CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Carbon Dioxide Emission

The emission of greenhouse gases (GHGs) has received widespread attention. Greenhouse gases are composed mainly of methane (CH_4), carbon dioxide (CO_2), chlorofluorocarbons (CFCs) and nitrous oxide (N_2O). Among the greenhouse gases, CO_2 contributes more than 60% to global warming (Albo et al., 2010). Since fossil fuel supplies the world of 81% of its commercial energy, CO_2 annually releases of 30×10^{12} kg (Hester et al., 2010). Nowadays, the CO_2 concentration in atmosphere is closed to 400 ppm which is significantly higher than the preindustrial level of about 300 ppm (Oh, 2010). The increasing level of global CO_2 is the major world concern.

For the global warming mitigation, Kyoto Protocol impulses European Union and 37 industrialized nations to decrease their greenhouse gas emissions to a level of 5.2% on average lower than those of 1990 during the period of 2008 to 2012. The mitigation options to reduce CO_2 greenhouse gas emissions include reducing energy consumption by using energy efficiency improvements, renewable energy sources, switching to less carbon-intensive fuels, nuclear power, and enhancement of biological sinks; however these options might not be the global warming mitigation in the coming future. Carbon capture is recognized as being a major technology to mitigating CO_2 emissions and protecting our environment for future generations, which could potentially reduce overall mitigation costs and increase flexibility in achieving the greenhouse gas emission reductions.

An anthropogenic carbon dioxide (CO_2) capture from fossil-fuel-based electricity generation utilities is of considerable importance because of the large point sources of CO_2 emission (Table 2.1).

Table 2.1 Industrial activity of worldwide large stationary CO_2 sources with emissions more than 0.1 million tonnes of CO_2 ($MtCO_2$) per year (*Intergovernmental Panel on Climate Change (IPCC), 2007*)

Process	Number of sources	Emissions $(MtCO_2yr^{-1})$
Fossil fuels		
Power	4,942	10,539
Cement production	1,175	932
Refineries	638	798
Iron and steel industry	269	646
Petrochemical industry	470	379
Oil and gas processing	Not available	50
Other sources	90	33
Biomass		
Bioethanol and bioenergy	303	91

2.2 Carbon Dioxide

Carbon dioxide (CO_2) is a naturally occurring gas in the atmosphere. Each CO_2 molecule consists of two oxygen atoms and one carbon atom (O=C=O). The bonding between carbon and oxygen atoms is covalently bonds. The properties of carbon dioxide are shown in Table 2.2.

Table 2.2 Properties of carbon dioxide (en.wikipedia.org)

Properties	Value
Molecular weight	44.01 g/mol
Density	1.977 kg/m^3 (gas at 1 atm and 0 °C)
Melting point	-78 °C

Table 2.2 (cont.) Properties of carbon dioxide (en.wikipedia.org)

Properties	Value
Boiling point	-57 °C at 5.185 bar
Viscosity	0.07 cP at -78.5 °C
Appearance	colorless gas
Acidity	6.35, 10.33 pK_a
Diameter	2.8-3.4 Å

2.3 Technologies of CO_2 Capture

The human and industrial activities that produce CO_2 are caused by burning fossil fuels, including coal, oil and natural gas. Carbon capture from fossil fuel power plants can be implemented in three different methods including post-combustion, pre-combustion, and oxyfuel capture (Figure 2.1).
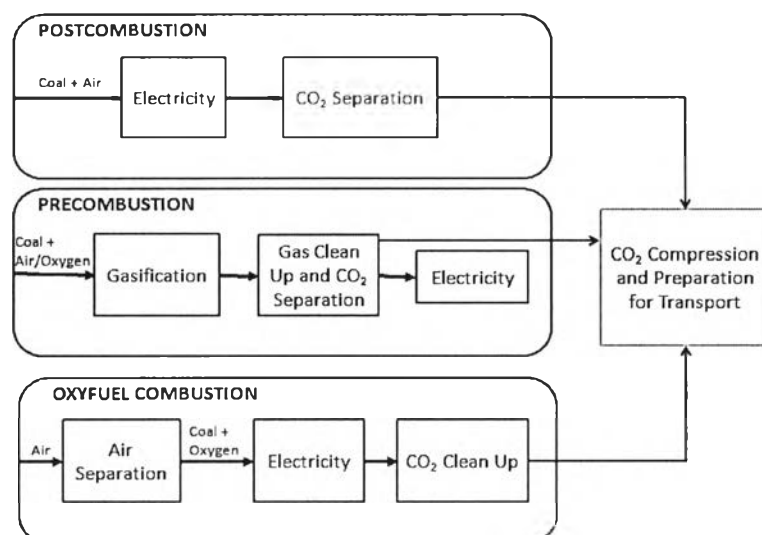

Figure 2.1 Technology alternatives for carbon dioxide capture in the power sector (*International Energy Agency (2009) Technology Roadmap*).
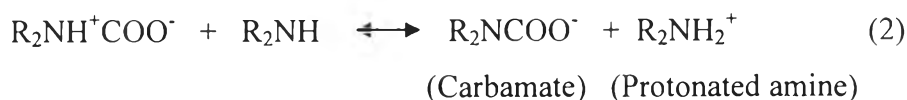
2.4 CO$_2$ Separation Reviews

According to the CO$_2$ capture technology, the post-combustion capture is a straightforward approach in the short-term (Chen *et al.*, 2012). It has been interested in various industrial applications, such as the power plants flue gases, because it can be retrofitted into the existing process without much modification of the existing plants. There are four main CO$_2$ separation approaches: membrane purification, cryogenic distillation, absorption with liquids, and adsorption using solids. Chemical absorption and physical adsorption are currently accepted to be the most suitable methods for post-combustion power plants because cryogenic distillation, although widely used for other gas separations, it requires high energy and membranes have been extensively studied, but are still at the development stage.

