Chapter II

Theoretical Backgrounds and Literature Review

2.1 Global warming and CO_2

2.1.1 Global warming and greenhouse gases

Global warming is an increase in average temperature of the world's atmosphere and oceans. Global warming has generally been known to be a consequence of an increase in concentrations of greenhouse gases resulting from human's activities e.g. fossil fuel combustion, deforestation and electricity generation from power plant. Global average temperature has increased by 0.6°C per year since 1900, and by the end of the twenty-first century, temperature may increase by a drastic figure of around 1.4–5.8°C in total (Pipitone and Bolland, 2009) resulting in the change of weather system, melting ice and also sea level rise. The greenhouse gases like nitrous oxide, methane and especially carbon dioxide are playing crucial role in the world's global warming phenomenon at the present time. The excessive emission of these gases is the major cause of global warming as these gases trap heat in the earth's atmosphere. To decrease the effect of global warming, greenhouse gases must be controlled or diminished from emitting sources. Global warming mitigation is becoming increasingly important as the effects of climate change are becoming apparent all around the world.

2.1.2 CO_2 as greenhouse gas

CO_2 gas is playing a major role in global warming. When CO_2 is released to the atmosphere, it acts like blanket over the planet by trapping long-wave radiation from leaving the Earth's surface and raising the average temperature. The growth rate of atmospheric carbon dioxide (CO_2), the largest human contributor to human-induced climate change, is increasing rapidly. Recent growth of the world economy combined with an increase in its carbon intensity has led to rapid growth in fossil fuel CO_2 emissions. CO_2 is the largest contributor to this effect as it is a long-lived gas and its emission increases each year. From these reasons, international courtesy rules for CO_2 reduction was proposed e.g. Kyoto protocol and EU's carbon credit regulations

2.2 CO_2 removal methods

2.2.1 CO_2 removal via absorption processes

There are several commercial available process technologies which can in principle be used for CO_2 capture from flue gases. However, comparative assessment studies have shown that absorption processes based on chemical solvents are currently the preferred option for post-combustion CO_2 capture (Je et al., 2009; You et al., 2008). At present, absorption processes offer high capture efficiency and selectivity, and lowest energy consumption and costs when compared with other existing post-combustion CO_2 capture system. Absorption processes in post-combustion capture make use of the reversible nature of the chemical reaction of an aqueous alkaline solvent, usually an amine, with an acid or sour gas. The process flow diagram is presented in Figure 2.1. After cooling the flue gas, it is brought into contact with the solvent in an absorber. A blower is required to overcome the pressure through the absorber. At absorber temperatures between 40 and 60°C, CO_2 is bound by chemical solvent in the absorber. The flue gas then undergoes a water wash section to balance water in the system and to remove any solvent droplets or solvent vapor carried over, and then it leaves the absorber. It is possible to reduce CO_2 concentration in the exit gas down to very low values, as a result of the chemical reaction in the solvent but lower exit concentrations tend to increase the height of the absorption vessel. The rich solvent which contains the chemically bound CO_2 is then pumped to the top of stripper (or regeneration of chemical solvent in the stripper at elevated temperatures (100-140 °C) at pressure not very much higher than atmospheric pressure. Heat is supplied to the reboiler to maintain the regeneration conditions. This leads to a thermal energy penalty as a result of heating up the solvent, providing the required desorption heat for removing the chemically bound CO_2 and for steam production which acts as a stripping gas. Steam is recovered in the condenser and fed back to stripper, whereas the CO_2 product leaves the stripper. The lean solvent, containing far less CO_2 is then pumped back to the absorber via the lean-rich heat exchanger and a cooler to bring it down to the absorber temperature level.

Reactions are described below:

$$2\ RNH_2 + CO_2 + H_2O \longleftrightarrow (RNH_3)_2CO_3 \qquad (2.1)$$

$$(RNH_3)_2CO_3 + CO_2 + H_2O \longleftrightarrow 2\ RNH_3HCO_3 \qquad (2.2)$$

$$2\ RNH_2 + CO_2 \longleftrightarrow RNHCOONH_3R \qquad (2.3)$$

$R = C_2H_4OH$ group

The key parameters determining the technical and economic operation of a CO_2 absorption system are

- Flue gas flow rate –The flue gas flow rate will determine the size of the absorber.

- CO_2 content in flue gas –Since flue gas is usually at atmospheric pressure, the partial pressure of CO_2 will be at 3-15 kPa. Under these low CO_2 partial pressure conditions, aqueous amines (chemical solvents) are the most suitable absorption solvents (Kohl and Nielsen, 1997).

- CO_2 removal –In practice, the exact recovery choice will lead to a taller absorption column, higher energy penalties, and hence, increasing cost.

- Solvent flow rate –The solvent flow rate will determine the size of most equipment apart from the absorber. For a given solvent, the flow rate will be fixed by the previous parameters described above and also the chosen CO_2 concentrations within the lean and rich solutions.

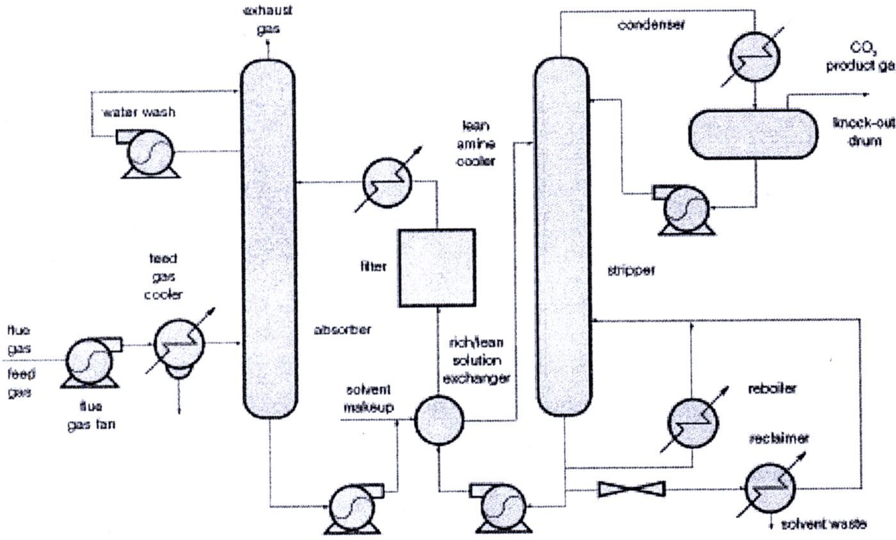

Figure 2.1 Process flow diagram for CO_2 recovery from the flue gas by chemical absorption (Metz et al., 2005)

