the heat of desorption be high, low or in between? *Current Opinion in Chemical Engineering*, **1**(1), pp. 55-63.

[90]. Miyake, J.; Wakayama, T.; Schnackenberg, J.; Arai, T.; Asada, Y. (1999): Simulation of the daily sunlight illumination pattern for bacterial photo-hydrogen production. *Journal of bioscience and bioengineering*, **88**(6), pp. 659-663.

[91]. Moazami-Goudarzi, M.; Colman, B. (2012): Changes in carbon uptake mechanisms in two green marine algae by reduced seawater pH. *Journal of Experimental Marine Biology and Ecology*, **413**, pp. 94-99.

[92]. Molina, E.; Fernández, J.; Acién, F. G.; Chisti, Y. (2001): Tubular photobioreactor design for algal cultures. *Journal of biotechnology*, **92**(2), pp. 113-131.

[93]. Murakami, M.; Ikenouchi, M. (1997): The biological CO2 fixation and utilization project by rite (2)—Screening and breeding of microalgae with high capability in fixing CO2. *energy conversion and Management*, **38**, pp. S493-S497.

[94]. Nagase, H.; Eguchi, K.; Yoshihara, K. I.; Hirata, K.; Miyamoto, K. (1998): Improvement of microalgal NOx removal in bubble column and airlift reactors. *Journal of fermentation and bioengineering*, **86**(4), pp. 421-423.

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

[96]. Nagase, H.; Yoshihara, K. I.; Eguchi, K.; Yokota, Y.; Matsui, R.; Hirata, K.; Miyamoto, K. (1997): Characteristics of biological NOx removal from flue gas in a Dunaliella tertiolecta culture system. *Journal of fermentation and bioengineering*, **83**(5), pp. 461-465.

[97]. Nedbal, L.; Červený, J.; Keren, N.; Kaplan, A. (2010): Experimental validation of a nonequilibrium model of CO2 fluxes between gas, liquid medium, and algae in a flat-panel photobioreactor. *Journal of industrial microbiology & biotechnology*, **37**(12), pp. 1319-1326.

[98]. Negoro, M.; Shioji, N.; Miyamoto, K.; Micira, Y. (1991): Growth of microalgae in high CO2 gas and effects of SOx and NOx. *Applied biochemistry and biotechnology*, **28**(1), pp. 877-886.

[99]. Ogbonna, J. C.; Tanaka, H. (1998): Cyclic autotrophic/heterotrophic cultivation of photosynthetic cells: a method of achieving continuous cell growth under light/dark cycles. *Bioresource technology*, **65**(1), pp. 65-72.

[100]. Olaizola, M. (2003): Microalgal removal of CO2 from flue gases: changes in medium pH and flue gas composition do not appear to affect the photochemical yield of microalgal cultures. *Biotechnology and Bioprocess Engineering*, **8**(6), pp. 360-367.

[101]. Olaizola, M.; Bridges, T.; Flores, S.; Griswold, L.; Morency, J.; Nakamura, T. (2004): Microalgal removal of CO2 from flue gases: CO2 capture from a coal combustor Third Annual Conference on Carbon Capture and Sequestration. *Alexandria, VA*.

[102]. Ong, S. C.; Kao, C. Y.; Chiu, S. Y.; Tsai, M. T.; Lin, C. S. (2010): Characterization of the thermal-tolerant mutants of Chlorella sp. with high growth rate and application in outdoor

photobioreactor cultivation. *Bioresource technology*, **101**(8), pp. 2880-2883.

[103]. Ota, M.; Kato, Y.; Watanabe, H.; Watanabe, M.; Sato, Y.; Smith, R. L.; Inomata, H. (2009): Fatty acid production from a highly CO 2 tolerant alga, Chlorocuccum littorale, in the presence of inorganic carbon and nitrate. *Bioresource Technology*, **100**(21), pp. 5237-5242.

[104]. Packer, M. (2009): Algal capture of carbon dioxide; biomass generation as a tool for greenhouse gas mitigation with reference to New Zealand energy strategy and policy. *Energy Policy*, **37**(9), pp. 3428-3437.

[105]. Park, J. B. K.; Craggs, R. J.; Shilton, A. N. (2011): Wastewater treatment high rate algal ponds for biofuel production. *Bioresource technology*, **102**(1), pp. 35-42.

[106]. Pronina, N. A.; Rogova, N. B.; Furnadzhieva, S.; Klyachko-Gurvich, G. L.; Semenenko, V. E. (1998): Effect of CO_2 concentrations of the fatty acid composition of lipids in Chlamydomonas reinhardtii Cia-3, a mutant deficient in the CO_2 concentrating mechanisms. Russian Journal of Plant Physiology, **45**: pp. 529-538.