2.4.1 Alkanolamine Absorption Technology

Various alkanolamines are applicable for amine based absorption for CO$_2$ removal. Alkanolamine structures (including primary, secondary, tertiary amines) contain at least one hydroxyl group, which is useful to reduce the vapor pressure and to increase their solubilities in an aqueous solution (Kohl and Reisenfeld, 1985) and one amino group which provide sufficient alkalinity to absorb CO$_2$. There are three types of alkanolamines: primary, secondary, and tertiary amines. These classifications are based on the substitution of hydrogen molecule on the nitrogen atom (Hendriks, 1994). Table 2.3 shows structures of common amines. Primary amines, e.g. monoethanolamine (MEA) and diglycolamine (DGA), are the most reactive amines towards CO$_2$. Secondary amines are less reactive with CO$_2$, e.g. diethanolamine (DEA) and diisopropanolamine (DIPA). Tertiary amines, e.g. triethanolamine (TEA) and methyldiethanolamine (MDEA), are the least reactive with CO$_2$. Triethanolamine (TEA) was the first commercially available alkanolamine and was used in early acid gas treating plants. As the result of its low capacity, reactivity, and poor stability, TEA has been mostly displaced by monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), and piperazine (PZ) due to commercial interests.
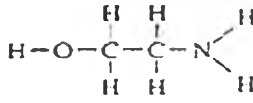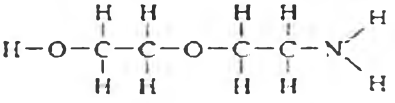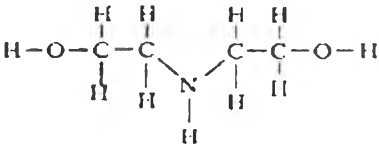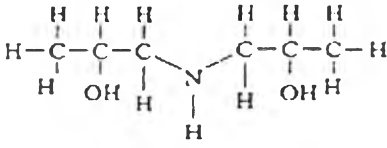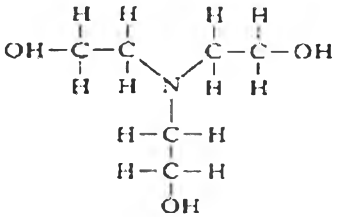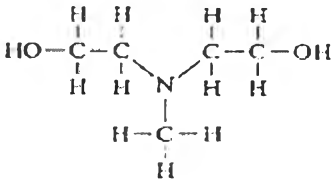
Primary and secondary amines can react with CO_2 directly to form zwitterion first and then to form carbamate.

$$CO_2 + R_2NH \longleftrightarrow R_2NH^+COO^- \quad \text{(Zwitterions)} \quad (1)$$

$$R_2NH^+COO^- + R_2NH \longleftrightarrow R_2NCOO^- + R_2NH_2^+ \quad (2)$$

$$\text{(Carbamate)} \quad \text{(Protonated amine)}$$

Tertiary amines react with CO_2 through a different mechanism. Instead of reacting directly with CO_2, the reaction is to form bicarbonate but cannot form carbamate, because the structure lacks of hydrogen to attach the nitrogen atom. The mechanism of tertiary amine reaction is shown in equation (3).

$$CO_2 + R_3N + H_2O \longleftrightarrow HCO_3^- + R_3NH^+ \quad (3)$$

$$\text{(Bicarbonate)}$$

Table 2.3 Structural formula of common alkanolamines (Kohl and Reisenfeld, 1985)

Industrially, MEA has been proven as a practical absorption solvent because MEA has the highest alkalinity and reacts most rapidly with CO_2. However,

MEA requires high energy consumption during high temperature absorbent regeneration. Since high heat of absorption is associated with carbamate formation reaction, the solvent regeneration costs are high when MEA is used. The other disadvantages of MEA include (Fauth *et al.*, 2005) (1) low carbon dioxide loading capacity, whereby two moles of primary amines or secondary amines can only absorb up to one mole of CO_2. Then, their loadings are limited to 0.5 mol of CO_2/ mol of amine regarding to corrosion, (2) degradation in the presence of oxygen (O_2), (3) have the highest equipment corrosion rate among commercial amines, and (4) have a substantially higher vapor pressure than other alkanolamines.

MEA, DEA and MDEA are regularly used as absorbents. The proposed mechanism of reactions between CO_2 and amines as shown in Figure 2.2 are formation of bicarbonate. In aqueous media, 2 mol of amine are used per mol of CO_2 for the formation of stable bicarbonate.
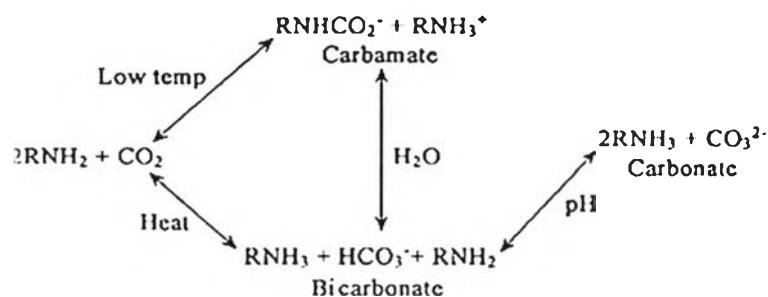
Figure 2.2 Proposed reactions of carbon dioxide in aqueous amine-based systems (Gray *et al.*, 2005).
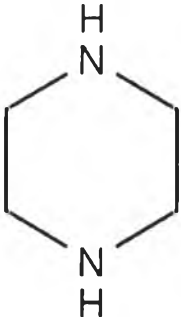
For MDEA, it not only has a low heat of regeneration, but also it has a maximum loading capacity of 1.0 mol of CO_2/ mol of amine. Furthermore, it is less corrosive than MEA. However, aqueous MDEA (a tertiary amine) does not react with CO_2 directly because it lacks the N-H bond required to form the carbamate ion with CO_2. Instead, an aqueous solution of MDEA will promote the hydrolysis of CO_2 to form bicarbonate and a protonated amine.

