CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Review of Carbon Dioxide Emission

Among greenhouse gases, CO_2 is mostly emitted into the atmosphere by human activities. Atmosphere concentration of CO_2 has increased by more than 25 percent since pre-industrial times. Not only CO_2 is greenhouse gas, but also include methane, nitrous oxide, methyl chloroform, ozone, carbon tetrachloride, carbon monoxide and chlorofluorocarbons, but these gases are emitted in much less amounts than CO_2 and their concentrations in the atmosphere are lower. Overall, about one-half of global warming potential is caused by the presence of CO_2 in the atmosphere. Many potential policy responses to climate change have concentrated on CO_2 emissions mainly because more data are known related to the sources and life cycle of CO_2 than the other greenhouse gases. (http://r0.unctad.org/ghg/download/other/controllingco2.pdf)

2.2 CO_2 Capture Technology

There are three major technologies for CO_2 capture from flue gases as pre-combustion, post-combustion and oxy-combustion. Advantages and drawbacks of these technologiees are shown in Table 2.1.

2.2.1 Pre-Combustion

In pre-combustion CO_2 capturing, CO_2 is recovered from process stream before the fuel is burned. Fuel is reacted with oxygen or air to give mainly CO and H_2. This process is known as gasification, partial oxidation or reforming. The mixture consisting mainly of CO and H_2 is passed through a catalytic reactor, called a shift converter, where the CO reacts with steam to give CO_2 and more H_2. The CO_2 is separated and the H_2 is used as fuel in a gas turbine combined cycle plant. The process is shown in Figure 2.1 (Figueroa *et al.,* 2008).
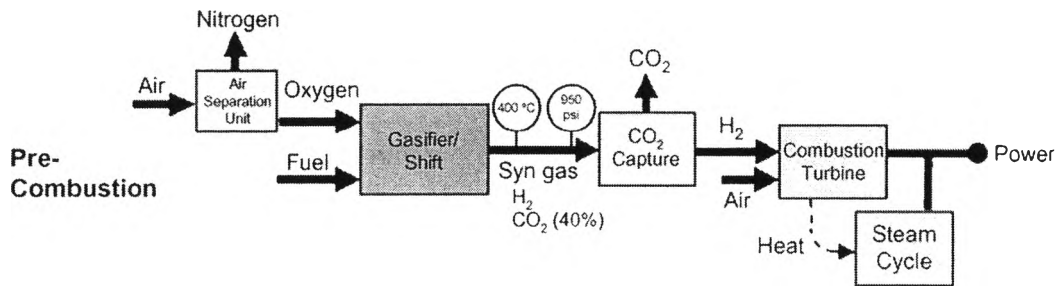
Figure 2.1 Block diagram for pre-combustion system (Figueroa *et al.*, 2008).

2.2.2 Post-Combustion

In post-combustion CO_2 capturing shown in Figure 2.2, the CO_2 is recovered from end of process stream (i.e. downstream). The most approved technique at present is to scrub the flue gases with an amine solution. This technique challenges for the development of cost effective advanced capture processes. Even with this difficulty, post-combustion carbon capture show high potential for reducing greenhouse gas emissions, because it can be retrofitted to existing power plants that generate two-thirds of the CO_2 emissions in the power sector. (Figueroa *et al.*, 2008).
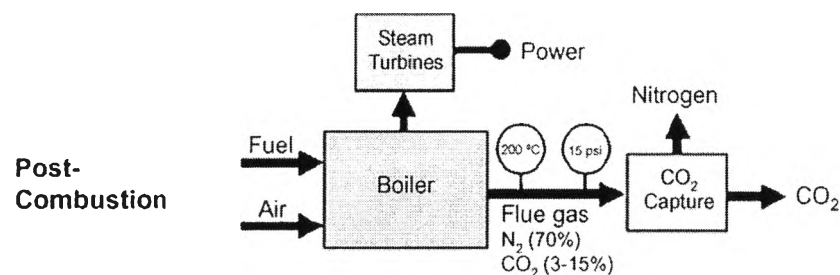

Figure 2.2 Block diagram for post-combustion system (Figueroa *et al.*, 2008).

2.2.3 Oxy-Combustion

In oxy-combustion CO_2 capture, the fuel is burned with nearly pure oxygen (greater than 95%) mixed with recycled flue gas. Oxyfuel combustion is substantially modified post-combustion method. The main attraction of this process is to produces a flue gas which is large amount CO_2 and water. The water is facilely

removed by condensation, and the remaining CO_2 can be purified relatively cheaply. The process that is given in Figure 2.3.
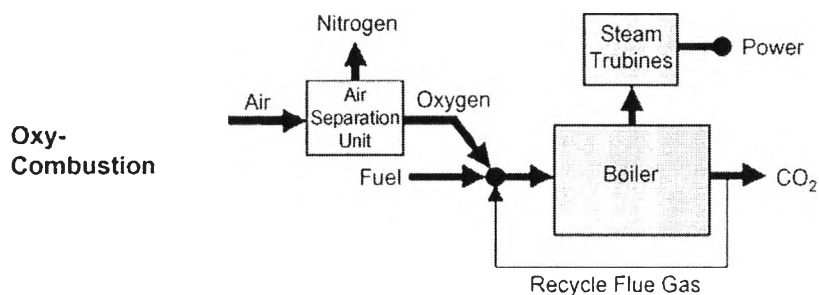
Nitrogen

Steam Trubines → Power

Air

Air Separation Unit

Oxygen

Oxy-Combustion

Fuel

Boiler → CO_2

Recycle Flue Gas

Figure 2.3 Block diagram for oxy-combustion system (Figueroa *et al.*, 2008).

Table 2.1 Advantages and disadvantages of different CO_2 capture approaches (Figueroa *et al.*, 2008)

Types of CO_2 Capture	Advantages	Barriers to Implementation
Post-combustion	- Applicable to the majority of existing coal-fired power plants - Retrofit technology option	Flue gas is - Dilute in CO_2 - At ambient pressure Resulting in - Low CO_2 partial pressure - Significantly higher performance or circulation volume required for high capture levels - CO_2 produced at low pressure compared to sequestration requirements

Table 2.1 Advantages and disadvantages of different CO_2 capture approaches (Figueroa *et al.*, 2008) (Cont'd)

Types of CO_2 Capture	Advantages	Barriers to Implementation
Pre-combustion	Synthesis gas is - Concentrated in CO_2 - High pressure Resulting in - High CO_2 partial pressure - Increased driving force for separation - More technologies available for separation - Potential for reduction in compression costs/loads	Applicable mainly to new plants, as few gasification - Barriers to commercial application of gasification are common to pre-combustion capture - Availability Resulting in - Cost of equipment - Extensive supporting systems requirements
Oxy-combustion	- Very high CO_2 concentration in flue - Retrofit and repowering technology option	- Large cryogenic O_2 production requirement may - Cooled CO_2 recycle required to maintain temperatures within limits of combustor materials - Decreased process efficiency - Added auxiliary load

2.3 Review of Possible CO$_2$ Separation Technology

The technologies are based on various physical and chemical processes including absorption, adsorption, membranes and cryogenics as showed in Figure 2.8. The choice of suitable technology depends on the characteristics of the flue gas stream and current status of CO$_2$ pathway given in Table 2.4.