[107]. Pulz, O. (2001): Photobioreactors: production systems for phototrophic microorganisms. *Applied microbiology and biotechnology*, **57**(3), pp. 287-293.

[108]. Radmann, E. M.; Costa, J. A. V. (2008): Lipid content and fatty acids composition variation of microalgae exposed to CO2, SO2 and NO. *Química Nova*, **31**(7), pp. 1609-1612.

[109]. Ramanan, R.; Kannan, K.; Deshkar, A.; Yadav, R.; Chakrabarti, T. (2010): Enhanced algal CO2 sequestration through calcite deposition by Chlorella sp. and Spirulina platensis in a mini-raceway pond. *Bioresource technology*, **101**(8), pp. 2616-2622.

[110]. Renuka, N.; Sood, A.; Ratha, S. K.; Prasanna, R.; Ahluwalia, A. S. (2013): Nutrient sequestration, biomass production by microalgae and phytoremediation of sewage water. *International journal of phytoremediation*, **15**(8), pp. 789-800.

[111]. Richmond A. (2004): Handbook of Microalgal Culture: Biotechnology and Applied Phycology. Oxford: Blackwell Science Ltd.

[112]. Rochelle, G. T. (2009): Amine scrubbing for CO2 capture. *Science*, (325), pp. 1652-4.

[113]. Rodolfi, L.; Chini Zittelli, G.; Bassi, N.; Padovani, G.; Biondi, N.; Bonini, G.; Tredici, M. R. (2009): Microalgae for oil: Strain selection, induction of lipid synthesis and outdoor mass cultivation in a low-cost photobioreactor. *Biotechnology and bioengineering*, **102**(1), pp. 100-112.

[114]. Ryu, H. J.; Oh, K. K.; Kim, Y. S. (2009): Optimization of the influential factors for the improvement of CO 2 utilization efficiency and CO2 mass transfer rate. *Journal of Industrial and engineering chemistry*, **15**(4), pp. 471-475.

[115]. Sakai, N.; Sakamoto, Y.; Kishimoto, N.; Chihara, M.; Karube, I. (1995): Chlorella strains from hot springs tolerant to high temperature and high CO2. *Energy Conversion and Management*, **36**(6), pp. 693-696.

[116]. Sánchez Mirón, A.; Garcia Camacho, F.; Contreras Gomez, A.; Grima, E. M.; Chisti, Y. (2000): Bubble-column and airlift photobioreactors for algal culture. *AIChE Journal*, **46**(9), pp. 1872-1887.

[117]. Santiago, D. E.; Jin, H. F.; Lee, K. (2010): The influence of ferrous-complexed EDTA as a solubilization agent and its auto-regeneration on the removal of nitric oxide gas through the culture of green alga Scenedesmus sp. *Process Biochemistry*, **45**(12), pp. 1949-1953.

[118]. Sato, T.; Usui, S.; Tsuchiya, Y.; Kondo, Y. (2006): Invention of outdoor closed type photobioreactor for microalgae. *Energy conversion and management*, **47**(6), pp. 791-799.

[119]. Sawayama, S.; Inoue, S.; Dote, Y.; Yokoyama, S. Y. (1995): CO2 fixation and oil production through microalga. *Energy Conversion and Management*, **36**(6), pp. 729-731.

[120]. Schenk, P. M.; Thomas-Hall, S. R.; Stephens, E.; Marx, U. C.; Mussgnug, J. H.; Posten, C.; ... Hankamer, B. (2008): Second generation biofuels: high-efficiency microalgae for biodiesel production. *Bioenergy research*, **1**(1), pp. 20-43.

[121]. Scragg, A. H.; Illman, A. M.; Carden, A.; Shales, S. W. (2002): Growth of microalgae with increased calorific values in a tubular bioreactor. *Biomass and Bioenergy*, **23**(1), pp. 67-73.

[122]. SEI. (2005): Emerging energy technologies in Ireland: a focus on carbon capture and Hydrogen. Dublin: Sustainable Energy Ireland.

[123]. Sierra, E.; Acien, F. G.; Fernández, J. M.; García, J. L.; González, C.; Molina, E. (2008): Characterization of a flat plate photobioreactor for the production of microalgae. *Chemical Engineering Journal*, **138**(1), pp. 136-147.

[124]. Singh, J.; Gu, S. (2010): Commercialization potential of microalgae for biofuels production. *Renewable and Sustainable Energy Reviews*, **14**(9), pp. 2596-2610.

[125]. Slade, R.; Bauen, A. (2013): Micro-algae cultivation for biofuels: cost, energy balance, environmental impacts and future prospects. *Biomass and Bioenergy*, **53**, pp. 29-38.