2.4.2 Piperazine Absorption

Piperazine (PZ, the other names are hexahydropyrazine, piperazidine, or diethylenediamine) is an organic compound containing six-membered ring with
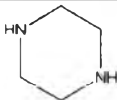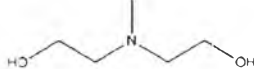
two amine groups, called diamine as shown in Table 2.4. PZ is the corresponding azine of piperadine and it is usually manufactured by reacting of 1,2-dichloroethane with alcoholic ammonia.

Table 2.4 Chemical data and structure of piperazine (Sigma-Aldrich, 2012)

	Molecular formula	$C_4H_{10}N_2$
	Molar mass	86.14 g/mol
	Appearance	White crystalline solid
	Melting point	109-112 °C
	Boiling point	145-146 °C
	Solubility in water	0.9 g/l at 20 °C
	Acidity (pKa)	9.73 (Cullinane and Rochelle, 2006)

Piperazine (PZ) has been used as a promoter to increase the absorption rate of CO_2 capture because of its rapid formation of carbamate with CO_2 (Freeman *et al.*, 2010). As being a good CO_2 capture promoter, the thermodynamic properties of PZ, such as CO_2 solubility, volatility, and heat capacity are listed in Table 2.5. In a recent report, PZ is observed not only to be used effectively for CO_2 absorption with fast kinetic rates, high absorption capacity, and beneficial solvent properties (Freeman *et al.*, 2010), but also to be an effective resistant to oxygen degradation and thermal degradation to a temperature up to 150 °C. However, the solubility of PZ in water is limited, for example, the solubility is 14 wt% at 20 °C, CO_2 capture by a high PZ content solution is therefore needed to carry out at high temperatures.

Table 2.5 Physical and chemical properties of the common used absorbents

Properties	MEA	PZ	MDEA
Molecular structure			
MW (g/mol)	61.08	86.14	119.16
Density at 293 K (g/cm^3)	1.012	1.1	1.038
Boiling point (K)	443	420	243
Vapor pressure at 293 K (kPa)	0.0085	0.1066	0.0013
Vapor pressure at 393 K (kPa)	15.9	41.66	N/A
Solubility (293 K)	Freely soluble	14 wt%	Freely soluble
Pesudo first order rate constant at 298 K (m^3/kmol/s)	7,000 (Hikita *et al.*, 1979)	53,700 (Bishnoi and Rochelle, 2000)	3.5 (Bishnoi and Rochelle, 2002)
CO_2 absorption capacity (mol of CO_2/ mol of absorbent)	0.5	1.0	1.0

Dugas *et al.* (2009) measured the absorption rate and desorption rate of carbon dioxide with monoethanolamine and piperazine in a wetted wall column at 40 °C and 60 °C. CO_2 loading, which represented the range of CO_2 in a coal-fired power plant system were 2, 5, 8, and 12 mole of piperazine (PZ) and 7, 9, 11, and 13 mole of monoethanolamine (MEA). They reported that 8 mole of PZ has about a 75% greater operational CO_2 capacity than 7 mole of MEA. The reaction rates (absorption and desorption) of CO_2 with PZ was 2–3 times faster than MEA at the equivalent CO_2 partial pressure.

Freeman *et al.* (2009) used piperazine as a promoter in amine systems to improve kinetics. PZ can be blended with different alkanolamine, such as MDEA/PZ or MEA/PZ because of its resistance to thermal and oxidative degradation at typical absorption/stripping conditions. The concentration of PZ when used as a promoter is limited to between 0.5 and 2.5 m PZ, because PZ is not highly soluble. Any possibility of precipitation ruled out PZ for use at concentrations above its room temperature solubility.

Cullinane and Rochelle (2006) compared overall rate constants of several amines at 1.0 M and 25 °C as shown in Table 2.6. Piperazine has the highest rate constant because of its structure and it may be attributed to the moderately high pKa. The cyclic diamine structure yields faster rates than would be expected from simple chemical classification or pKa correlation, as it can be observed from other diamine for example; ethylenediamine (EDA) and heterocycles, for example, piperidine and morphorine.

Table 2.6 Overall rate constants for 1.0 M amine at 25 °C (Cullinane and Rochelle, 2006)

Amine	pKa	Rate constant $(s^{-1} \times 10^3)$	$\triangle$Ha (kJ/mol)	Reference
Piperazine	9.73	102.2	35.5	Cullinane and Rochelle, 2006
Monoethanolamine	9.55	5.9	41.2	Hikita *et al.*, 1997 ; Perrin *et al.*, 1981
Diethanolamine	8.88	1.3	53.1	Hikita *et al.*, 1977 ; Christensen *et al.*, 1969
Diglycolamine	9.46	4.52	39.4	Alper *et al.*, 1990 ; Littel *et al.*, 1990
		6.7	40.1	Al-Juaied *et al.*, 2004; Littel *et al.*, 1990

Table 2.6 (cont.) Overall rate constants for 1.0 M amine at 25 °C (Cullinane and Rochelle, 2006)

Amine	pKa	Rate constant $(s^{-1} \times 10^3)$	$\triangle Ha$ (kJ/mol)	Reference
Ethylenediamine	9.91	15.1		Jensen *et al.*, 1995; Christensen *et al.*, 1969
Piperidine	11.12	93.3		Sharma *et al.*, 1969; Christensen *et al.*, 1969
		60.3		Jensen *et al.*, 1952; Christensen *et al.*, 1969
Morpholine (MOR)	8.94	20.6	23.3	Alper *et al.*, 1990 ; Christensen *et al.*, 1969
		20.0		Sharma *et al.*, 1965; Christensen *et al.*, 1969
		22.3		Al-Juaied *et al.*, 2004; Christensen *et al.*, 1969