2.3.1 Absorption

2.3.1.1 Physical Absorption

Physical absorption uses organic solvents to physically absorb acid gas components rather than reacting chemically. Extraction of CO$_2$ by physical absorption processes are based on the solubility of CO$_2$ within the solvents. The solubility depends on the partial pressure and on the temperature of the feed gas. The interaction between CO$_2$ and the absorbent is weak compared to chemical solvents that resulting in low energy requirement for regeneration (Chakravati *et al.*, 2001). Physical absorption is used commercially to remove acid gases e.g. CO$_2$ and H$_2$S from natural gas and to remove CO$_2$ from syngas in the production of hydrogen, ammonia and methanol (Olajire, 2010).
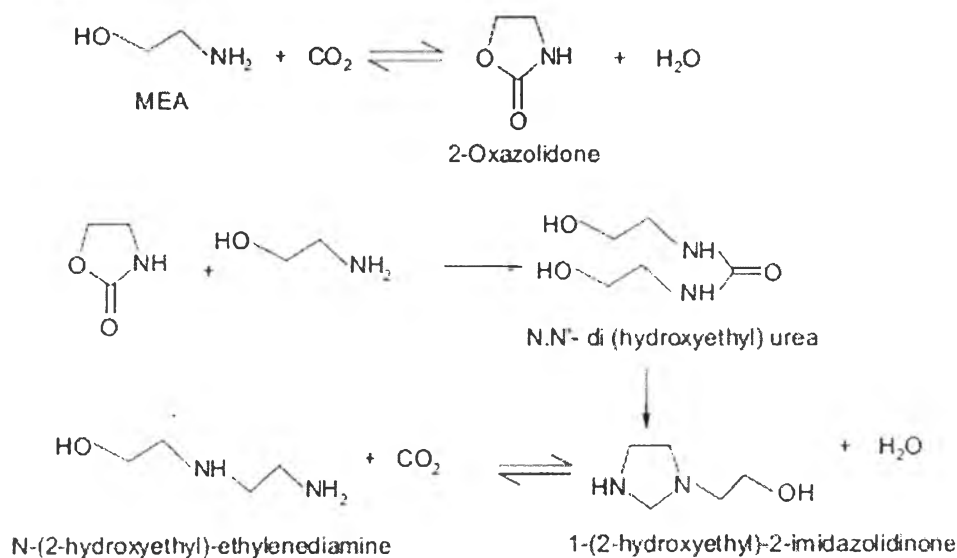
2.3.1.2 Chemical Absorption

Chemical absorption is preferred for low to moderate CO$_2$ partial pressure. Reaction of CO$_2$ with a chemical solvent forms weakly bonded intermediate compounds which may be regenerated with the application of heat producing pure CO$_2$ stream while recycling the solvent to the process. The selectivity of chemical absorption is relatively high. In addition, a relatively pure CO$_2$ stream could be produced. These factors make chemical absorption well appropriated for CO$_2$ capture for industrial flue gases (Wang *et al.*, 2010).

- Amine Absorption

Chemical absorption with amines has been effectively used in processes such as natural gas sweetening and hydrogen production for the rejection of carbon dioxide. This method having been used for many years is regarded as the most mature technology (Olajire, 2010). However, the technology still suffers from several problems including needs to handle large amounts of

hazardous waste, equipment corrosion, tower entrainment, and amine solution flooding and weeping. The proposed reactions of amines reacting with CO_2 are shown in Figure 2.4 (Chakravati *et al.*, 2001). The proposed reactions of amines and CO_2 during absorption process are shown below.

Figure 2.4 Proposed reaction sequence for The capture of CO_2 by liquid amine-based systems (Olajire, 2010).

For amine absorption, monoethanolamine (MEA) is commercially used. MEA has disadvantages such as low carbon dioxide loading capacity (weights of CO_2 absorbed / weights of absorbent), high equipment corrosion rate, amine degradation induced by CO_2, SO_2, NO_2, HCl and HF and oxygen in flue gas resulting in a high absorbent makeup rate and high energy consumption during high temperature absorbent regeneration. Absorption reactions of amine and are shown in Figure 2.4. The cost of MEA makeup is high because of degradation, even after most of the SO_2 is removed from the flue gas in an upstream flue gas desulphurization unit. NO_x must also be eventually removed from the flue gas before it is discharged into the air in order to meet present and future gaseous emission limits (Chakravarti *et al.*, 2001). Therefore, the scientists develop mixed amines to fix drawbacks of MEA. Mixtures of amines are generally mixtures of methyldiethanolamine (MDEA), diethanolamine (DEA) triethanolamine (TEA) and 2-amino-2-methyl-1-propanol (AMP) (Yan *et al.*, 2009). The development of solvents aims at selecting the alternative solvents to replace the single MEA, which should provide the equivalent or greater CO_2 absorption rate, higher CO_2 loading capacity and lower regeneration energy consumption than MEA (Polasek and Bullin, 2006). Mechanisms of MEA degradation with are given CO_2 and O_2 in Figure 2.5.

CO$_2$ - induced MEA Degradation :

MEA

2-Oxazolidone

N.N'- di (hydroxyethyl) urea

N-(2-hydroxyethyl)-ethylenediamine

1-(2-hydroxyethyl)-2-imidazolidinone

O$_2$ - Induced MEA Degradation:
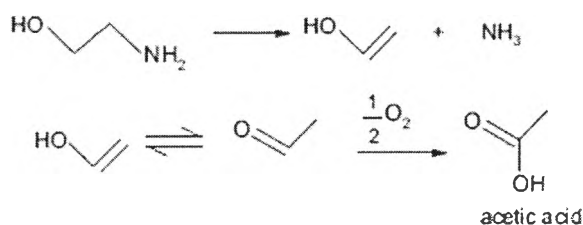

acetic acid

Figure 2.5 Degradetion MEA by CO$_2$ and O$_2$ (Olajire, 2010).

2.3.2 Adsorption

"Adsorption is the term used to describe the tendency of molecules from an ambient fluid phase to adhere to the surface of a solid. This is a fundamental property of matter, having its origin in the attractive forces between molecules. The force field creates a region of low potential energy near the solid surface and, as a result, the molecular density close to the surface is generally greater than in the bulk gas. Furthermore, and perhaps more importantly, in a multicomponent system the composition of this surface layer generally differs from that of the bulk gas since the surface adsorbs the various components with different affinities. Adsorption may

also occur from the liquid phase and is accompanied by a similar change in composition, although, in this case, there is generally little difference in molecular density between the adsorbed and fluid phases.

The enhanced concentration at the surface accounts, in part, for the catalytic activity shown by many solid surfaces, and it is also the basis of the application of adsorbents for low pressure storage of permanent gases such as methane. However, most of the important applications of adsorption depend on the selectivity, i.e., the difference in the affinity of the surface for different components. As a result of this selectivity, adsorption offers, at least in principle, a relatively straightforward means of purification (removal of an undesirable trace component from a fluid mixture) and a potentially useful means of bulk separation.

2.3.2.1 Fundamental Principles

Adsorption may be classified as chemisorption or physical adsorption, depending on the nature of the surface forces. In physical adsorption the forces are relatively weak, involving mainly van der Waals (induced dipole-induced dipole) interactions, supplemented in many cases by electrostatic contributions from field gradient-dipole or -quadrupole interactions. By contrast, in chemisorption there is significant electron transfer, equivalent to the formation of a chemical bond between the sorbate and the solid surface. Such interactions are both stronger and more specific than the forces of physical adsorption and are obviously limited to monolayer coverage. The differences in the general features of physical and chemisorption systems (Table 2.2) can be understood on the basis of this difference in the nature of the surface forces.

