CHAPTER II

LITERATURE REVIEW

2.1 Carbon Dioxide Emission

Global warming is major environmental problems of the world that come from emissions of greenhouse gases (GHG), such as carbon dioxide (CO_2) and methane (CH_4), and the pollution of fuel combustion such as NO_x, SO_x. The increased concentration of greenhouse gases directly is the consequence of human activities and industry evolution, especially in 15 years ago. CO_2 is the largest contributor of all the GHG. 60% of global warming effects results from a lot of CO_2 emission (Yang *et al.*, 2008). The concentration of CO_2 (379 ppmv in 2005) was about 35% higher than that in the mid-1800s (280ppm) with the fastest growth occurring in the last ten years (1.9 ppmv/year) (International Energy Agency, 2010). It is estimated that roughly 26 to 30 percent of all CO_2 emissions is derived from human activities related to fossil fuels use for generating electricity. Moreover, a variety of other industrial processes such as oil refineries, fertilizer and cement plants also emit large amounts of CO_2 (Zanganeh *et al.,* 2009). Total CO_2 emission in atmosphere has to be reduced which can be done generally through 3 methods. The first is to reduce energy intensity, which requires efficient use of energy. The second is to reduce carbon intensity by switching to non-fossil fuels and the last is to enhance the sequestration of CO_2 which includes development of technology to capture and sequester CO_2 (Olajire, 2010).

2.2 Carbon Dioxide Capture Technology

Generally, CO_2 is often released by burning fossil fuels. To capture CO_2 from industries, there are three operating options namely pre-combustion, post-combustion and oxy-fuel combustion as illustrated in Figure 2.1. Concentration and partial pressure of CO_2 in gas stream and fuel type are the main factors in selecting the capture system (Olajire, 2010).

Pre Combustion Capture

Fuel ⟶ [Gasifier] $\frac{CO}{H_2}$ ⟶ [Catalytic Shift Reactor] ⟶ CO_2 for storage

O_2/Air ⟶

H_2 as fuel

Post Combustion Capture

CO_2containing flue gas

Fuel ⟶ [Combustion] ⟶ [CO_2 Capture] ⟶ CO_2 for storage

Air ⟶

Oxy Fuel Combustion

Fuel ⟶ [Combustion] ⟶ CO_2 for storage

O_2 ⟶
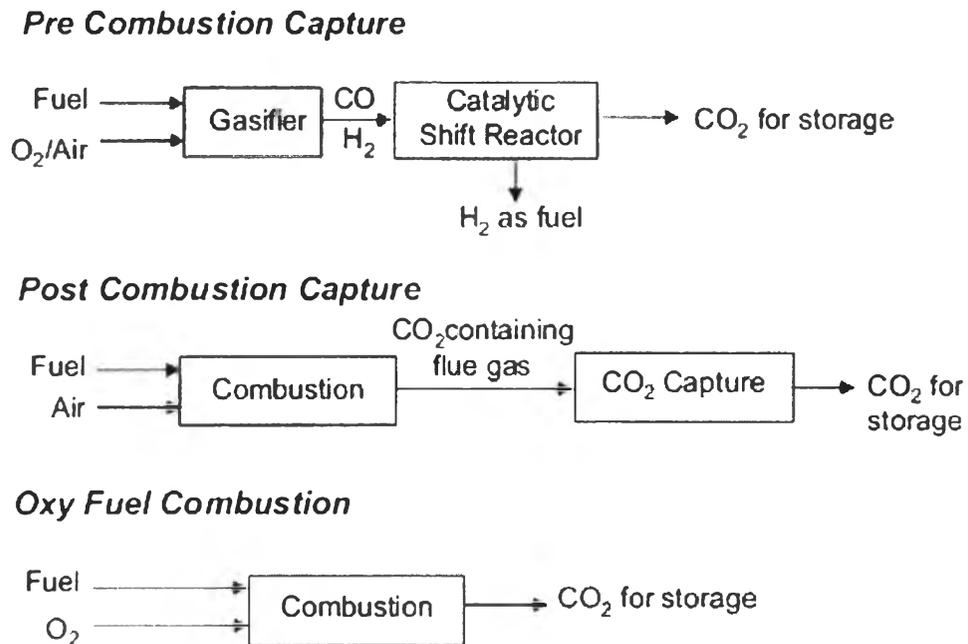
Figure 2.1 Block diagrams illustrating post-combustion, pre-combustion, and oxy-combustion systems (Thiruvenkatachari *et al.*, 2009).