2.2.2 CO_2 removal via carbonation processes

There are post-combustion systems being proposed that make use of regenerable solid sorbents to remove CO_2 at relatively high temperatures. The use of high temperatures in the CO_2 separation step has the potential to reduce efficiency penalties with respect to wet-absorption methods. In principle, they all follow the scheme shown in Figure 2.2, where the combustion flue gas is put in contact with the sorbent in a suitable reactor to allow the gas-solid reaction of CO_2 with the sorbent (usually the carbonation of metal oxide). The solid can be easily separated from gas stream and sent for regeneration in a different reactor. One key component for the development of these systems is obviously the sorbent itself with good CO_2 absorption capacity and chemical and mechanical stability for long period of operation in repeated cycle. Solid sorbents investigated for large-scale CO_2 capture purposes are sodium and potassium dioxides and carbonates (to produce bicarbonate). They are usually supported on a solid substrate (Hoffman et al., 2002; Green et al., 2002). Also, high temperature Li-based and CaO-based sorbents are suitable candidates. The use of lithium-containing compounds (lithium, lithium-zirconia and lithium-silica oxides) in a carbonation-calcination cycle, was first investigated in Japan (Nakagawa and Ohashi, 1998). They reported that the performance of these sorbents was very good, with very high reactivity in wide range of temperatures below 700°C, rapid regeneration at higher temperatures and durability in repeated capture-regeneration cycles. The use of CaO as a regenerable CO_2 sorbent has been proposed in several processes in the 19th century. The carbonation reaction of CaO to separate CO_2 from hot gases (T> 600 °C) is very fast and the regeneration of the sorbent by calcining the CaCO3 into CaO and pure CO_2 is favoured at T>900 °C (at a partial pressure of CO_2 of 0.1 MPa). The basic separation principle using this carbonation-calcination cycle for post-combustion system was first proposed by Shimizu et al. (1999). The effective capture of CO_2 by CaO has been demonstrated in a small pilot fluidized bed (Abanades et al., 2004a). Other combustion cycles incorporating capture of CO_2 with CaO that might not need O_2 are being developed, including one that works at high pressures with simultaneous capture of CO_2 and SO_2 (Wang et al., 2004). One weak point in all these processes is that natural sorbents (limestones and dolomites) deactivate rapidly, and a large make-up flow of sorbent (of the order of the mass flow of fuel entering the plant) is required to maintain the activity in the capture-regeneration loop (Abanades et al., 2004b). Although the deactivated sorbent may find application in the cement industry and the sorbent cost is low, many ranges of method to enhance the activity of Ca-based CO_2 sorbents are being pursued by several research around the world. To improve CO_2 absorption mass transfer and to inhibit corrosion, proprietary activators and inhibitors are added. These systems known as "activated hot potassium carbonate" (AHPC) systems including the original Benfield activator, DEA (Diethanolamine) show that the full capacity of the "hot pot" family of processes requires a feed CO_2 partial pressure of about 700 kPa.

Reactions are described below:

$$CaO + CO_2 \longleftrightarrow CaCO_3 \qquad (2.4)$$

$$CaCO_3 + CO_2 + H_2O \longleftrightarrow Ca(HCO_3)_2 \qquad (2.5)$$

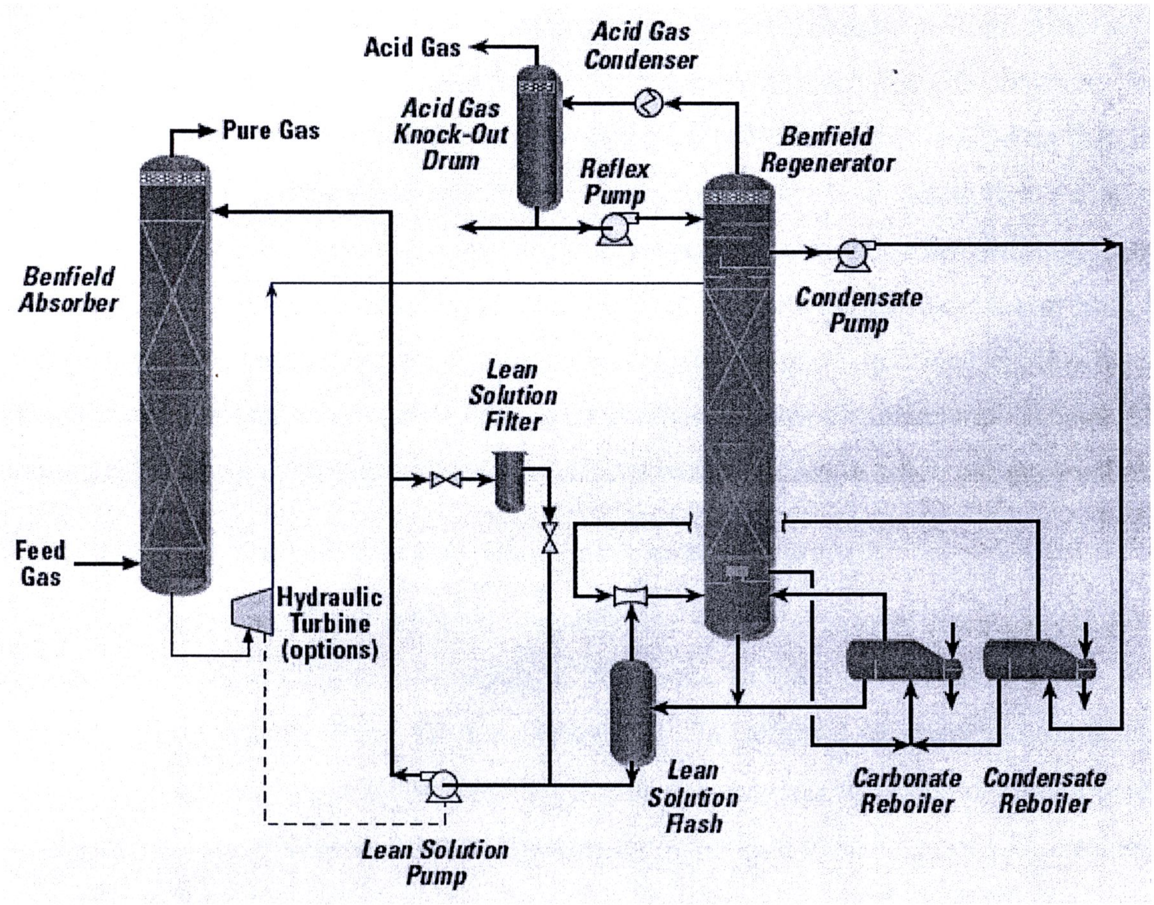

Figure 2.2 Process flow diagram for CO_2 recovery from the flue gas by Benfield process or carbonation process (UOP LLc, 2000)

2.2.3 CO_2 removal via adsorption processes

In the adsorption process for flue gas CO_2 recovery, molecular sieves or activated carbons are used in adsorbing CO_2. Desorbing CO_2 is then by the pressure swing operation (PSA) or temperature swing operation (TSA). Most applicants are associated with pressure swing adsorption (Ishibashi et al., 1999 and Yokoyama, 2003). Much less attention has been focused on CO_2 removal via temperature swing adsorption due to the longer cycle ties needed to heat up the bed of solid particles during sorbent regeneration. For bulk separations at large scale, it is also essential to limit the length of the unused bed and therefore opt for faster cycle times.

Adsorption processes have been employed for CO_2 removal from synthesis gas for hydrogen production. It has not yet reached a commercial stage for CO_2 recovery from flue gases. It can be concluded based on mathematical models and pilot-scale data that industrial adsorption process might be feasible. A serious drawback of all adsorptive methods is the necessity to treat the gaseous feed before CO_2 separation in an adsorber. In many cases gases have to be also cooled and dried, which limits the attractiveness of PSA, TSA or ESA (electric swing adsorption) compared with capture by chemical absorption described in previous sections. The development of a new generation of materials that would efficiently adsorb CO_2 will undoubtedly enhance the competiveness of adsorptive separation in a flue gas application.

2.2.4 CO_2 removal methods via membrane contactors

Membrane processes are used commercially for CO_2 removal from natural gas at high pressure and at high CO_2 concentration. In flue gases, the low CO_2 partial pressure difference provides a low driving force for gas separation. The removal of carbon dioxide using gas separation with polymeric membranes results in not only energy penalties compared with a standard chemical absorption process, but also the maximum percentage of CO_2 removed which is lower than for a standard chemical absorption processes (Herzog et al., 1991, Van der Sluijs et al., 1992 and Feron, 1994).

The membrane option currently receiving the most attention is a hybrid membrane-absorbent (or solvent) system. These systems are being developed for flue gas CO_2 recovery. Hybrid membrane systems enhance membrane to provide a very high surface to volume ratio for mass exchange between gas stream and solvent resulting in a very compact system. This results in membrane contactor system in which the membrane forms a gas permeable barrier between a liquid and a gaseous phase. In cases of non-porous membranes, CO_2 dissolves in the membrane and diffuse through the pores and are absorbed by the liquid. The contact surface area between gas and liquid phases is maintained by the membrane and is independent of the gas and liquid flow rate. The selectivity of the partition is primarily determined by the absorbent (solvent). Absorption in the liquid phase is determined either by physical partition or by a chemical reaction.

The advantage of membrane/solvent systems are avoid of operation problems where gas and liquid flows are in direct contact. Operation problems avoided include foaming, flooding and channeling. Furthermore, the use of compact membranes result in a smaller equipment sizes with capital cost reductions. The alternative of a suitable combination of solvent and membrane material is very important. The material characteristics should be avoided at operating pressure gradients of typically 50-100 KPa while the transfer of gas is not hindered. Membrane/solvent systems can be both used in the absorption as well as in desorption step.

Research and development efforts have also been reported in the area of facilitated transport membranes. An important class of facilitated transport membranes is the so-called liquid membrane in which carrier is dissolved into a liquid contained in a membrane. For CO_2 separation, carbonates, amines and molten salt hydrates have been suggested as carriers (Feron, 1992). Porous membranes and ion-exchange membranes have been employed as the support. Until now, supported liquid membranes have been only study in a laboratory scale. Practical problems associated with supported liquid membranes are membrane stability and liquid volatility. Recent development work has focused on the following technological options that are applicable to both CO_2/N_2 (i.e. Amine process) and CO_2/H_2 (i.e. Fuel cell and Syngas purification) separations, examples include:

- Amine-containing membranes (Teramoto et al., 1996),
- Membranes containing potassium carbonate polymer gel membrane

  (Okabe et al., 2003),
- Membranes containing potassium carbonate-glycol (Chen et al., 1999),
- Dendrimer-containing membranes (Kovvali and Sirkar, 2001),
- Poly-electrolyte membranes (Quin and Laciak, 1997).

2.2.5 CO_2 removal via algal cultivation

The biological method using microalgal photosynthesis is recently considered as an effective method to remove CO_2 from stack or flue gas. By this approach, CO_2 is turned into the form of microalgal biomass by photosynthesis. Carbon fixation refers to process through which gaseous carbon dioxide is converted into a solid compound. It mostly refers to the processes found in autotrophs (organisms that produce their own food), usually driven by photosynthesis. Most microalgae use CO_2 as an inorganic source for their growth through photosynthetic pathway, and CO_2 naturally is transformed to oxygen, biomass and many useful chemical substances such as lipids and proteins. Microalgae can fix carbon dioxide from different sources, such as CO_2 from the atmosphere and from industrial exhaust gases (e.g. flue gas and flaring gas), and fixed CO_2 in the form of soluble carbonates (e.g., $NaHCO_3$ and Na_2CO_3). Photosynthetic organisms are called photoautotroph, since they can create their own food. In plants, algae and cyanobacteria, photosynthesis uses carbon dioxide and water and converts to sugar (glucose), releasing oxygen as a waste product. Glucose may be used directly by the plant for its own metabolic needs during cellular respiration. Excess glucose also can be converted into other molecules (fiber, starch, protein and fat) for structural or energy-storage purposes.