[126]. Smit A. (2011): Personal communication. The Netherlands, Zeist: director Emissiebeurs BA.

[127]. Soletto, D.; Binaghi, L.; Ferrari, L.; Lodi, A.; Carvalho, J. C. M.; Zilli, M., Converti, A. (2008): Effects of carbon dioxide feeding rate and light intensity on the fed-batch pulse-feeding cultivation of Spirulina platensis in helical photobioreactor. *Biochemical Engineering Journal*, **39**(2), pp. 369-375.

[128]. Stepan, D. J.; Shockey, R. E.; Moe, T. A.; Dorn, R. (2002): *Carbon dioxide sequestering using microalgal systems*. University of North Dakota.

[129]. Stephens, E.; Ross, I. L.; Mussgnug, J. H.; Wagner, L. D.; Borowitzka, M. A.; Posten, C.; ... Hankamer, B. (2010): Future prospects of microalgal biofuel production systems. *Trends in plant science*, **15**(10), pp. 554-564.

[130]. Stumm, W.; Morgan, J.J. (1981): Aquatic Chemistry. 2nd ed. New York: John Wiley & Sons.

[131]. Su, Z.; Kang, R.; Shi, S.; Cong, W.; Cai, Z. (2010): Study on the destabilization mixing in the flat plate photobioreactor by means of CFD. *Biomass and bioenergy*, **34**(12), pp. 1879-1884.

[132]. Sung, K. D.; Lee, J. S.; Shin, C. S.; Park, S. C. (1999): Isolation of a new highly CO 2 tolerant fresh water Microalga Chlorella sp. KR-1. *Renewable energy*, **16**(1), pp. 1019-1022.

[133]. Sung, K. D.; Lee, J. S.; Shin, C. S.; Park, S. C.; Choi, M. J. (1999): CO2 fixation by Chlorella sp. KR-1 and its cultural characteristics. *Bioresource technology*, **68**(3), pp. 269-273.

[134]. Tababa, H. G.; Hirabayashi, S.; Inubushi, K. (2012): Media optimization of Parietochloris incisa for arachidonic acid accumulation in an outdoor vertical tubular photobioreactor. *Journal of applied phycology*, **24**(4), pp. 887-895.

[135]. Takagi, M.; Yoshida, T. (2006): Effect of salt concentration on intracellular accumulation of lipids and triacylglyceride in marine microalgae Dunaliella cells. *Journal of bioscience and bioengineering*, **101**(3), pp. 223-226.

[136]. Tang, D.; Han, W.; Li, P.; Miao, X.; Zhong, J. (2011): CO2 biofixation and fatty acid composition of Scenedesmus obliquus and Chlorella pyrenoidosa in response to different CO2 levels. *Bioresource Technology*, **102**(3), pp. 3071-3076.

[137]. Tredici, M. R.; Zittelli, G. C. (1998): Efficiency of sunlight utilization: tubular versus flat photobioreactors. *Biotechnology and bioengineering*, **57**(2), pp. 187-197.

[138]. Tsai, D. D. W.; Ramaraj, R.; Chen, P. H. (2012): Growth condition study of algae function in ecosystem for CO 2 bio-fixation. *Journal of Photochemistry and Photobiology B: Biology*, **107**, pp. 27-34.

[139]. Tsuzuki, M.; Ohnuma, E.; Sato, N.; Takaku, T.; Kawaguchi, A. (1990): Effects of CO2 concentration during growth on fatty acid composition in microalgae. *Plant physiology*, **93**(3), pp. 851-856.

[140]. Ugwu, C. U.; Ogbonna, J. C.; Tanaka, H. (2005): Light/dark cyclic movement of algal culture (Synechocystis aquatilis) in outdoor inclined tubular photobioreactor equipped with static mixers for efficient production of biomass. *Biotechnology letters*, **27**(2), pp. 75-78.

[141]. Van Den Hende, S.; Vervaeren, H.; Desmet, S.; Boon, N. (2011a): Bioflocculation of microalgae and bacteria combined with flue gas to improve sewage treatment. *New biotechnology*, **29**(1), pp. 23-31.

[142]. Van Den Hende, S.; Vervaeren, H.; Saveyn, H.' Maes, G.; Boon, N. (2011b): Microalgal bacterial floc properties are improved by a balanced inorganic/organic carbon ratio. *Biotechnology and bioengineering*, **108**(3), pp. 549-558.

[143]. Vargas, M. A.; Rodriguez, H.; Moreno, J.; Olivares, H.; Del Campo, J. A.; Rivas, J.; Guerrero, M. G. (1998): Biochemical composition and fatty acid content of filamentous nitrogen-fixing cyanobacteria. *Journal of phycology*, **34**(5), pp. 812-817.