2.2.1 Pre-combustion Technology

The system is removal the CO_2 before combustion process. Fossil fuel is partially combusted (gasified or reformed) with oxygen or air (in some cases steam) to give synthesis gases that is mixture of CO and H_2. This process perform about 30-60 bar (Gibbins and Chalmers, 2008). Then CO undergoes a shift reaction to generate H_2 and CO_2 in a catalytic reactor. CO_2 is separated and H_2 is used as fuel in a gas turbine combined-cycle plant (Olajire, 2010).

2.2.2 Post-combustion Technology

The system involves the removal of CO_2 in flue gas produced by combustion before it is vented to atmosphere. Flue gas is passed though equipment, which separates/captures most of CO_2. A variety of techniques described latter can be used for separation. Post combustion capture requires a significant design process due to the relatively low partial pressure of CO_2 in flue gas (Olajire, 2010).

2.2.3 Oxy-combustion Technology

Fuel is combusted in nearly pure oxygen instead of air which is modified technology from post combustion process, thereby eliminating nitrogen resulting in high concentration of CO_2 and water in flue gases. The flame temperature in oxy combustion is too high, but CO_2–rich flue gas is recycle to the combustor to lower the flame temperature to the same level as normal air blown combustor (Thiruvenkatachari *et al.*, 2009).

Advantages and disadvantages of the post-combustion, pre-combustion and oxy-fuel technologies are compared in Table 2.1.

Table 2.1 Advantages and disadvantages of CO_2 capture technologies (Olajire, 2010; Thiruvenkatachari *et al.*, 2009)

capture technologies	Advantages	Disadvantages
Pre-combustion	• Synthesis gas is concentrated in CO_2 at high pressure • High CO_2 partial pressure • High driving force for separation due to the partial pressure of CO_2 • More technologies available for separation • Potential for reduction in compression costs/loads	• Cooling of gas to capture CO_2 is necessary. • Efficiency loss in water-gas shift section • Barriers to commercial application of gasification are common to pre combustion capture • Availability • Cost of equipment • Extensive supporting systems requirements
Post-combustion	• Applicable to the majority of existing coal-fired power plants • Retrofit technology option • Extra removal NO_x and SO_x	• Energy penalty due to solvent regeneration • Low CO_2 partial pressure so have to use the powerful chemical solvent • Loss of solvent
Oxy- combustion	• Absence of nitrogen provides low volume of gasses and so reduced size of entire process • Very high CO_2 concentration in flue gas • Absence of nitrogen eliminates NO_x emission • Retrofit and repowering technology option	• High energy input for air separation • Combustion of pure oxygen is complicated • expensive, both in terms of capital cost and energy consumption • Cooled CO_2 recycle required to maintain temperatures within limits of combustor materials

2.3 Review of Possible CO_2 Separation Techniques

A wide range of technologies currently exist for separation of CO_2 from gas steams although has not been designed for the power-plant scale operation. They are based on different physical and chemical processes including absorption, adsorption, membrane and cryogenic separations, the choice of suitable technology depends on the characteristics of the flue gas steam, economical investment and many factor of industrial plant.