Photosynthetic reaction is described below:

$$6CO_2 + 6H_2O \xrightarrow{\text{sunlight}} C_6H_{12}O_6 + 6O_2 \text{ (in the presence of chlorophyll)} \qquad (2.6)$$

More informative CO_2 removal via algal cultivation is described in Section 2.3.

2.3 CO_2 Removal via algal cultivation (CO_2 Bio-mitigation)

Biological CO_2 mitigation has attracted much attention as an alternative strategy because it leads to production of biomass energy in the process of CO_2 fixation through photosynthesis (Ryu et al., 2008; de Morais and Costa et al., 2007). Biological CO_2 mitigation can be carried out by plants and photosynthetic microorganisms (photosynthesis reaction is described in Section 2.2.5). However, the potential for increased CO_2 capture in agriculture by plants has been estimated to contribute only 3–6% of fossil fuel emissions (Skjanes et al., 2007), largely due to the slow growth rates of conventional terrestrial plants

Microalgae, a group of fast-growing unicellular or simple multicellular microorganisms, have the ability to fix CO_2 while capturing solar energy with an efficiency of 10 to 50 times greater than that of terrestrial plants (Li et al., 2008). The microalgae-for-CO_2-mitigation or CO_2 fixation via microalgae cultivation provides numerous advantages.

Firstly, microalgae have much higher growth rates and CO_2 fixation abilities compared to conventional forestry, agricultural, and aquatic plants (Li et al., 2008). Secondly, it could completely recycle captured CO_2 because carbon dioxide is converted into the chemical substances via photosynthesis. In comparison, the chemical reaction-based CO_2 removal approaches as previous discussed above, have disposal problems because both the captured CO_2 and the wasted absorbents need to be disposed (Bonenfant et al., 2003). Thirdly, as mentioned in the previous section, chemical reaction-based CO_2 mitigation approaches are energy-consuming and costly processes (Lin et al., 2003; Resnik et al., 2004). On the other hand, CO_2 bio-mitigation using microalgae could be made profitable from the production of biofuels and other useful bioproducts. Finally, the microalgal CO_2 bio-mitigation could be made more economically cost-effective and environmentally sustainable, especially when it is combined with other processes such as wastewater treatment integrated with other facilities.

A number of microalgal species have been shown to be able to utilize carbonates such as Na_2CO_3 and $NaHCO_3$ as inorganic sources for cell growth (Huertas et al., 2000a). They fix CO_2 by chemical reaction to produce bicarbonates and carbonates and use as the latter carbon source for microalgal cultivation. These bicarbonates and carbonates uptake pathway by active transport in microalgae are mainly described in Section 2.4.

There are two main methods in which algae can be cultivated. One of the methods is to cultivate algae in an open pond or lake. This type of system is considerably cheap and allows for large production capacities. However, because this is an open system, the algae are exposed to natural, uncontrolled conditions such as water temperature and lighting conditions. There is also a risk of contamination by other organisms. This often causes problems with the open pond cultivating systems. A cover or greenhouse may be used to cover the pond to increase production by eliminating some of the disturbances associated with open systems.

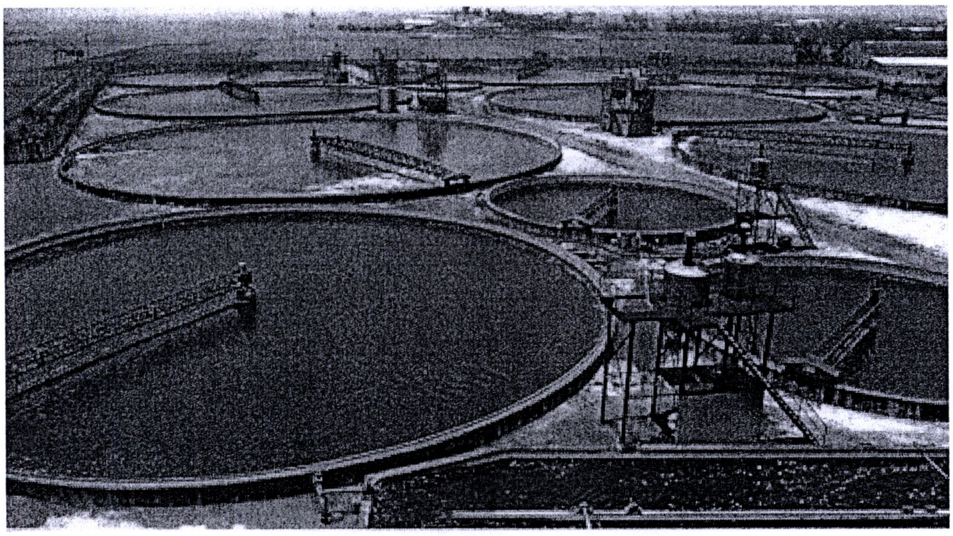

Figure 2.3.1 *Chlorella sp.* open system cultivation ponds (Continex, 2009)

Another method in which microalgae can be cultivated is by using a photobioreactor. A photobioreactor contains a light source and is a closed system. The photobioreactor can be set up like a batch reactor or a continuously harvesting reactor. As a microalgal photobioreactor is a totally enclosed system it is generally more expensive than an open system. However, there are several major advantages as the bioreactor can prevent or at least minimize contamination and allows easier cultivation of one algae strain. It also offers better control over a range of other growing conditions, like pH, light, carbon dioxide, and temperature. To enhance productivity of microalgae with CO_2, flue gases from emitting sources can be directed through the integrated microalgal reactor. CO_2 is taken up by the microalgae, directly recycled in the form of biomass and derived products. Several algal cultivation systems are equipped with CO_2 fixation to increase the algal productivity, such as *Chlorella sp.* (Hyun et al., 2008) and *Dunaliella tertiolecta* (Sydney et al., 2010).