Samanta *et al.* (2008) studied on the absorption of CO_2 into PZ activated aqueous 2-amino-2-methyl-1-propanol (AMP) solutions at various temperatures with different relative compositions of AMP/PZ in the solutions and various CO_2 partial pressures. It was found that PZ acts as a rate accelerator in combining with 2-amino-2-methyl-1-propanol (AMP). The solubility and diffusivity of CO_2 in the aqueous amine and activated amine solution containing 30wt % total amine and with PZ concentrations of 2, 5 and 8wt % were estimated in a temperature range of 298 K to 313 K using the N_2O- analogy method.

Chemical absorption by alkanolamine is widely used at low partial pressures of CO_2 because of their high reactivity (Donaldson *et al.*, 1980). These amines react with CO_2 at low temperatures and the gas is consequently released at high temperatures, with a complicated chemistry. Many alkanolamine/water

solutions are corrosive and energy consumption in regeneration, thus, the absorption process is costly due to the high heat capacity of amine/ammonia and large amount of water involving in the process. Furthermore, amine and water may enter the gas stream, which limits the process applicability to the environment and a large absorber volume required (Knudsen *et al.*, 2009).

2.4.3 Adsorption Process Technology

Since the aqueous amine absorption processes display some drawbacks, for example, low CO_2 loading and severe absorbent corrosion. The adsorption process technology may be an alternative method to achieve the CO_2 capture purpose.

Alternatively, adsorption is considered as one of the potential options because of possibly low energy requirement, cost advantage, and ease of applicability over a relatively wide range of temperatures and pressure. For the success, this method is dependent on the development of adsorbent with a high CO_2 selectivity and adsorption capacity (Shafeeyan *et al.*, 2010). The development for CO_2 capture adsorbent should satisfy low-cost raw materials, low heat capacity, fast kinetics, high CO_2 adsorption capacity, high CO_2 selectivity and thermal, chemical, and mechanical stabilities under extensive cycling (Sayari *et al.*, 2011). Adsorbent in term of supported amines have the advantages over liquid amines: (1) solvent loss due to evaporation can be less problem for supported amines compared to amine solutions and (2) vessel corrosion is less problematic with supported amines than liquid amines used (Yan *et al.*, 2011).

On account of industrial application, an effective and less energy-consumed regeneration of the CO_2 captured adsorbents is needed. The regeneration techniques are considered by two main adsorption technologies: pressure swing (PSA) and temperature swing adsorption (TSA). The difference between both technologies lies in the strategy to regenerate the adsorbent after the adsorption step. In PSA applications, the pressure of the bed is reduced, whereas in TSA, the temperature is raised while pressure is maintained approximately constant (Plaza *et al.*, 2010).

Pressure swing adsorption (PSA) is an adsorption process using solid sorbent and it is well known as one of the most promising method to recover CO_2.

This technology has gained interest because of its low energy requirements and low capital investment (Liu *et al.*, 2007). In PSA, adsorption is typically performed at pressures higher than atmospheric pressure, while desorption is performed at atmospheric pressure.

2.4.3.1 Chemisorption

There are two types of adsorption depending on the interaction between the adsorbate and adsorbent. Firstly, chemisorption or chemical adsorption, is a kind of adsorption which involves a chemical reaction between the adsorbate and the surface of adsorbent. The chemical bonding, ionic or covalent, depending on the reactive chemical species, is generated on the surface of the adsorbent. The chemical identity and the surface structure are indicating the ability of chemisorption process.

2.4.3.2 Physisorption

Physisorption or physical adsorption is one of the adsorption processes that are absence of the chemical bonding interaction. The interacting force of physisorption is caused by van der Waals force including attractions and repulsions between atoms, molecules, and surfaces. The interaction energy is relatively low (~10-100 meV) in physisorption as compared to the chemisorption (~1-10 eV). The differences between chemisorption and physisorption are summarized in Table 2.7.

Table 2.7 Comparison between chemisorption and physisorption (Ruthven, 1984)

Properties	Chemisorption	Physisorption
Temperature	high temperature	close to boiling point of adsorbate
Interaction	covalent bond	van der Waal force
Binding energy	1-10 eV	10-100 meV
Adsorption rate	maybe slow and irreversible	rapid and reversible
Types of adsorption	monolayer	monolayer or multilayer

The adsorption ability is dependent on the properties of the adsorbent. The adsorbents should have high resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and high surface capacity for adsorption. Most of the solid adsorbents of the industrial applications have a complex porous structure that consists of pores of different sizes and shapes. If the pores are slit shaped measurement used are in term of width but for the pores with a cylindrical shape the term diameter is normally used. The significance of pores in the adsorption processes generally depends on their sizes. Because sizes of micropores are comparable to those of adsorbate molecules, all atoms or molecules of the adsorbent can interact with the adsorbate species. That is the fundamental difference between adsorption in micropores and larger pores like mesopores and macropores. Accordingly, the adsorption in micropores is essentially a pore-filling process in which their volume is the main controlling factor as the important parameter characterizing micropores is their volume usually referred to a unit mass of the solid and characteristics of their sizes.

2.4.3.3 Specific surface area determination, the BET method

The most frequently used method to determine the surface area of a porous material is the Brunauer-Emmet-Teller (BET) method. The method has evolved from the Langmuir theory with multilayer corrections. It is assumed that the adsorbent surface is uniform, adsorbed molecules do not interact, and only a monolayer is formed at the maximum adsorption.