2.3.1 Absorption Processes

Absorption is a common process in the chemical industry and used among others in the treatment of the industrial gas stream containing acid gases such as H_2S, NO_x and CO_2. The process can be divided into two categories, chemical and physical absorption. Chemical absorption process uses solvent to chemically react with the acid gases to form a weakly bonded intermediate compound (Ritter and Ebner, 2004). This compound may be regenerated with the application of heat producing the original solvent and CO_2 stream. The alkanolamines are commonly used as reactive absorbents (Wang *et al.*, 2010). On the other hand, Physical absorption only allows interacting physically with the acid gases. Typical physical solvents are methanol (Rectisol Process) and glycol ethers (Selexol Process) (Ritter and Ebner, 2004). Physical solvents are not economical for flue gas streams with CO_2 partial pressure lower than 15% (Wang *et al.*, 2010).

2.3.1.1 Amine Absorption Technologies

Amines have been used efficiently to treat of industrial gas stream for decades (Wang *et al.*, 2010). Industrially important amines for CO_2 removal are primary amines (e.g. monoethanolamine (MEA) and diglycolamine (DGA)), the secondary amines (e.g. diethanolamine (DEA) and diisopropanolamine (DIPA)) and the tertiary amine (e.g. methyldiethanolamine (MDEA) and triethanolamine (TEA)). Typical operating conditions of the amine system are presented in Table 2.2.

Table 2.2 Typical operating conditions and data for amines. (Polasek and Bullin, 2006)

Properties	Amine type			
	MEA	DEA	DGA	MDEA
Solution Strength , wt.%	15-20	25-35	50-70	20-50
Acid gas loading, mole/mole (carbon steel)	0.3-0.35	0.3-0.35	0.3-0.35	Unlimited
Ability to selectivity absorb H_2S	No	Under Limited Condition	No	Under Most Conditions

MEA absorption is a commercial process which CO_2 is removed by reacting with MEA solution in an absorber. The CO_2-rich MEA solution is then sent to a stripper where it is reheated to release almost pure CO_2. The MEA is then recycled to the absorber (Herzog, 1999). MEA concentration is generally used in range of 10 to 20 % wt solution in water. The acid gas loading is usually limited to 0.3 to 0.35 moles acid gas per mole of amine due to corrosion problems for carbon steel equipment. If stainless steel is used, CO_2 loading can be as high as 0.7-0.9 moles per mole of amine with no corrosive problem in stainless steel equipment (Polasek and Bullin, 2006).

The MEA process is uneconomic as it has high energy consumption for solvent regeneration, high equipment corrosion rate and low CO_2 loading capacity, amine degradation by SO_2, NO_2, HCl, HF and oxygen in flue gas. Thus, it requires a high make up rate of MEA solution to maintain the CO_2 capture efficiency of the process (Yang et al., 2008). Alternatively, less reactive amines, such DEA and MDEA are often used (Gray et al., 2005). However there have been efforts to modify the absorbents, improve the process design and optimize processes operation. The proposed mechanism of reaction between CO_2 and amines are shown in Figure 2.2. The CO_2 initially reacts with primary and secondary amines to form carbamate. Carbamates can hydrolysis to produce the bicarbonate and if the pH of the system is suitable, bicarbonate can form carbonate species. The degree of hydrolysis was evaluated by many parameters such as amine concentration, solution pH, and the chemical stability of the carbamate. At the low temperature the

equilibrium will favor the formation of carbamate and bicarbonate, but upon heating it will favors the liberation of amine and carbon dioxide (Hook et al., 1997).
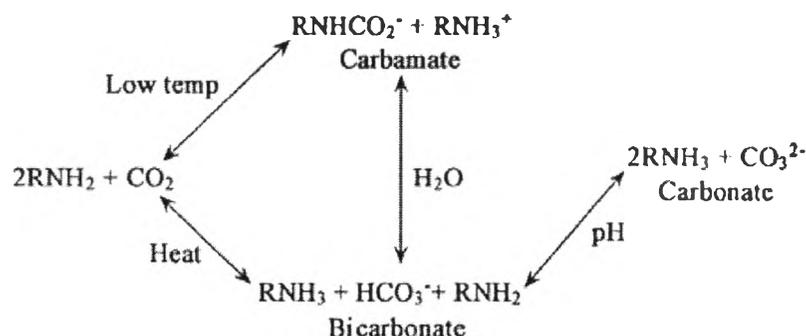
Figure 2.2 Proposed reaction sequence for the capture of CO_2 by liquid amine-based systems (Gray *et al.*, 2005).