Traditionally, microalgae are cultivated in closed systems or open ponds, which are aerated or exposed to air to allow microalgae to capture carbon dioxide from the atmosphere for cell growth. Industrial exhaust gases such as flue gas contains up to 15% CO_2 provide a CO_2-rich source for microalgal cultivation and a potentially cheap source for CO_2 bio-fixation. Therefore, it would be beneficial if microalgae are tolerant to elevated CO_2 level should they be used for CO_2 fixation from flue gases (Maeda et al., 1995). An early review on flue gas tolerance by microalgae indicated that high levels of CO_2 were tolerated by many microalgal species and that moderate levels of SO_x and NO_x (up to 150 ppm) were also well-tolerated (Matsumoto et al., 1997). However, the excess CO_2 leaving as unused gas to the atmosphere is the factor that should be considered and optimized CO_2 fed to the cultivation system.

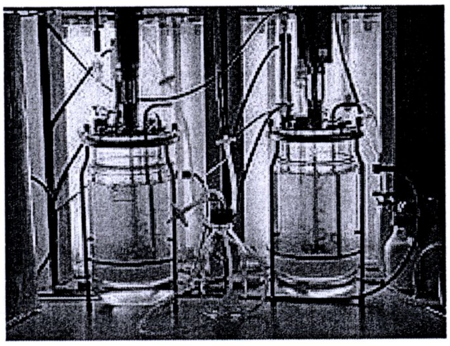

Figure 2.3.2 *Physcomitrella patens* photobioreactor for biophamaseutical (Eva, 2007)

2.4 CO_2 and bicarbonate as inorganic carbon source for microalgal uptake

Higher terrestrial plants usually depend entirely on CO_2 as their only source of inorganic carbon for photosynthesis, whereas marine microalgae acquire their inorganic carbon from the dissolved inorganic carbon (DIC) system in sea water. The DIC system contains four forms of carbon, i.e. CO_2, H_2CO_3, HCO_3^- and CO_3^{2-}, their interconversion being governed by a complex equilibrium:

$$CO_2 + H_2O \longleftrightarrow H_2CO_3 \longleftrightarrow H^+ + HCO_3^- \longleftrightarrow CO_3^{2-} + 2H^+ \qquad (2.7)$$

which is controlled primarily by pH and to a lesser degree by temperature and alkalinity (Merrett et al., 1996). Aquatic photosynthetic organisms face a number of problems in obtaining a supply of CO_2 for photosynthesis, causing largely from the physical chemistry of the water phase. The rate of diffusion of CO_2 in water is 1x 10^4 times slower than it is in air, and at alkaline pH. HCO_3^- is the dominant dissolved inorganic carbon (DIC) species and the rate of spontaneous conversion of HCO_3^- to CO_2 is slow in this pH range. The low availability of CO_2 is particularly acute in seawater, which has a high ionic strength and an average pH of 8.0 to 8.2; most of the DIC (99%) is present in the form of HCO_3^- (about 2mM), whereas the CO_2 concentration is very low (10 mM at 20°C) (Round, 1981) and modeling of the diffusive CO_2 flux from the bulk phase to the plasmalemma suggests that the availability of CO_2 may be rate-limiting for the growth of marine diatoms (Riebesell et al., 1993).

Many photosynthetic microalgae achieve high photosynthetic rates via mechanisms that raise the intracellular CO_2 concentration (Kaplan and Reinhold,, 1999). Many marine phytoplankton species possess a CO_2-concentrating mechanism (CCM), which consists of active CO_2 uptake, HCO_3- uptake, and the presence of an external carbonic anhydrase (CA). Although it is not required for either CO_2 or HCO_3^- transportation, the presumed role of external CA is to maintain the CO_2/HCO_3^- equilibrium at the cell surface and thus ensure the availability of substrate for the CO_2 transporter (Williams and Turpin, 1987). These microalgae can therefore acquire inorganic carbon by the direct uptake of bicarbonate or the active uptake of CO_2 derived from bicarbonate by the action of external CA.

A number of species have been found to display the characteristics of a CCM in that they have the capacity to accumulate inorganic carbon during photosynthesis. Leggat et al. (1999) showed a 7- to 26-fold accumulation over that in the external medium in *Amphidinium carterae* and a 5- to 24-fold accumulation in the symbiotic species *Symbiodinium sp.* A 10-fold accumulation has been reported in the marine species *Procentrum micans* (Nimer et al., 1999), and a 5- to 70-fold accumulation has been demonstrated in the freshwater species *Peridinium gatunense* (Berman-Frank et al., 1998). This capacity to accumulate inorganic carbon may be required to maintain photosynthetic CO_2 fixation.

At present, most ecophysiological studies of marine diatoms have focused on the ability of these organisms to take up macronutrients and trace metals and grow under various light regimes (Sarthou et al., 2005). By comparison, relatively few studies have examined the physiological mechanisms of inorganic C acquisition in this group. Early work suggested that the rate of diffusive CO_2 supply could significantly limit diatom growth as a result of the low CO_2 concentrations in marine surface waters and the poor CO_2 affinity of the principal RubisCO - carboxylating enzyme ribulose bisphosphate carboxylase/oxygenase (RubisCO; Riebesell et al. 1993).

However, subsequent studies demonstrated the presence of inorganic carbon-concentrating mechanisms (CCMs) in a number of marine diatom species (Rotatore et al. 1995; Korb et al. 1997; Burkhardt et al., 2001; Morel et al., 2002). The CCM acts to concentrate CO_2 in close proximity to RubisCO via the active uptake of CO_2 and/or HCO_3^- (the dominant C form in seawater) and the use of carbonic anhydrase to catalyze the interconversion between these C species (Colman et al., 2002; Giordano et al., 2005).