2.4.3.4 Micropore volume, the t-plot method

Each adsorbate-adsorbent system yields a unique isotherm due to variations in the interaction between the species. As a result, each system needs a standard isotherm to estimate the micropore volume, internal and external surface area. The standard isotherm can also be used as a reference for adsorbed layer thickness. The micropore volume is estimated by using a t-plot method.

2.4.3.5 Mesopore size analysis

There are the several methods, i.e. BJH, and KJS. The KJS method was developed to improve the BJH method. But most calculation methods are still based on the Barrett-Joyner-Halenda (BJH) method that assumed all pores

have a cylindrical shape. However, different methods are suitable for different pore and sizes.

There are many types of solid adsorbent used for gas separation, such as zeolites, activated carbon, mesopore supports and metal-organic frameworks.

2.4.3.6 Types of Physisorbent

2.4.3.6.1 Zeolite Structural Characteristic and CO_2 Adsorption Capacity (Chemsuschem, 2009)

Zeolite, a group of porous crystalline aluminosilicates built of a periodic array of TO_4 tetrahedral (T=Si or Al), have been widely used in separation applications mainly because of their unique ability of molecular sieving. The presence of aluminum atoms in these silicate-based molecular sieve materials introduces negative framework charges that are compensated with exchangeable cations in the pore space (alkali cations), and these structural characteristic of zeolites enable them to adsorb wide variety of gas molecules, including acidic gas molecules. The CO_2 adsorption properties of zeolites are also influenced by the porous characteristics of the framework. In comparison, a number of commercially available zeolites including 4A, 5A, 13X, APG-II, and WE-G 592 are being studied. It was reported that the highest adsorption capacities was observed in zeolite 13X, having the largest pore diameter and volume with a surface area of approximately 790 m^2/g.

The adsorption efficiencies of zeolites are largely affected by their size, charge density, and chemical composition of cations in their porous structures (Wang et al., 2011). Accordingly, a number of reports focus on zeolites with highly crystalline structure, high surface area, and 3-dimensional pore structures by altering their composition as Si/Al ratio. Another research field focuses on the exchange with alkali and alkaline-earth cations in the structure of zeolites to enhance the CO_2 adsorption. Though CO_2 adsorption can be enhanced by these approaches, they exist several drawbacks. The CO_2 adsorption capacity and the CO_2/N_2 selectivity are relatively low (Sayari et al., 2011). Besides, the CO_2 adsorption capacity greatly declines in the presence of moisture in gas because of their highly hydrophilic character, thus a high regeneration temperature (often above 300°C) is needed.

2.4.3.6.2 Activated Carbon Structural Characteristic and CO_2

Adsorption (Chemsuschem, 2009)

Activated carbons (AC) are well-known for adsorbent materials for many gas separations. These meso- or microporous carbonaceous structures have an advantage over other adsorbents due to their relatively low cost raw materials. AC can be produced from coals (e.g., bituminous coal, lignite) from industrial byproducts, (e.g., scraps of polymeric materials, petroleum, coke pitch), and wood or other biomass sources (e.g., saw dust, coconut shells, olive stones). Activated carbon can be prepared from raw materials consisting two steps: carbonization and activation. According to their large variations in the textural properties of activated carbons, such as pore size distribution, pore structure and active surface area, making the adsorption characteristics highly variable (Sircar *et al.*, 1996). A gram of activated carbon can have a surface area in excess of 500 m^2, with 1500 m^2 being readily reachable.

As a consequence, current research focuses on how to improve the CO_2 adsorption capacity and selectivity via two ways: (1) to improve surface area and pore structure of the carbonaceous adsorbents either using different precursors or fabricating different structures (2) to increase alkalinity by chemical modification on surface (Yu *et al.*, 2012).

2.4.3.6.3 Mesoporous Silica Structural Characteristic and CO_2

Adsorption

Mesoporous silica is a form of silica and a recent development in nanotechnology. The most common type of mesoporous nanoparticles are MCM-41 (Mobil Composition of Matter No.41) and SBA-15 mesoporous silica with pore size between 2-50 nm. Since mesoporous silica has uniform and large pore size as well as high surface area, a large number of active sites or adsorption sites can be introduced uniformly on pore walls of mesoporous silica by its surface modification with organosilane molecules (Pankaj *et al.*, 2011). SBA-15 has a surface area in a range of 400-900 m^2/g (Beilstein, 2011) whereas MCM-41 has a surface area of 600-1000 m^2/g (Meziani *et al.*, 1997).

2.3.3.6.4 Biopolymer Structural Characteristic and CO_2 Adsorption

Chitosan (CTS) (hetero polymer constituted of glucosamine and a fraction of acetylglucosamine residues) is a well-known biopolymer characterized by its sorption properties due to its high nitrogen content (Krishnapriya et al., 2010). They have become interesting not only because they are made from an abundant renewable resource, but because they are compatible and effective biomaterials that are used in many applications. Chitosan is a linear copolymer of β-(1–4) linked 2-acetamido-2-deoxy-d-glucopyranose and 2- amino-2-deoxy-d-glycopyranose (Dash et al., 2011).

Keramati et al. (2014) studied activated carbon (AC) functionalization by chitosan and triethylenetetramine for improving CO_2 adsorption. In this study activated carbon was functionalized by two different amines, chitosan and triethylenetetramine. The adsorption of CO_2 onto raw and amine functionalized AC was investigated using volumetric technique in the temperature range of 293 K to 313 K and pressure range of 1 bar to 40 bar. Results indicated that amine functionalization of the adsorbent significantly improved the adsorption of CO_2. The adsorption capacity of CO_2 achieved by the amine functionalized AC with triethylenetetramine (AC-TETA) was more than the amount reached by amine functionalized AC with chitosan (AC-chitosan). The maximum amount of CO_2 uptake achieved by AC-TETA and AC-chitosan was16.16 and 13.65 mmol/g at 298 K and 40 bar which shows 90% and 60% increase compared to raw AC, respectively.