Table 2.2 Parameters of physical adsorption and chemisorption (Kirk-Othmer, 2004)

Parameter	Physical Adsorption	Chemisorption
heat of adsorption (DH)	low, < 2 or 3 times latent heat of evaporation	high, > 2 or 3 times latent heat of evaporation
specificity	nonspecific	highly specific
nature of adsorbed phase	monolayer or multilayer, no dissociation of adsorbed species	monolayer only may involve dissociation
temperature range	only significant at relative low temperatures	possible over a wide range of temperature
forces of adsorption	no electron transfer, although polarization of sorbate may occur	electron transfer leading to bond formation between sorbate and surface
reversibility	rapid, nonactivated, reversible	activated, may be slow and irreversible

In contrast, physical adsorption is a very rapid process, so the rate is always controlled by mass transfer resistance rather than by the intrinsic adsorption kinetics. However, under certain conditions the combination of a diffusion-controlled process with adsorption equilibrium constant that can give the appearance of activated adsorption.

As illustrated in Figure 2.6, a porous adsorbent in contact with a fluid phase offers at least two and often three distinct resistances to mass transfer: external film resistance and intraparticle diffusional resistance. When the pore size distribution has a well-defined bimodal form, the latter may be divided into macropore and micropore diffusional resistances. Depending on the particular system and the conditions, any one of these resistances may be dominant or the overall rate

of mass transfer may be determined by the combined effects of more than one resistance.
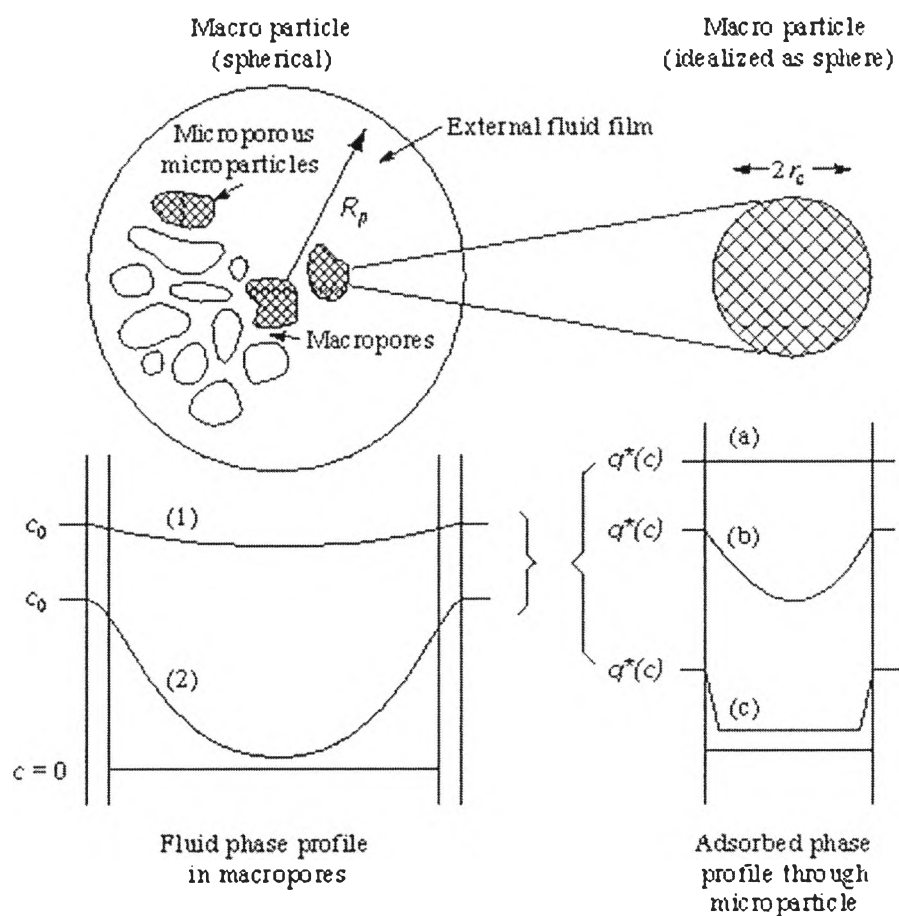
Figure 2.6 Concentration profiles through an idealized biporous adsorbent particle showing some of the possible regimes. (1) (a) rapid mass transfer, equilibrium throughout particle; (1) (b) micropore diffusion control with no significant macropore or external resistance; (1) (c) controlling resistance at the surface of the microparticles; (2) (a) macropore diffusion control with some external resistance and no resistance within the microparticle; (2) (b) all three resistances (micropore, macropore, and film) significant; (2) (c) diffusional resistance within the macroparticle and resistance at the surface of the microparticle with some external film resistance.

2.3.2.2 Adsorption Separation and Purification Processes

The main area of current application of adsorption is in separation and purification processes. Many different ways of operating such processes have been devised and it is helpful to consider the various systems according to the mode of fluid-solid contact (see Figure 2.7). In a cyclic batch process at least two beds are employed and each bed is successively saturated with the preferentially adsorbed species (or class of species) during the adsorption step and then regenerated during a desorption step in which the direction of mass transfer is reversed to remove the adsorbed species from the bed. In the continuous countercurrent process the adsorbent can be regarded as circulating continuously between the adsorption and desorption beds, in both of which fluid and solid contact in countercurrent flow. More commonly, as in the Sorbex type of process, the adsorbent is not physically circulated but the same effect is achieved in a fixed adsorbent bed equipped with multiple inlet and outlet ports to which the fluid streams are directed in sequence. Such systems can achieve a close approximation to counter-current flow without the problems inherent in circulating the solid adsorbent. However, the system is relatively expensive, so it is generally used only for difficult separations (low separation factor) which cannot be carried out efficiently in a simple batch process.
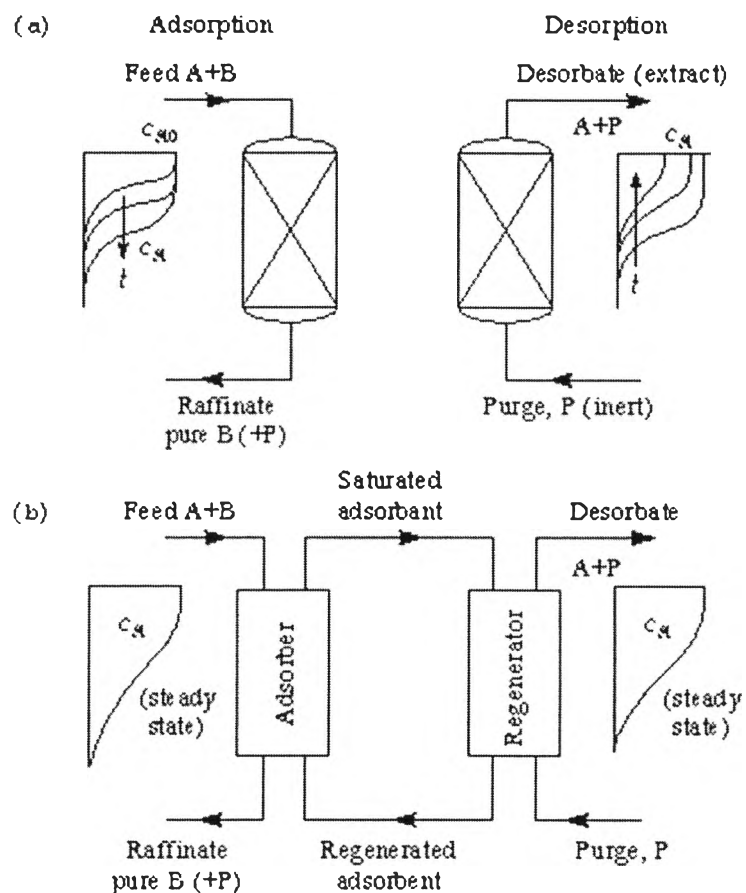
Figure 2.7 The two basic modes of operation for an adsorption process: (a) cyclic batch system; (b) continuous counter current system with adsorbent recirculation (Kirk-Othmer, 2004).