There is a variety of inorganic carbon acquisition mechanisms in marine microalgae. Some have been shown to take up both CO_2 and HCO_3^- by active transport, with or without the involvement of an external CA (Colman and Rotatore 1995; Bozzo et al., 2000), whereas others have been found to take up only a single species of inorganic carbon (Rotatore et al. 1992, Huertas and Lubian 1998; Huertas et al., 2000b). These algae therefore display all the combinations of inorganic carbon uptake that could be expected from the existence of two active inorganic carbon transporters and an external CA (Colman et al., 2002). The utilization of HCO_3^- may occur either by direct uptake or by CA catalysing the conversion of HCO_3^- to CO_2 and OH^- externally to the plasmalemma. Both mechanisms have been reported for marine macro- and microalgae. (Nimer and Merrett 1992; Dong et al., 1993)

2.5 Solubility of carbon dioxide in the water

As carbon dioxide causing the global warming, oceans represent in the largest carbon storage capacity in the world as a buffer. The natural uptake of CO_2 from the atmosphere by the ocean occurs on an enormous scale, and the ocean offers the world's most powerful long-term buffer against the rise of both temperature and CO_2 emissions (Brewer et al., 1995). Dissolved inorganic carbon in the ocean is increasing because of higher release of CO_2 to the atmosphere. Open ocean water in equilibrium with the atmosphere at 0° C contains about 2200 micromoles/liter CO_2, which is about 75 times as much as that in fresh water and about 1% of the dissolved CO_2 in seawater is in the form of CO_2 (aqueous form) or H_2CO_3, and 97% is in the form of HCO_3^-. Since the degree of ionic dissociation changes with pH, the solubility of CO_2 in seawater is a function of not only temperature but also pH (Round, 1981).

To enhance CO_2 capture and storage in the water, the solubility of CO_2 is essential to be understood and according to the occurring of mass transfer between gas and liquid phase, how CO_2 soluble in the water depends on these important factors influencing the gas solubility in the water i.e. (1) chemical property, (2) temperature and (3) pressure. Firstly, the solubility of one substance in another is determined by the balance of intermolecular forces between the solvent and solute, and the entropy change that accompanies the dissolution. The various characteristics of chemical substance e.g. polarity, enthalpy of formation and reactivity affect efficiently the solubility of gas in the liquid. Secondly, Due to the differences between gas and solid, solid substances are able to be dissolved well at higher temperature but contrary to the gas. Gas is dissolved better at lower temperature. As CO_2 solubility is temperature dependant, colder water can dissolve more CO_2 and increasing water temperature reduces the solubility as demonstrated in Figure 2.5.1. Last, solubility is direct proportional to pressure so increasing in pressure causes more gas to dissolve in a liquid. At higher pressure, gas molecules are forced to be more dissolved into the liquid phase. Furthermore, Henry's law is commonly used to quantify the solubility of gases in solvents. The solubility of a gas in a solvent is directly proportional to the partial pressure of that gas above the solvent. This relationship is written as:

$$p = k_H c \tag{2.8}$$

where p is the partial pressure of the solute in the gas above the solution, c is the concentration of the solute and k_H is a constant with the dimensions of pressure divided by concentration

However, it should also be noted the use of Henry's Law is a limited only to low soluble gases, e.g. O_2 and N_2 where the solubility could be assumed to linearly vary with pressure. For relatively high soluble gases like CO_2, failure of Henry' law is observed because indirect proportion between solubility and pressure is often the case, and particularly for CO_2, the soluble CO_2 could undergo carbonation reaction leading to a formation of its carbonate derivatives like HCO_3^- and CO_3^{2-} according to the following reactions (Wilhelm et al., 1977):

$$CO_2\,(g) \xleftrightarrow{1} CO_2\,(aq) \xleftrightarrow{2} H^+ + HCO3^- \tag{2.9}$$

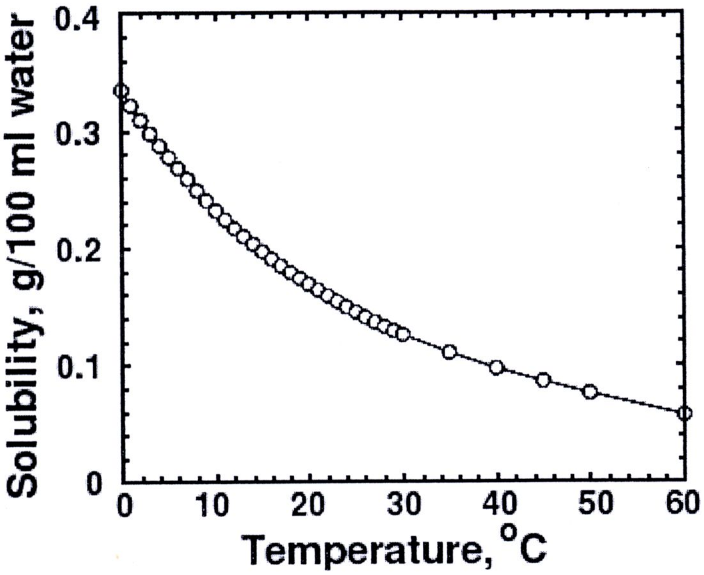

Figure 2.5.1 The relationship between solubility of CO_2 in the water (in g·10^{-2}ml^{-1}) at various temperature (°C) at 1 atm pressure (Nielson, 2003)

Any water-soluble gas becomes more soluble as the temperature decreases, due to the thermodynamics of the reaction, the entropy change, ΔS, of this reaction is positive because the gas molecules are less constrained than the gas molecules in solution. This effect is particularly large for gases like CO_2 that undergo specific reactions with water. Then, equilibrium is established between the dissolved CO_2 and H_2CO_3, carbonic acid.

$$CO_2\ (l) + H_2O\ (l) \longleftrightarrow H_2CO_3\ (l) \tag{2.10}$$

This reaction is kinetically slow. At equilibrium, only a small fraction (ca. 0.2 - 1%) of the dissolved CO_2 is actually converted to H_2CO_3. Most of the CO_2 remains as solvated molecular CO_2. As equation:

$$K_r = \frac{[H_2CO_3]}{[CO_2]_l} \approx 1.7.10^{-3} \tag{2.11}$$

In fact, the pK_a (the symbol for the acid dissociation constant at logarithmic scale) most reported for carbonic acid ($pK_{a1} = 6.37$) is not really the true pK_a of carbonic acid. Rather, it is the pK_a of the equilibrium mixture of CO_2 (l) and carbonic acid. Carbonic acid is actually a much stronger acid than this, with a true pK_{a1} value of 3.58. However, these values are also temperature dependent (Wang et al., 2008). Carbonic acid is a weak acid that dissociates in following two steps (Lide et al., 1990):

$$H_2CO_3 + H_2O \longleftrightarrow H_3O^+ + HCO_3^- \qquad (2.12)$$

$$HCO_3^- + H_2O \longleftrightarrow H_3O^+ + CO_3^{2-} \qquad (2.13)$$

which are controlled primarily by pH and alkalinity and described in interconversion of CO_2 in Equation (2.7) (Merrett et al., 1996).