2.4.3.7 Chemical Adsorbent: Amine-Based

Many studies have been devoted to improve CO_2 adsorption and selectivity by chemical modification on the surface of solid materials possessing high surface area. The basic organic group (amine) and inorganic metal oxide (alkali metal or alkali-earth metal) are of particular interest. The interaction between the acidic CO_2 molecules and modified basic active sites on the surface facilitates CO_2 adsorption through the formation of covalent bonding. Amine-based adsorbents have widely been studied and exhibited the advantage as low heat of regeneration over aqueous amines due to the low heat capacity of solid supports. Their low CO_2 adsorption capacity and high cost, however, are the major challenges to

commercialize. Recently, the improvement of amine-based adsorbents was proposed by the approaches: (1) the preparation of supports with high amine loading, (2) the use of amine with high nitrogen content and (3) the effective methods for amine introduction (Wang *et al.*, 2011). According to the type of the interactions between amines and supports, the amine-based adsorbents can be categorized as amine-impregnated and amine-grafted materials via weak interactions and strong covalent bonding, respectively (Sayari *et al.*, 2011). Typically, the amine-grafted adsorbents exhibit comparatively higher adsorption rate and higher stability in cyclic runs than the amine-impregnated ones. However, the grafted amount of amine depends on surface silanol groups, sometimes leading to a comparatively lower amine loading as compared with the impregnated amount.

Maroto-Valer *et al.* (2008) studied sorbents for CO_2 capture from high carbon fly ashes. The samples were steam activated at 850 °C, resulting in a significant increase of the surface area (1075 m^2/g). The activated samples were impregnated with different amine compounds methyldiethanolamine (MDEA), diethanolamine (DEA), monoethanolamine (MEA) and MDEA + MEA (MM) and the resultant samples were tested for CO_2 capture at different temperatures. The impregnation process with MDEA, DEA, MEA, and MDEA + MEA, results in a decrease of the micro and mesopore volumes, resulting from pore filling effects. The mechanism of pore filling using different amine is not well understood, but it is assumed that the different pore filling effect was due to the difference in the molecular size and shape of the amines used. The highest adsorption capacity was at 30 °C and 70 °C (68.6 and 49.8 mg CO_2/g sorbent) for the amine impregnated activated carbons, it was probably due to the combination of physical adsorption inherent from the parent sample and chemical adsorption of loaded amine groups.

Wang *et al.* (2011) reported the effects of polyethylenimine (PEI) loading, gas conditions, temperature, moisture and supports on CO_2 adsorption capacity for the PEI-impregnated mesoporous silica and carbonaceous materials. A higher PEI loading significantly enhanced CO_2 adsorption capacity together with the decreases of surface area, pore size and pore volume of the PEI impregnated supports. The highest CO_2 adsorption capacity of 3.02 mmol/g for the PEI-impregnated MCM-41 (PEI/MCM-41) with 75 wt% of PEI loading was observed

under pure CO_2 at 75°C, although the highest amine efficiency (CO_2/N molar ratio) occurred at 50 wt% PEI loading and was reduced with an increase of PEI loading. Generally, the amine loading is not directly related to the amines for CO_2 adsorption because the formation of the aggregated amine on supports would reduce the amine accessible to CO_2. When the PEI/MCM-41 with 50 wt% PEI loading was used to treat an anhydrous gas at 75°C containing 15% CO_2, 75% N_2. The adsorption capacity was decreased to 2.03 mmol/g. When the temperature was decreased from 75 to 25°C, the adsorption capacity of CO_2 was found to decrease as well. It is known that CO_2 adsorption is an exothermic process, the increasing temperature is unfavorable for CO_2 adsorption capacity. However, the formation of bulk-like PEI inside the pore at low temperature leads to CO_2 adsorption as a diffusion-limited process (Sayari *et al.*, 2011). At high temperature, the high CO_2 adsorption capacity is possibly due to the high diffusion rate of CO_2 into bulk-like PEI and the increasing reaction rate of CO_2 with PEI.

Khalil *et al.* (2012) studied on the improvement of the capacity of amine-impregnated commercial activated carbon beds for CO_2 adsorbing. In order to improve the ability and selectivity of CO_2 adsorption from gas mixture stream, amine-based chemicals were impregnated onto activated carbon particles. The amine-based chemicals used in this study were, monoethanolamine (MEA) and 2-amino-2-methyl-1-propanol (AMP). Characterization results achieved by measuring the surface area with ASAP 2020 showed that the amine-based chemicals blocked the mostly micropore pores of the activated carbon particles which is reflected by the high reduction in the surface area of the activated carbon particles. However, the process enhanced the adsorption capacity and selectivity of the activated carbon for CO_2 adsorption. Elemental analysis results using energy-dispersive X-ray spectroscopy showed that the impregnation process managed to attach the reactive N_2 molecules onto the surface and inside the pores of the activated carbon particles. Images from field emission scanning electron microscope showed that most of the pores of the activated carbon particles had been blocked by the MEA and AMP molecules because of the impregnation process. The results presented that MEA molecules distributed in better manner than AMP molecules onto the surface and the pores of activated carbon particles due to the size and shape differences

between the two molecules, impregnation with MEA molecules created more active sites on the surface of the activated carbon particles than AMP molecules would do. Sweeping exhausted non-impregnated activated carbon beds with 60 mL/min pure nitrogen for 4 h was enough for these beds to recover their original adsorption capacity. However, it was not enough to regenerate exhausted AMP, MEA-impregnated activated carbon beds to regain their original adsorption capability.