The other major difference between adsorption processes lies in the method by which the adsorbent bed is regenerated. The advantages and disadvantages of three different methods - temperature swing, pressure swing, and displacement are summarized in Table 2.3. For efficient removal of trace impurities it is normally essential to use a highly selective adsorbent on which the sorbate is strongly held. Temperature swing regeneration is therefore generally used in such applications. However, in bulk separations all three regeneration methods are widely used" (Kirk-Othmer, 2004).

Table 2.3 Factors governing choice of regeneration method (Kirk-Othmer, 2004)

Method	Advantages	Disadvantages
thermal swing	- good for strongly adsorbed species; small change in T gives large change in q* - desorbate may be recovered at high concentration - gases and liquids	- thermal aging of adsorbent - heat loss means inefficiency in energy usage unsuitable for rapid cycling, so adsorbent cannot be used with maximum efficiency - in liquid systems the latent heat of the interstitial liquid must be added
pressure swing	- good where weakly adsorbed species is required at high purity - rapid cycling efficient use of adsorbent	- very low P may be required - mechanical energy more expensive than heat -desorbate recovered at low purity
displacement desorption	- good for strongly held species - avoids risk of cracking reactions during regeneration	- product separation and recovery needed (choice of desorbent is crucial)

Table 2.3 Factors governing choice of regeneration method (Kirk-Othmer, 2004) (Cont'd)

Method	Advantages	Disadvantages
displacement desorption	- avoids thermal aging of adsorbent	

In 2009, Lu *et al.* studied thermodynamics and regeneration of CO_2 adsorption from mesoporous spherical-silica particles (MSPs) modified by N-[3-(trimethoxysilyl) propyl]ethylenediamine (EDA). The thermodynamic analysis gave low isosteric (having the same number of valence electrons in the same configuration but differing in the kinds and numbers of atoms.) heats of adsorption, which are typical for physical adsorption. The adsorption process was endothermic in 20–60 °C but exothermic in 60–150 °C. The cyclic CO_2 adsorption via MSP (EDA) showed that the adsorbed CO_2 can be effectively desorbed at 120 °C for 25 min while the adsorbed CO_2 due to physical interaction can be effectively desorbed at 0.145 bar for 30 min. The desorption time of spent MSP (EDA) can be further shortened to 7.5 min via a combination of thermal treatment and vacuum suction. The adsorption performance, the crystal phase and the surface functional groups of MSP (EDA) were preserved during 15 cycles of adsorption and regeneration. This suggests that the MSP (EDA) can be employed in the prolonged cyclic CO_2 adsorption with low energy penalty for desorption process. The MSP (EDA) is thus possibly cost-effective sorbents for CO_2 capture from flue gases in the foreseeable future.

In 2010, Hsu *et al.* studied thermodynamics and regeneration of CO_2 adsorption from multiwalled carbon nanotubes (CNTs) that were fabricated and modified by 3-aminopropyl-triethoxysilane (APTS) solutions. The results showed thermodynamic analysis indicated that the CO_2 adsorption on CNTs and CNT (APTS) is exothermic and typical for physical adsorption. The cyclic CO_2 adsorption on CNT(APTS) showed that the adsorbed CO_2 can be effectively desorbed at 120°C for 25 min while the adsorbed CO_2 due to physical interaction can

be effectively desorbed at 0.145 atm for 30 min. The regeneration time can be further shortened to 5 min via a thermal/vacuum desorption and thus reduces a significant amount of energy penalty. The adsorption capacity, the pore structure, the crystal phase and the surface functional groups of CNT (APTS) were preserved in the 20 cycles of adsorption and regeneration. This suggests that the CNT (APTS) can be used in prolonged cyclic operation. The CNT (APTS) are thus possible cost-effective CO_2 sorbents in the predictable future.

2.3.3 Membrane

Membranes are semi-permeable barriers able to separate substances by various mechanisms (adsorption/diffusion, solution/diffusion, molecular sieve and ionic transport) (Olajire, 2010). Their separation efficiency depends on the CO_2 partial pressure. Although membranes have several advantages over absorption and adsorption processes (no regeneration energy required, simple modular systems, no waste streams). Membranes cannot always achieve high degrees of separation, which makes multiple stages or recycling necessary. Another disadvantage of membranes is the sensitivity to sulphur compounds and other trace elements (Figueroa *et al.*, 2008).

2.3.4 Cryogenic

The cryogenic method of purification involves the separation of the gas mixtures by fractional condensation and distillation at low temperature (Olajire, 2010). This physical process is proper for treating flue gas streams with high CO_2 concentrations considering the costs of refrigeration. This is regularly used for CO_2 capture for oxyfuel process. The process has the preference that it allows recovery of pure CO_2 in the form of a liquid, which can be transported (Wang *et al.*, 2010).
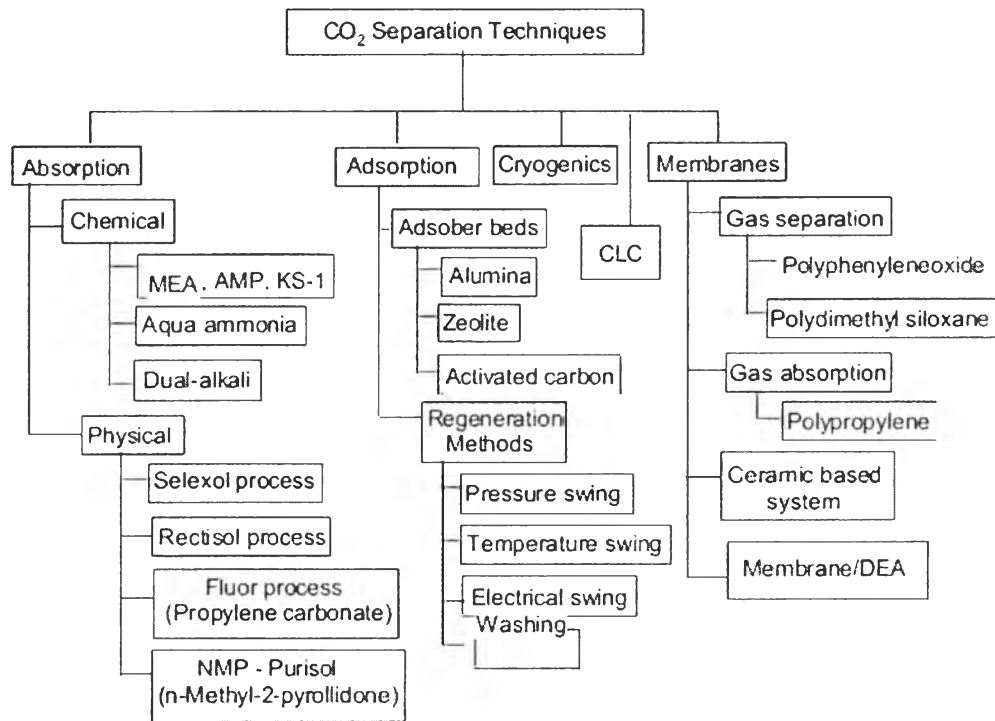
Figure 2.8 Technology options for CO_2 separation (Olajire, 2010).