Carbonate species are found in different pH range as shown in Figure 2.5.2. At high pH values, carbonic acid exists only in the form of carbonate ions. If the pH value decreases, the fraction of bicarbonate increases proportionally. At a pH around 10.3, both ions exist at equal amounts. Furthermore, low pH values, only bicarbonate exists at equilibrium. (Fleischer et al., 1998)

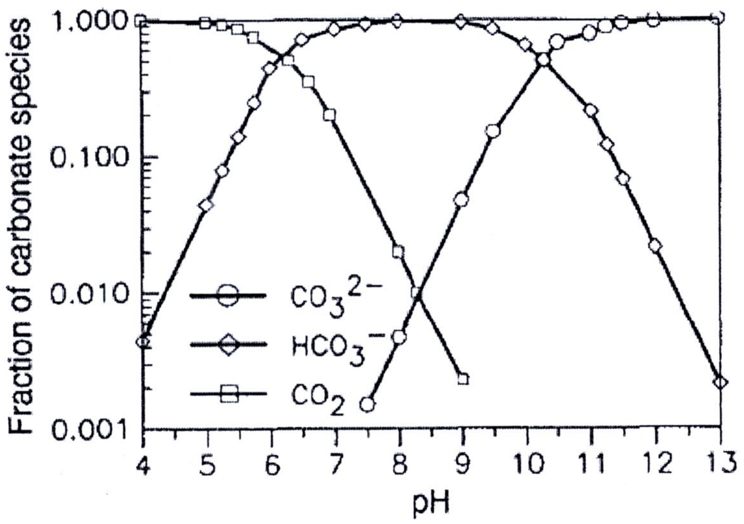

Fig 2.5.2 The various fraction of carbonate species in pH range from 4 to 13 (Fleischer et al., 1998)

2.6 Literature Review

From early twentieth century, Amine process using MEA (Monoethanolamine) as absorbent was found for CO_2 removal from pre-treated natural gas and then it was improved for removing CO_2 from coal-fired power plant and other purposes. However, MEA can cause energy penalty during absorption and regeneration cycle that relatively low temperature and high temperature are needed (described in Section 2.1). Furthermore, there are studies about alternative amine absorbent for substituting MEA e.g. NH_3 (ammonia) (Je et al., 2009; You et al., 2008; Bai et al., 2005; James et al., 2005; Yeh et al., 1999; Hsunling et al., 1997). Ammonia seems to be a promising alternative solvent for removing CO2 from flue gas (Yeh et al., 1999).

From literature study, Amine processes using MEA and NH_3 in various important aspects e.g. fed CO_2 flow rate, flue gas composition, operating condition, maximum absorption capacity and averaged absorption rate were compared as shown in Table 2.6.1. MEA showed acceptable CO_2 absorption rate for commercial use. Furthermore, there was a study of chilled MEA (Temperature at -4°C) enhancing CO_2 removal (Yeh et al., 1999). However, it shows sign of energy penalty during cycle as mentioned above. Many NH_3 as absorbent studies were compared because NH_3 represents the better CO_2 capacity and absorption rate than MEA as shown in Table 2.6.1. The highest averaged absorption rate at room temperature and atmospheric pressure was presented at 12.01 kg $CO_2 \cdot kg\ NH_3^{-1} day^{-1}$ (Je et al., 2009) and maximum absorption capacity at 0.98 kg of $CO_2 \cdot kgNH_3^{-1}$ (James et al., 2005). Moreover, chilled NH_3 process (at Temperature=-4°C) was also compared representing the highest maximum absorption capacity and averaged absorption rate at 1.20 kg of $CO_2 \cdot kSg\ NH_3^{-1}$ and 14.4 kg $CO_2 \cdot kg\ NH_3\ ^{-1}\ day^{-1}$ respectively (Yeh et al., 1999). This implied that temperature effect greatly yields better CO_2 absorption rate and capacity for NH_3 but considering energy penalty is required.

Table 2.6.1 Summary of CO_2 removal rate via amine processes

Absorbent	CO_2 flowrate (l/min)	Flue gas composition (%v/v)	Absorbent concentration	Condition	Maximum Absorption Capacity	Averaged Absorption rate	Reference
NH_3 MEA	2-10 2-10	40	7-35 %MEA, NH_3	Temperature =-4 °C Pressure =101.3 kPa	1.20 kg CO_2 kg NH_3^{-1} 0.40 kg CO_2 kg MEA^{-1}	14.4 kg CO_2kg NH_3^{-1} d^{-1} 4.80 kg CO_2kg MEA^{-1} d^{-1}	Yeh et al., 1999
NH_3	0.12	12.81	8.8 % NH_3	Temperature =25°C Pressure =101.3 kPa	0.152 kg CO_2 kg NH_3^{-1}	7.30 kg CO_2kg NH_3^{-1} d^{-1}	You et al., 2008
NH_3	3	14.7	15 % NH_3	Temperature =25°C Pressure =101.3 kPa	0.24 kg CO_2kg $NH3^{-1}$	11.52 kg CO_2kg NH_3^{-1} d^{-1}	Bai et al., 2005
NH_3	2	100	28 % NH_3	Temperature = 25°C Pressure =101.3 kPa	0.9 kg of CO_2kg NH_3^{-1}	10.8 kg CO_2kg NH_3^{-1} d^{-1}	Hsunling et al., 1997
MEA	n/a	100	30 % MEA	Temperature = 25°C Pressure =101.3 kPa	0.36 kg of CO_2kg MEA^{-1}	4.32 kg CO_2kg MEA^{-1} d^{-1}	Jou et al., 1995
NH_3	7.5	15	7-14 % NH_3	Temperature =27 °C Pressure =101.3 kPa	0.98 kg CO_2 kg NH_3^{-1}	5.88 kg CO_2kg NH_3^{-1} d^{-1}	James T. et al., 2005
NH_3	20-30	25	2-7 % NH_3	Temperature =25°C Pressure =101.3 kPa	0.252 kg CO_2 kg NH_3^{-1}	12.01 kg CO_2kg NH_3 $^{-1}d^{-1}$	Je et al., 2009