Sayari *et al.* (2011) reviews adsorbents used for flue gas treatment via CO_2 adsorption with a) physical adsorbents including carbons, zeolites and metal organic frameworks (MOFs) and b) chemical adsorbents, amine-functionalized materials with the aim of developing suitable CO_2 adsorbents. Suitable adsorbents for CO_2 removal from flue gas implies of combining several attributes, including i) high CO_2 adsorption capacity, ii) fast kinetics, iii) high CO_2 selectivity, iv) mild condition for regeneration, v) stability during extensive adsorption, vi) tolerance to the presence of moisture and other impurities in the feed, vii) low cost. As a result, at low CO_2 partial pressure, activated carbons exhibits lower adsorption capacity and selectivity than zeolites due mainly to their less favorable adsorption isotherms. In spite of the hydrophobic character of carbon-based adsorbents, their CO_2 adsorption ability is adversely affected by the presence of water vapor. Zeolites and zeolite-like materials with low Si/Al ratios are among the most promising adsorbents for CO_2 capture from flue gas but needs extensive drying prior to capture CO_2. Metal organic frameworks (MOFs), zeolite-like MOFs (ZMOFs) and covalent organic frameworks (COFs) may be promising material for CO_2 removal provided that more favorable CO_2 adsorption isotherms obtained but their selectivity and capacity at low pressure of CO_2 in gas mixtures are quite low and more likely to be suitable for CO_2 storage rather than CO_2 separation from flue gas. Apart from the physical adsorbents, the selectivity of amine-functionalized materials is not significantly affected by temperature within the range of flue gas treatment. In addition, their stability may be dramatically enhanced during thousands of adsorption-desorption cycles providing that the feed and purge gases contain moisture. Tables 2.8-2.12 summarize the CO_2 adsorption capacity from literature review with different types of adsorbents(Bates, Mayton *et al.*, 2002).

Table 2.8 Literature review on CO_2 adsorption properties of activated carbons and carbon nanotubes at low pressure (Sayari *et al.*, 2011)

Carbon material	Temperature (K)	CO_2 adsorption capacity at 0.1-0.4 bar (mmol/g)	N_2 adsorption capacity at 0.9-1.6 bar (mmol/g)	CO_2/N_2 capacity molar ratio	Reference
AC	298	0.6-1.5	0.5-0.75	1.2-2	Na *et al.* (2001)
AC	328	0.25-0.8	0.2-0.35	1.25-2.28	Na *et al.* (2001)
SWCNT	308	0.5-1.25	-	-	Cinke *et al.* (2003)
MWCNT	333	0.34-0.91	-	-	Su *et al.* (2009)

Table 2.9 Literature review on CO_2 adsorption properties of some zeolites and zeolite-like materials at low pressure (Sayari *et al.*, 2011)

Zeolite/Si/ Al ratio	CO_2 adsorption temperature (K)	Adsorption capacity at 0.1-0.4 bar (mmol/g)	N_2 adsorption capacity at 0.9-1.6 bar (mmol/g)	CO_2/N_2 capacity molar raito	Reference
NaX/1	298	2.8-3.9	0.264-0.46	11-8.5	Cavinati *et al.* (2004)
NaX/1	323	1.43-2.49	-	-	Cavinati *et al.* (2004)
LiX/1	303	3.1-4.6	-	-	Walton *et al.* (2006)

Table 2.9 (cont.) Literature review on CO_2 adsorption properties of some zeolites and zeolite-like materials at low pressure (Sayari *et al.*, 2011)

Zeolite/Si/ Al ratio	CO_2 adsorption temperature (K)	Adsorption capacity at 0.1-0.4 bar (mmol/g)	N_2 adsorption capacity at 0.9-1.6 bar (mmol/g)	CO_2/N_2 capacity molar raito	Reference
NaY/2.4	323	0.45-1.17	-	-	Maurin *et al.* (2007)
CsY/2.4	333	0.86-1.2	-	-	Pirngruber *et al.* (2010)
KY/2.4	333	0.75-1.6	-	-	Pirngruber *et al.* (2010)
Silicalite/∞	334	0.16-0.45	0.1	1.6	Dunne *et al.* (1996)
H-ZSM-5/30	313	0.7-1.5	0.23	3	Harlick *et al.* (2002)
Li-MCM-22/15	333	0.68-1	-	-	Zukal *et al.* (2009)

Table 2.10 Literature review on CO_2 adsorption properties of some MOFs and ZMOFs (Sayari *et al.*, 2011)

MOFs	Temperature (K)	CO_2 adsorption capacity (mmol/g at 0.1-0.4 bar)	N_2 adsorption capacity (mmol/g at 0.9-1.6 bar)	CO_2/N_2 selectivity	Reference
MOF-508	323	0.1-0.7	0.6-0.9	2	Bastin *et al.* (2008)
Cu-BTC	298	0.5-2	0.25	15	Yang *et al.* (2007)

Table 2.10 (cont.) Literature review on CO_2 adsorption properties of some MOFs and ZMOFs (Sayari *et al.*, 2011)

MOFs	Temperature (K)	CO_2 adsorption capacity (mmol/g at 0.1-0.4 bar)	N_2 adsorption capacity (mmol/g at 0.9-1.6 bar)	CO_2/N_2 selectivity	Reference
MIL-53	303	0.5-1.15	-	-	Finsy *et al.* (2009)
Ni/DOBDC	296	2.7-4.01	-	-	Caskey *et al.* (2008)
CO/BOBDC	296	2.8-5.36	-	-	Caskey *et al.* (2008)
Mg/DOBDC (Mg-MOF-74)	296	5.36-6.8	-	-	Britt *et al.* (2009)
ZIF-78	298	0.77-1.36	-	50	Banerjee *et al.* (2009)