Table 2.4 Summary of current status of CO_2 separation techniques (Olajire, 2010)

Separation Techniques	Type	Status
Chemical absorption	MEA KS-1	Commercially available
Physical adsorption	PSA method PTSA method	Under research
Membranes	Polymeric Inorganic Zeolite	Commercially available

Table 2.4 Summary of current status of CO_2 separation techniques (Olajire, 2010) (Cont'd)

Separation Techniques	Type	Status
Membranes	Silica	Commercially available
Amine and membranes	Amine solvent + membrane	Under research
CLC	MeO {Me = Ni, Cu, Mn or Fe}	Commercially available
Cryogenic	Cryogenic	Commercially available

2.4 Biopolymer

Biopolymers are polymers produced by living organisms. Since they are polymers, Biopolymers contain monomeric units that are covalently bonded to form larger structures. There are three main classes of biopolymers based on the differing monomeric units used and the structure of the biopolymer formed. Polynucleotides long polymers which are composed of thirteen or more nucleotide monomers, polypeptides short polymers of amino acids, and polysaccharides which are often linear bonded polymeric carbohydrate structures.

2.4.1 Chitosan
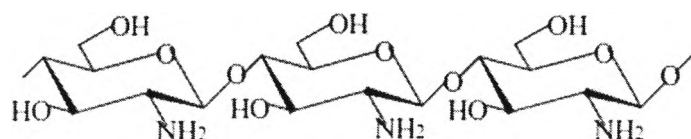
Figure 2.9 Structure of Chitosan (Krajewska, 2004).

Chitin has been found in a wide range of natural sources e.g. crustaceans, fungi, insects, annelids, molluscs, and coelenterata. However chitosan is only manufactured from crustaceans e.g. crab, krill, and crayfish primarily because a large amount of crustacean exoskeleton is available as a byproduct of food processing (Shepherd *et al.*, 1997). Chitosan as its structure shown in Figure 2.9 is deacetylated product of chitin, which soluble in dilute acids such as acetic acid, formic acid. Chitosan is used as a ß-flocculant, clarifier, thickener, fibre, film, affinity chromatography column matrix, gas-selective membrane, plant disease resistance promotor, anti-cancer agent, wound healing promoting agent and antimicrobial agent. It is used as a processing aid for applications in fruit preservation, wound dressings, cosmetics, artificial organs and pharmaceuticals (Kumar, 2000). Applications of chitosan are given in Table 2.5.

Table 2.5 Principal applications for chitosan (Rinaudo, 2006)

Types of Usage	Applications
Agriculture	- Defensive mechanism in plants - Stimulation of plant growth - Seed coating, Frost protection - Time release of fertilizers and nutrients into the soil
Water & waste Treatment	- Flocculant to clarify water (drinking water, pools) - Removal of metal ions - Ecological polymer (eliminate synthetic polymers) - Reduce odors

Table 2.5 Principal applications for chitosan (Rinaudo, 2006) (Cont'd)

Types of Usage	Applications
Food & beverages	- Not digestible by human (dietary fiber) - Bind lipids (reduce cholesterol) - Preservative - Thickener and stabilizer for sauces - Protective, fungistatic, antibacterial coating for fruit
Cosmetics & toiletries	-Maintain skin moisture -Treat acne -Improve suppleness of hair -Reduce static electricity in hair -Tone skin -Oral care (toothpaste, chewing gum)
iopharmaceutics	-Immunologic, antitumoral -Hemostatic and anticoagulant -Healing, bacteriostatic

In 2007, Hoven *et al.* studied positive and negative charges that were introduced to chitosan surfaces via methylation using methyl iodide (MeI) and reductive alkylation using 5-formyl-2-furan sulfonic acid (FFSA). The Results showed the presence of N-sulfofurfuryl and quaternary ammonium groups has a remarkable impact on how the chitosan film responds to charged proteins in terms of adsorbed quantity and selectivity. It is interesting that the surface-modified chitosan films having similar wettability as judged by the contact angle analysis but distinguishable charge characteristics essentially possess different responses to proteins. The ability to sustain their charges in a broader pH range should make these

surface-charged chitosan films more versatile for applications than the native chitosan films for which the charge is altered as a function of environmental pH.

In 2009, Aranaz *et al.* studied the physicochemical properties of the polymers and their behaviour. A functional characterization of chitin and chitosan regarding some biological properties and some specific applications is presented. These results are shown in Table 2.6.

Table 2.6 General recommendations for the use of chitin and chitosan in several applications (Aranaz *et al.*, 2009)

Application	General Recommendations
Wound healing	- High DD chitosan preferred over chitin - Low Mw samples (oligomers)
Drug delivery systems	- High DD - High Mw
Gene Delivery	- DD $\leq$ 80 - Low Mw (around 10 kDa)
Scaffolds (tissue engineering)	- DD around 85 (good proliferation and structure) - High Mw (prolonged biodegradation)
Cell immobilization	- Chitosan preferred over chitin (high DD)
Enzyme immobilization	- Depend on the enzyme, immobilization method and reaction media - Low ash content - β-chitin preferred over α-chitin in organic reaction media

Table 2.6 General recommendations for the use of chitin and chitosan in several applications (Aranaz *et al.,* 2009)

Application	General Recommendations	
Enzyme immobilization	Adsorption	- Chitin for neutral or positively charged proteins - Chitosan for negatively charged proteins. High DD
	Covalent	- Chitosan for multipoint immobilization. High DD - Chitin or chitosan with low DD for single point immobilization
	Encapsulation	- Chitosan-TPP High Mw, high DD better retention - Chitosan-Alginate PECs Medium Mw better stability
Dietary ingredient	- High DD; high Mw (viscosity) - Fine particle	
Food preservative	- High DD - Medium-low Mw (5-80 kDa)	
Emulsifying agent	- Low DD for emulsion stability - High viscosity	
Waste water treatment	- Depend on pollutant and water conditions (pH, ionic strenght) - In general, chitosan preferred over chitin. High DD Low cristallinity	

Table 2.6 General recommendations for the use of chitin and chitosan in several applications (Aranaz *et al.*, 2009) (Cont'd)

Application	General Recommendations	
Molecular imprinting	- Not yet tested - High DD is expected to improve crosslinking - In general, low Mw chitosan is used	
Metal reduction	- Metal reduction depends on chitosan characteristics (not yet fully tested) - High DD and low Mw seems to stabilize the nanoparticles	
	Clear relationship between morphology and Mw	- Low Mw chitosan 2D chains - Medium Mw chitosan: single nanoparticles - High Mw chitosan: nanoplates

2.5 Amino Acids

Amino acids are molecules containing an amine group, a carboxylic acid group and a side-chain that varies between different amino acids. The key elements of an amino acid are carbon, hydrogen, oxygen, and nitrogen. They are particularly important in biochemistry, where the term usually refers to *alpha-amino acids*.