CO_2 sequestration by photosynthetic organisms or autotrophs is being interesting throughout the world. Forestry, sea and fresh water plant are considered as alternative options for CO_2 removal. Because of highly potential growth rate of algae compared with other plants and some use CO_2 as their inorganic carbon for their growth. Furthermore, according to its substantial CO_2 removal benefit, captured CO_2 is completely transformed to biomass and some high-valued products. There are many studies on CO_2 for algal cultivation and global warming mitigation purposes. CO_2 fixation rates were compared in different living organisms and operating conditions as shown in Table 2.6.2. Literature recommends the range of condition for CO_2 fixation in the photobioreactors at: light intensity at range 40-250 $\mu E\ m^{-2}\ s^{-1}$ (Sydney et al., 2010; Hyun et al., 2008; de Morais et al., 2007; Yeoung et al., 1997; Kurano et al., 1995), various low to medium CO_2 flow rate at range 6.94-83.33 $ml \cdot min^{-1}$ (Eduardo et al. 2010; Hyun et al. 2008; de Morais et al., 2007), high CO_2 flow rate at range 400-1000 $ml \cdot min^{-1}$ (Yeoung et al., 1997; Kurano et al., 1995), different flue gas composition from 5 to 34 %v/v and a variety of mediums for algal cultivation were provided. Various algae are cultivated in fresh water and sea water in which they can naturally grow. Besides, Yeoung applied steel-making facility waste water for *Chlorella vulgaris* cultivation as substituted nutrients in which high value CO_2 fixation (0.624 $g\ l^{-1}d^{-1}$) was taken (Yeoung et al., 1997). If only fresh water or artificial sea water are considered without pH effect, Sea water *Chlorococcum Littora* represents the highest CO_2 fixation among other sea water algae at 0.900 $g\ l^{-1}d^{-1}$ (Kurano et al., 1995) and fresh water *Chlorella sp.* shows the second highest CO_2 fixation at 0.570 $g\ l^{-1}d^{-1}$. Note that in many cases, CO_2 supplied to algal culture is wasted to the atmosphere as CO_2 consumption rate at which the alga can uptake is relatively low.

From Tables 2.6.1 and 2.6.2, CO_2 removal via amine process and algal cultivation can be compared in many diverse aspects, e.g. CO_2 removal rate per day, chemical utilization and unit operation. CO_2 removal rate per day in amine process representing in averaged absorption rate (in kg CO_2 kg absorbent^{-1} day^{-1}) are clearly better than in algal cultivation (in $g\ l^{-1}d^{-1}$). Nevertheless, amine process costs a chemical expenditure and need energy provided for absorption and regeneration cycle via costly absorber and desorber columns. On the contrary,

CO_2 removal via algal cultivation requires little chemical for medium, no need for regeneration cycle and reacted CO_2 is completely transformed into biomass by simple photobioreactors. Eventually, Amine process is still reliable and effective for industrial scale use and CO_2 removal via algal cultivation need to be more improved for competitive CO_2 removal for substantial development.

Table 2.6.2 Summary of CO_2 removal rate via algal cultivation

Microalgae	Reactor type / volume	Condition	CO_2 rate (ml/min)	Flue gas Composition (%v/v)	CO_2 fixation ($g\ l^{-1}d^{-1}$)	Remark	Reference
Chlorella vulgaris	Photobioreactor / 0.25 l	Temperature = 27 °C Medium : N8 Medium Light intensity = 110 $\mu E\ m^{-2}\ s^{-1}$	400	15	0.624	Using suspended solid removed wastewater from steel-making facility	Yeoung et al., 1997
Haematococcus pluvialis	Photobioreactor / 180 l	Temperature = 16-18 °C Medium : n/a Light intensity >2200 $\mu E\ m^{-2}\ s^{-1}$	n/a	16-34	0.143	Commercial scale, outdoor and using daylight Addition of CO_2 until pH in range of 7.3-7.8	Huntley et al., 2007
Spirulina sp.	Photobioreactors (3)/ total volume 5.4 l	Temperature = 30 °C Medium : modified Zarrouk medium Light intensity = 43.24 $\mu E\ m^{-2}\ s^{-1}$	55.56	12	0.413	-	de Morais et al., 2007
Chlorella sp.	Photobioreactors (4)/ total volume 2.4 l	Temperature = 20 °C Medium : Allen medium Light intensity = 40 $\mu E\ m^{-2}\ s^{-1}$	83.33	5	0.570	-	Ryu et al., 2008
Botryococcus braunii	Photobioreactor / 8 l	Temperature = 25 °C Medium : 3N-MBM medium Light intensity = 47.30 $\mu E\ m^{-2}\ s^{-1}$	6.94	5	0.500	Artificial sea water pH 7.2±0.2 adjusted by acid/base injection	Sydney et al., 2010
Spirulina platensis	Photobioreactor / 8 l	Temperature = 30 °C Medium : Zarrouk medium Light intensity = 47.30 $\mu E\ m^{-2}\ s^{-1}$	6.94	5	0.320	Artificial sea water pH 9.0±0.2 adjusted by acid/base injection	Sydney et al., 2010
Dunaliella tertiolecta	Photobioreactor / 8 l	Temperature =25 °C Medium : DUN medium Light intensity = 47.30 $\mu E\ m^{-2}\ s^{-1}$	6.94	5	0.270	Artificial sea water pH 7.2±0.2 adjusted by acid/base injection	Sydney et al., 2010
Chorella. vulgaris	Photobioreactor / 8 l	Temperature = 30 °C Medium : modified Britol medium Light intensity = 47.30 $\mu E\ m^{-2}\ s^{-1}$	6.94	5	0.250	Artificial sea water pH 7.2±0.2 adjusted by acid/base injection	Sydney et al., 2010
Chlorococcum Littora	Culture vessel / 20 l	Temperature = 25 °C Medium : Allen medium Light intensity = 250 $\mu E\ m^{-2}\ s^{-1}$	1000	6.25	0.900	Artificial sea water pH was not adjusted	Kurano et al., 1995