Table 2.11 Literature data on CO_2 adsorption capacity of amine-impregnated adsorbent (Sayari *et al.*, 2011)

Support	Amine	Amine loading (wt %)	CO_2 adsorption capacity (mmol/g)	CO_2/N	CO_2 concentration (%)	T (°C)	Reference
MCM-41	PEI	50	2.1	0.18	10	75	Xu *et al.* (2002)
MCM-41	PEI	50	2.84	0.27	13(13% H_2O)	75	Xu *et al.* (2005)
SBA-15	PEI	50	3.18	0.27	15	75	Ma *et al.* (2009)

Table 2.11 (cont.) Literature data on CO_2 adsorption capacity of amine-impregnated adsorbent (Sayari *et al.*, 2011)

Support	Amine	Amine loading (wt %)	CO_2 adsorption capacity (mmol/g)	CO_2/ N	Experimental condition		Reference
					CO_2 concentration (%)	T (°C)	
KIT-6	PEI	50	1.95	0.17	5	75	Son *et al.* (2008)
Monolith	PEI	65	3.75	0.25	5	75	Chen *et al.* (2009)
As-synthesized SBA-15	TEPA	50	3.25	0.28	10	75	Yue *et al.* (2006)
As-synthesized MCM-41	TEPA	50	4.54	0.34	5	75	Yue *et al.* (2008)
As-synthesized SBA-15	TEPA+ DEA	50(30% TEPA, 20% DEA)	3.77	0.38	5	75	Yue *et al.* (2008)
PE-MCM-41	DEA	76	3	0.41	5	25	Franchi *et al.* (2005)
Mesoporous Al_2O_3	DETA	40	1.4	0.12	100	57	Plaza *et al.* (2008)
Mesoporous SiO_2	PEI	40	2.4	0.26	15	70	Sayari *et al.* (2010)
SBA-15	PEI	50	1.36	0.12	12	75	Dasgupta *et al.* (2009)

Table 2.11 (cont.) Literature data on CO_2 adsorption capacity of amine-impregnated adsorbent (Sayari *et al.*, 2011)

Support	Amine	Amine loading (wt %)	CO_2 adsorption capacity (mmol/g)	$CO_2/$ N	Experimental condition		Reference
					CO_2 concentration (%)	T (°C)	
PMMA	TEPA	41	13.88	1.28	15 (2.6% H_2O)	70	Lee *et al.* (2008)
PMMA	Ethylen eamine + acrylon itrile	Propriet ary informa tion	4.18	Prop rieta ry infor mati on	10 (humid)	25	Gray *et al.* (2005)
PMMA	DBU	30	2.34	0.59	10 (2% H_2O)	65	Gray *et al.* (2008)
SiO₂ (CARiA CT)	PEI	40	3.95	0.42	10 (2% H_2O)	40	Jadhav *et al.* (2007)
PMMA (Diaion)	PEI	40	3.60	0.39	10 (2% H_2O)	40	Gray *et al.* (2009)
AOS carbon	PEI	5	1.98	1.70	100	25	Plaza *et al.* (2009)
13X	MEA	25	0.45	0.11	15	75	Jadhav *et al.* (2007)
Beta-zeolite	TEPA	38	2.08	0.21	10	30	Fisher *et al.* (2009)
Silica gel	AP	0.89	1.26	0.71	100% (100% RH)	50	Leal *et al.* (1995)
MCM-48	AP	2.3	2.3	1	10% (100% RH)	25	Huang *et al.* (2003)

Table 2.12 Literature data on CO_2 adsorption of amine-grafted adsorbent (Sayari *et al.*, 2011)

Support	Amine	CO_2 adsorption capacity (mmol/g)	Amine loading (mmol/ g)	CO_2/ N	Experimental conditions		Reference
					CO_2 concentration	T (^oC)	
HMS	AP	1.59	2.29	0.69	90%	20	Knowles *et al.* (2006)
HMS	TRI	1.34	4.57	0.29	90%	20	Knowles *et al.* (2006)
PE-MCM-41	TRI	1.59	7.9	0.20	10%	50	Serna-Guerrero *et al.* (2010)
SBA-15	TRI	1.80	5.80	0.31	15% (humid)	60	Hiyoshi *et al.* (2005)
MS	TRI (co-cond)	1.74	5.18	0.34	100%	25	Kim *et al.* (2008)
SBA-16	EDA	1.4	0.76	1.84	100%	27	Knofel *et al.* (2007)
SBA-15	AP	0.45	2.56	0.18	10%	65	Wang *et al.* (2007)
SBA-16	EDA	0.727	3.06	0.24	15%	60	Wei *et al.* (2008)
SBA-15	AP	1.54	2.72	0.57	10%	25	Zelenak *et al.* (2008)
SBA-12	AP	1.04	2.13	0.49	10%	25	Zelenak *et al.* (2008)
MS	AP	0.24	1.6	0.15	10%	30	Knofel *et al.* (2009)

Table 2.12 (cont.) Literature data on CO_2 adsorption of amine-grafted adsorbent (Sayari *et al.*, 2011)

Support	Amine	CO_2 adsorption capacity (mmol/g)	Amine loading (mmol/g)	CO_2/N	Experimental conditions		Reference
					CO_2 concentration	T (°C)	
MSP	EDA	0.73	0.99	0.73	10%	60	Lu *et al.* (2009)
MCM-48	TREN	1.36	4	0.34	100%	50	Bhagiyala kshmi *et al.* (2010)
ITQ-6	AP	0.67	1.26	0.53	12%	20	Zukal *et al.* (2009)
SBA-15	Amine-dendri mers	1	1.25	0.40	90%	20	Liang *et al.* (2008)
SBA-15	Azirid ine polym er	4	9.78	0.41	10% (humid)	75	Drese *et al.* (2009)