An alpha-amino acid has the generic formula $H_2NCHRCOOH$, where R is an organic substituent; the amino group is attached to the carbon atom immediately adjacent to the carboxylate group (the α–carbon). Other types of amino acid exist when the amino group is attached to a different carbon atom; for example, in gamma-

amino acids (such as gamma-amino-butyric acid) the carbon atom to which the amino group attaches is separated from the carboxylate group by two other carbon atoms. The various alpha-amino acids differ in which side-chain (R-group) is attached to their alpha carbon. and can vary in size from just one hydrogen atom in glycine to a large heterocyclic group in tryptophan.

Amino acids are critical to life, and have many functions in metabolism. One particularly important function is to serve as the building blocks of proteins, which are linear chains of amino acids. Amino acids can be linked together in varying sequences to form a vast variety of proteins. Twenty-two amino acids are naturally incorporated into polypeptides and are called proteinogenic or standard amino acids. Of these, twenty are encoded by the universal genetic code. Eight standard amino acids are called "essential" for humans because they cannot be created from other compounds by the human body, and so must be taken in as food.

Due to their central role in biochemistry, amino acids are important in nutrition and are commonly used in food technology and industry. In industry, applications include the production of biodegradable plastics, drugs, and chiral catalysts. Types of amino acids can be divided into twenty types as shown in Table 2.7

Table 2.7 Types of amino acids (http://www.bioscience.org/urllists/aminacid.html)
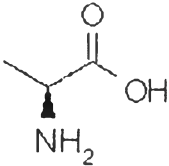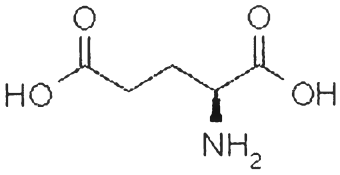
Name Abbreviation	Mol Wt.	pI	CAS Registry Number	Structure formula
Alanine ala, a	89.09	6.00	56-41-7	CH3-CH(NH2)-COOH

Table 2.7 Types of Amino Acids(http://www.bioscience.org/urllists/aminacid.htm) (Cont'd)

Name Abbreviation	Mol Wt.	pI	CAS Registry Number	Structure formula
Arginine arg, r	174.20	11.15	74-79-3	HN=C(NH2)-NH-(CH2)3-CH(NH2)-COOH
Asparagine asn, n	132.12	5.41	5794-13-8	H2N-CO-CH2-CH(NH2)-COOH
Cysteine cys, c	121.15	5.02	52-90-4	HS-CH2-CH(NH2)-COOH
Glutamine gln, q	146.15	5.65	56-85-9	H2N-CO-(CH2)2-CH(NH2)-COOH

Table 2.7 Types of amino acids (http://www.bioscience.org/urllists/aminacid.htm)
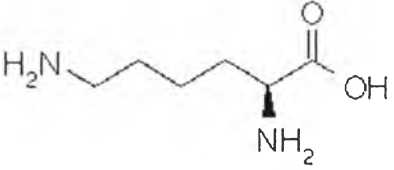(Cont'd)
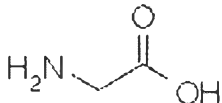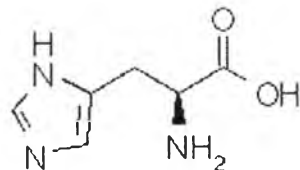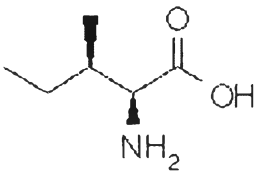
Name Abbreviation	Mol Wt.	pI	CAS Registry Number	Structure formula
Glutamic acid glu, e	147.13	3.22	56-86-0	HOOC-(CH2)2-CH(NH2)-COOH
Glycine gly, g	75.07	5.97	56-40-6	NH2-CH2-COOH
Histidine his, h	155.16	7.47	71-00-1	N=C-NH-C=C-CH2-CH(NH2)-COOH
Isoleucine ile, i	131.17	5.94	73-32-5	CH3-CH2-CH(CH3)-CH(NH2)-COOH

Table 2.7 Types of amino acids (http://www.bioscience.org/urllists/aminacid.htm) (Cont'd)
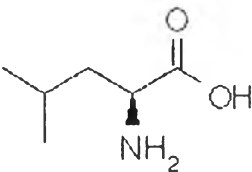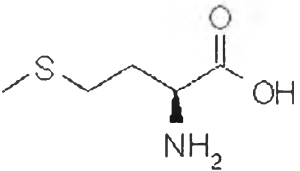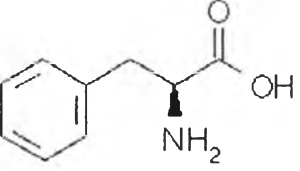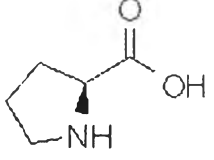
Name Abbreviation	Mol Wt.	pI	CAS Registry Number	Structure formula
Leucine leu, l	131.17	5.98	61-90-5	(CH3)2-CH-CH2-CH(NH2)-COOH
Lysine lys, k	146.19	9.59	39665-12-8	H2N-(CH2)4-CH(NH2)-COOH
Methionine met, m	149.21	5.74	63-68-3	CH3-S-(CH2)2-CH(NH2)-COOH
Phenylalanine phe, f	165.19	5.48	63-91-2	Ph-CH2-CH(NH2)-COOH
Proline pro, p	115.13	6.30	147-85-3	NH-(CH2)3-CH-COOH

Table 2.7 Types of amino acids (http://www.bioscience.org/urllists/aminacid.htm) (Cont'd)
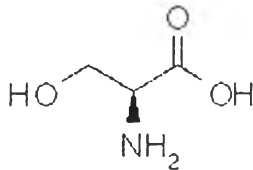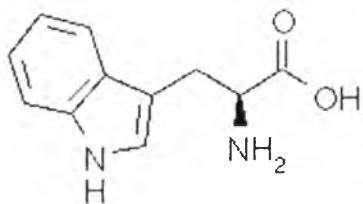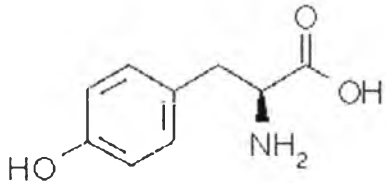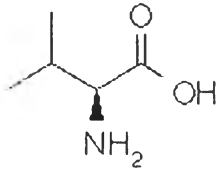
Name Abbreviation	Mol Wt.	pI	CAS Registry Number	Structure formula
Serine ser, s	105.09	5.68	56-45-1	HO-CH2-CH(NH2)-COOH
Threonine thr, t	119.12	5.64	72-19-5	CH3-CH(OH)-CH(NH2)-COOH
Tryptophan trp, w	204.23	5.89	73-22-3	Ph-NH-CH-C-CH2-CH(NH2)-COOH
Tyrosine tyr, y	181.19	5.66	60-18-4	HO-p-Ph-CH2-CH(NH2)-COOH

Table 2.7 Types of amino acids (http://www.bioscience.org/urllists/aminacid.htm)
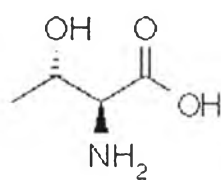(Cont'd)

Name Abbreviation	Mol Wt.	pI	CAS Registry Number	Structure formula
Valine val, v	117.15	5.96	72-18-4	CH3-CH(CH2)-CH(NH2)-COOH

2.5.1 Arginine

Arginine ($C_6H_{14}N_4O_2$ or (*S*)-2-Amino-5-guanidinopentanoic acid) is an α-amino acid. The L-form is one of the twenty most common natural amino acids. At the level of molecular genetics, in the structure of the messenger ribonucleic acid mRNA, CGU, CGC, CGA, CGG, AGA, and AGG, are the triplets of nucleotide bases or codons that codify for arginine during protein synthesis.