[144]. Viswanath, B.; Mutanda, T.; White, S.; Bux, F. (2010): The microalgae–a future source of biodiesel. *Dyn Biochem Process Biotech Mol Biol*, **4**, pp. 37-47.

[145]. Vonshak, A.; Torzillo, G.; Accolla, P.; Tomaselli, L. (1996): Light and oxygen stress in Spirulina platensis (cyanobacteria) grown outdoors in tubular reactors. *Physiologia Plantarum*, **97**(1), pp. 175-179.

[146]. Wang, B.; Li, Y.; Wu, N.; Lan, C. Q. (2008): CO2 bio-mitigation using microalgae. *Applied Microbiology and Biotechnology*, **79**(5), pp. 707-718.

[147]. Wang, L.; Li, Y.; Chen, P.; Min, M.; Chen, Y.; Zhu, J.; Ruan, R. R. (2010): Anaerobic digested dairy manure as a nutrient supplement for cultivation of oil-rich green microalgae Chlorella sp. *Bioresource technology*, **101**(8), pp. 2623-2628.

[148]. Wang, L.; Min, M.; Li, Y.; Chen, P.; Chen, Y.; Liu, Y.; ... Ruan, R. (2010): Cultivation of green algae Chlorella sp. in different wastewaters from municipal wastewater treatment plant. *Applied biochemistry and biotechnology*, **162**(4), pp. 1174-1186.

[149]. Wilde, E. W.; Benemann, J. R. (1993): Bioremoval of heavy metals by the use of microalgae. *Biotechnology Advances*, **11**(4), pp. 781-812.

[150]. XIA, J. R.; GAO, K. S. (2005): Impacts of elevated CO2 concentration on biochemical composition, carbonic anhydrase, and nitrate reductase activity of freshwater green algae. *Journal of integrative plant biology*, **47**(6), pp. 668-675.

[151]. Xiong, W.; Li, X.; Xiang, J.; Wu, Q. (2008): High-density fermentation of microalga Chlorella protothecoides in bioreactor for microbio-diesel production. *Applied Microbiology and Biotechnology*, **78**(1), pp. 29-36.

[152]. Xu, M.; Chen, S.; Liu, G.; Hu, Z. (2003): Pilot study of physiological and morphological acclimation of {sl Scenedesmus armatus} under Extreme--High—CO(2)--Stress. *Wuhan botanical research*, **22**(5), pp. 439-444.

[153]. Yanagi, M.; Watanabe, Y.; Saiki, H. (1995): CO2 fixation by Chlorella sp. HA-1 and its utilization. *energy conversion and Management*, **36**(6), pp. 713-716.

[154]. Yang, S.; Wang, J.; Cong, W.; Cai, Z.; Ouyang, F. (2004): Effects of bisulfite and sulfite on the microalga Botryococcus braunii. *Enzyme and microbial technology*, **35**(1), pp. 46-50.

[155]. 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), pp. S71-S74.

[156]. Yoshihara, K. I.; Nagase, H.; Eguchi, K.; Hirata, K.; Miyamoto, K. (1996): Biological elimination of nitric oxide and carbon dioxide from flue gas by marine microalga NOA-113 cultivated in a long tubular photobioreactor. *Journal of fermentation and bioengineering*, **82**(4), pp. 351-354.

[157]. Yu, G.; Li, Y.; Shen, G.; Wang, W.; Lin, C.; Wu, H.; Chen, Z. (2009): A novel method using CFD to optimize the inner structure parameters of flat photobioreactors. *Journal of Applied Phycology*, **21**(6), pp. 719-727.

[158]. Yue, L.; Chen, W. (2005): Isolation and determination of cultural characteristics of a new highly CO 2 tolerant fresh water microalgae. *energy conversion and Management*, **46**(11), pp. 1868-1876.

[159]. 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**(4), pp. 451-455.

[160]. Yun, Y. S.; Park, J. M.; Yang, J. W. (1996): Enhancement of CO2 tolerance of Chlorella vulgaris by gradual increase of CO2 concentration. *Biotechnology techniques*, **10**(9), pp. 713-716.

[161]. Zamalloa, C.; Vulsteke, E.; Albrecht, J.; Verstraete, W. (2011): The techno-economic potential of renewable energy through the anaerobic digestion of microalgae. *Bioresource technology*, **102**(2), pp. 1149-1158.

[162]. Zeiler, K. G.; Heacox, D. A.; Toon, S. T.; Kadam, K. L.; Brown, L. M. (1995): The use of microalgae for assimilation and utilization of carbon dioxide from fossil fuel-fired power plant flue gas. *Energy Conversion and Management*, **36**(6), pp. 707-712.

[163]. 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), pp. 428-433.