The amino acid side chain of arginine consists of a 3-carbon aliphatic straight chain, the distal end of which is capped by a complex guanidinium group. With a pK_a of 12.48, the guanidinium group is positively charged in neutral, acidic and even most basic environments, and thus imparts basic chemical properties to arginine. Because of the conjugation between the double bond and the nitrogen lone pairs, the positive charge is delocalized, enabling the formation of multiple H-bonds as shown in Figure 2.10.
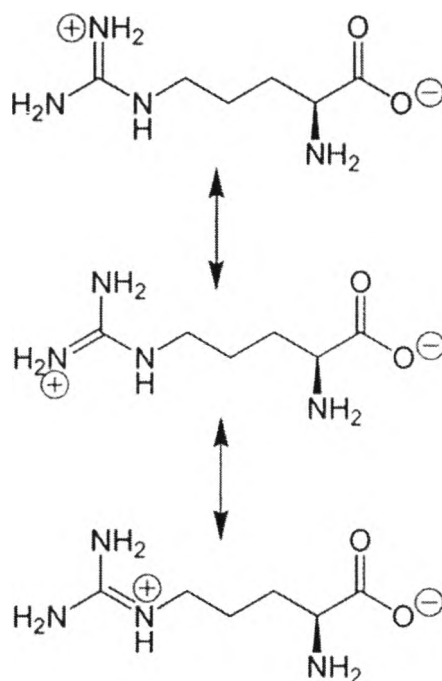
Figure 2.10 Delocalization of charge in guanidinium group of L-arginine.

Arginine plays an important role in cell division, the healing of wounds, removing ammonia from the body, immune function, and the release of hormones. Arginine taken in combination with proanthocyanidins or yohimbine, has also been used as a treatment for erectile dysfunction.

The benefits and functions attributed to oral supplementation of L-arginine include:

- Precursor for the synthesis of nitric oxide (NO)
- Reduces healing time of injuries (particularly bone)
- Quickens repair time of damaged tissue
- Helps decrease blood pressure

In 2004, Liu *et al.* studied anticoagulation biomaterial from Chitosan (CS) that was modified with arginine using N-hydroxysuccinimide (NHS) and 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) as coupling agents. FT-IR and NMR spectra showed that arginine was chemically coupled to CS to form a chitosan-arginine conjugate (CS-ArgC). Results showed that the substitution

degree of arginine in CS estimated from elemental analysis was 20.1%. In summary, this work demonstrated that chitosan-arginine could be synthesized using EDC and NHS as coupling agents. EDC and NHS can significantly prolong activated partial thromboplastin time (APTT). The APTT of CS-ArgC membrane was prolonged two times as that of CS counterpart. The CS-ArgC has potential as a new anticoagulation biomaterial.

In 2009, El-Azzami and Grulke. studied CO_2-selective membranes that obtain high CO_2 permeabilities accompanied with high CO_2/H_2 and CO_2/N_2 separation factors at industrial temperatures and pressures applicable to fuel cell operations and flue gas purification. By separation of carbon dioxide from a mixed gas stream of hydrogen and nitrogen by a chitosan membrane containing 40 wt% sodium arginate. Continuous membrane separations were done for a feed gas with 10% carbon dioxide, feed gas total pressures of 152 and 507 pa (1.5 and 5 atm), and temperatures ranging from 20 to 150 °C. Results showed that at 152 pa (1.5 atm) feed pressure and 110 °C, there are maximum in the carbon dioxide permeabilities (1500 barrers), and the separation factors for CO_2/N_2 (852) and CO_2/H_2 (144). At higher pressure (507 pa or 5 atm), there were no maximum in the carbon dioxide permeabilities or separation factors, and there was less bound water in the membrane. The addition of arginine salts increases the number of amino groups for facilitated transport of CO_2 and increases the water levels in the arginine salt–chitosan membranes compared to swollen chitosan membranes at the same humidification conditions. The enhanced membrane performance could be correlated with membrane water contents at the various operating conditions. As with the performance of swollen chitosan membranes, free water in arginine salt–chitosan membranes decrease with temperature and increase with feed stream pressure. When operating conditions excluded free water from the membrane (T=150°C), carbon dioxide permeability and selectivities correlated directly with bound water levels. Similar to swollen chitosan membranes, the arginine salt–chitosan membranes had a maximum CO_2 permeability at 110 °C; above this temperature, all free water was lost from the membrane, reducing the facilitated transport pathway.

In 2009, Holst. studied towards the kinetics of CO_2 with several aqueous salts of amino acids at temperature of 298 K. In a preliminary screening at a

concentration of 0.5 mol/L the potassium salts of 6-aminohexanoic acid, β-alanine, l-arginine, l-glutamic acid, dl-methionine, l-proline and sarcosine were investigated. The aqueous potassium salts of sarcosine and proline were considered to be the most promising solvents. For these solvents and the corresponding lithium solvents, the physical distribution coefficient of N_2O was determined for various temperatures and concentrations. Subsequently, the kinetics were studied at 298 K in which the concentration of the amino acid salts was varied between 0.5 and 3 $molL^{-1}$. Results showed that the kinetics for the sarcosine salts seem to be independent on the counter-ion (Li^+ or K^+), potassium prolinate solutions seems to have a substantially higher apparent rate constant than the lithium salt.

In 2011, Xiao *et al.* studied a series of water-soluble chitosan-N-arginine (CS-N-Arg) with various degrees of substitution (DSs) synthesized by reacting amino groups of chitosan with arginine. Results showed that CS-N-Arg had a more amorphous structure than that of chitosan, and the thermal stability of CS-N-Arg was slightly lower than that of chitosan. The degrees of substitution of arginine could be changed from 8.7 to 28.4% under the various reaction periods from 12 to 48 h. It was found that CS-N-Arg samples were able to inhibit almost all the bacteria (Staphylococcus aureus and Escherichia coli) at a concentration higher than 150 ppm, whereas they could promote the growth of bacteria at a concentration lower than 50 ppm.

2.6 Literatures

In 2002, Gray *et al.* studied how to impregnate amine group on fly, silica gel, activated carbon, molecular sieve. These samples were place in a H_2O / CO_2 / He stream and DRIFTS, TPD, and MS analyses were used to determine the CO_2 capture capacity. The adsorption / desorption of CO_2 for these samples were determined over the temperature range of 25 to 120 °C. Results of CO_2 capture on amine grafted adsorbents are compared to the normal adsorbents as shown in Table 2.8.

Table 2.8 Alternative oxygen-rich solid substrates tested as amine-enriched sorbents for the capture of CO_2 (Gray *et al.*, 2002)

Sample	μ mole / g CO_2 captured
Fly ash	24.4
Amine-fly ash	174.6
Silica gel	4.9
Amine-silica gel	31.6
Activated carbon	8.0
Amine-Activated carbon	28.7
Molecular sieve 13X	13.6
Amine-molecular sieve 13X	15.8

In 2009, Gray *et al.* used 40% polyethylenimine (PEI) immobilized in the CARiACT and Diaion adsorbents to approach the projected performance target of a delta loading of 3 mol of CO_2/kg of sorbent with a heat of reaction 580 Btu/lb. CO_2 was substrates by PEI immobilized in the CARiACT and Diaion under low humidity conditions. Results showed the CARiACT sorbent has shown acceptable thermal stability over 10 cycle test periods under dry CO_2 conditions. Furthermore, application of CO_2 as the sweep gas during the regeneration stage significantly reduced the delta loading, and steam could be considered as an alternative sweep gas. To make available optimized reaction conditions for the design of reactors capable of capturing CO_2, the total effect of moisture on the sorbents must be determined over the range of concentrations anticipated for such a capture process. In addition, the total regeneration heat duty for these sorbents must not exceed the value of 500-1,000 Btu/lb to be significantly better than existing MEA liquid amine systems.

In 2009, Singh *et al.* determined structure and activity relationships of various amine-based CO_2 absorbents in which the absorption of pure CO_2 at atmospheric pressure was measured to assess the total absorption rates and capacities. Steric hindrance effect was noticed when side chain with alkyl group was present at the α-carbon to the amine group in the absorbent structure. An increase in the number of amine groups in absorbent structure, results in a higher capacity of up to 3.03 moles CO_2/moles amine. Aromatic amines substituted with alkyl groups at the 2nd and 5th position show an increase in both absorption rate and capacity.

In 2009, Wang *et al.* studied adsorption and desorption of carbon dioxide, methane and other gases on coals using representative Zhongliangshan coals. Gas adsorption is one of the major concerns for both CO_2 sequestration and methane recovery processes. The experiments were carried out using both single and multi-component mixtures at 25 °C and 30 °C with the highest pressure of 12 MPa. The coal was under moisture equilibrated conditions. This provides experimental data from which a predictive assessment of CO_2 sequestration and/or methane recovery can be conducted. The results showed that for pure gasses the CH_4 adsorption capacity is higher than the N_2 adsorption capacity but lower than the CO_2 adsorption capacity. The irregular variance is observed in the CH_4 and CO_2 components at pressures over 6.14-6.42 MPa. Under these experimental conditions this is due to the supercritical nature of the CO_2. Otherwise, the desorbed CH_4 is maximum at pressures of 6.14-6.42 MPa. Then it decreases slightly as the pressure drops. Therefore, it sequesters large amounts of CO_2, or other gases, which can significantly affect the CH_4 desorption and allow enhanced CH_4 recovery from coals.

In 2011, Darde *et al.* measured a rate of absorption of carbon dioxide by aqueous ammonia and by performing process simulation. The overall mass transfer coefficient was measured at temperatures from 279 to 304 K for 1 to 10 wt% ammonia solutions at loading up to 0.6. The results were compared with those found for 30wt% monoethanolamine (MEA) solutions. Results showed that the rate of absorption of carbon dioxide by 10 wt% ammonia solutions at 304 K is in the same range as the one observed with 30 wt% MEA solutions at 314 K. However, at low temperature, the rate of absorption with ammonia solutions is significantly lower than with MEA solutions at 314 K. Therefore, a higher contact area between the

liquid and the gas is required for the chilled ammonia process where absorption occurs at low temperature.

In 2011, Ko *et al.* studied reversible capture of CO_2 is aprominent feature of CO_2 organic-inorganic hybrid adsorbent to sequester CO_2, Herein, (3-aminopropyl) trimethoxysilane (APTMS), [3-(methylamino) propyl] trimethoxysilane (MAPTMS), and [3-(diethylamino) propyl] trimethoxysilane (DEAPTMS) are immobilized on highly ordered mesoporous silicas (SBA-15) to catch CO_2 on primary, secondary, and tertiary aminosilica adsorbents. This result was first discovered using CO_2 adsorption kinetics and thermodynamics. APTMS, MAPTMS, and DEAPTMS were immobilized on highly ordered mesoporous silicas (SBA-15) to compare CO_2 capturing effects as primary (1°), secondary (2°), and tertiary (3°) amino-adsorbents, respectively. The results showed the maximum capacities of SBA-15-NH_2, SBA-15-NH-CH_3, and SBA-15-N(CH_2CH_3)$_2$ were 0.95, 0.75, 0.17 mmol CO_2/g adsorbent, respectively. While the CO_2 adsorption rate constants for three types of adsorbents were comparable, the desorption rate constant for the SBA-15-NH_2 was almost 4 times lower than that for the SBA-15-N(CH_2CH_3)$_2$. This implies that the adsorbate molecules were more tightly bound to the adsorbent, consistent with the increased interaction potential within the mesopores. In summary, the adsorbed CO_2 is easily desorbed from the adsorbent with the low energy consumption in the order of tertiary (3°), secondary (2°), and primary (1°) amino-adsorbents while the adsorption amount and the bonding-affinity increase in the reverse order.

In 2011, Maiti *et al.* explored new amine-based chemistry for CO_2 capture at large industrial scales that performed atomistic modeling of CO_2 chemisorption in aqueous solutions of primary and tertiary amines. The density functional theory (DFT)-based quantum chemical solvation calculations are shown to yield a number of important results, including the relative stability of ion species (carbamate versus bicarbonate), heat of absorption, and density and volumes changes as a function of CO_2 loading. Good agreement of simulation results with available experimental data provides confidence in the accuracy of such computational methods in predicting properties of new solvent systems and capture designs as shown in Table 2.9-2.10

Table 2.9 Computed heats of CO_2 absorption (ΔH) per mole of CO_2 at 25 °C in 30 wt% MEA and 45 wt% MDEA solutions (Maiti *et al.*, 2011)

Reaction	Amine/water ratio	CO₂ loading	ΔH (kJ/mol)
R1	30 wt% MEA	0.0	-78.8
		0.25	-82.1
		0.5	-81.1
R2	30 wt% MEA	0.0	-60.6
		0.25	-63.0
		0.5	-64.8
		0.75	-66.3
		1.0	-67.6
R3	45 wt% MDEA	0.0	-47.2
		0.25	-46.6
		0.5	-45.6
		0.75	-44.4
		1.0	-42.8

Table 2.10 Computed vs. experimental density at 25 °C in various amine solutions and CO_2 loading levels (Maiti *et al.*, 2011)

System	Computed Density (MD) (g/cm3) †	Experimental Density (g/cm³)
Pure MEA	1.020	1.012
Pure MDEA	1.035	1.038
30 wt% MEA, 0 CO2 loading	1.015	1.013 , 1.010
45 wt% MDEA, 0 CO2 loading	1.040	1.039 , 1.040
30 wt% MEA, 0.5 CO2 loading	1.165,* 1.030**	1.117 , 1.121
45 wt% MDEA, 0.5 CO2 loading	1.150,* 1.050**	1.115

†Rounded to 0.005 g/cm3

$*CO_2$ 100% chemisorbed (i.e. ions formed)

$**CO_2$ 100% physisorbed, no ions

In 2011, Nuchitprasittichai and Cremaschi. studied the impact of different amine absorbents and their concentrations, the absorber and stripper column heights and the operating conditions on the cost of CO_2 recovery plant for post-combustion CO_2 removal. The results showed that the absorber height, solvent circulation rate and reboiler duty have the highest impacts on the cost while the stripper height and the regenerator-inlet temperature does not show significant effects. The addition of primary or secondary amines to tertiary amines improves the CO_2 absorption capacity of the mixture. Among the solvents of this study, the 48 wt% DGA with 96% CO_2 removal amount was found to be the lowest cost process due to its high CO_2 absorption capability and low energy consumption.