Vaidya and Kenig (2007) studied the kinetics of the reaction of CO_2 with aqueous solutions of alkanolamines. Primary and secondary alkanolamines (i.e. MEA, DEA, DGA) react rapidly with CO_2 to form carbamates which usually described by the zwitterions mechanism while tertiary alkanolamines (MDEA) facilitate to hydrolysis with CO_2 to from bicarbonate.

2.3.1.2 Mixed Amine

Mixed amine is an alternative to maximize the desirable quality of individual amine. Tertiary amine is mixed with primary or secondary amines in comparison with single amine systems to reduce regeneration cost of process. The mix amines remain high in reactivity of primary or secondary amine at similar or reduced circulation rate (Idem *et al.*, 2006). There are many literatures reporting substantial reduction in energy requirements and modest reduction in circulation rate for amine blends relative to the corresponding single amine system as similar total concentration.

Idem *et al.* (2006) studied the CO_2 capture performance of aqueous MEA and mixed MEA-MDEA solvents in terms of the heat requirement for solvent regeneration, lean and rich loadings, CO_2 production, and solvent stability.

They compared the performance of aqueous 5 kmol/m³ MEA with that of an aqueous 4:1 molar ratio MEA/MDEA blend of 5 kmol/m³ total amine concentration as a function of the operating time using two pilot CO_2 capture plants. It showed that a huge heat-duty reduction can be achieved by using a mixed MEA/MDEA solution instead of a single MEA solution in an industrial environment of a CO_2 capture plant. However, this benefit is dependent on whether the chemical stability of the solvent can be maintained.

Vaidya and Kenig (2007) showed that the released heat of bicarbonate formation which is the reaction between tertiary amine with CO_2 is lower than carbamate formation, which is the reaction between primary amine or secondary amine with CO_2 so that tertiary amine can reduce regeneration cost. Researcher emphasized the acceleration of the CO_2 reaction with MDEA, 2-amino-2-methyl-1-propanol (AMP) and diethylmonoethanolamine (DEMEA) by promoters such as MEA, DEA. Mixed amine are found to be attractive for the enhancement of CO_2 capture

Aroonwilas and Veawa b (2007) focused on the performance of MEA and MEA-MDEA blending as CO_2 capture solvent for coal field power plants. The study was done at steady state and full loading of power plant. It was found that when MEA-MDEA is mixed at a reasonable ratio, operating the CO_2 capture unit at high removal efficiency can be obtained at acceptable value of CO_2 avoided per energy penalty. When compared with MEA only, the power plant can improve thermal efficiency around 3%.

2.3.1.3 Piperazine Absorption Technologies

Piperazine (PZ) is an organic compound that consists of a six-membered ring containing two opposing nitrogen atoms that are the same amine groups so that piperazine is compound in diamine types. Its structural formula is shown in Figure 2.3. PZ has been studied as a solvent for absorption/stripping systems for the removal of CO_2 from the flue gas of coal-fired power plants. The concentration of PZ when used as a promoter is low, between 0.5 to 2.5 m PZ, because PZ is not highly soluble in water. It has been studied as a promoter for amine system in CO_2 capture process Piperazine help to increase CO_2 mass transfer rates in amine system such as MEA/PZ or MDEA/PZ (Freeman *et al.*, 2010).
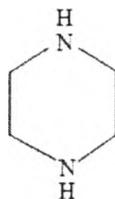
Figure 2.3 Structural formula of piperazine (PZ).

      Bishnoi and Rochelle (2002) studied simulation of carbon dioxide absorption of 0.6 M piperazine/4 M MDEA in a wetted wall column using a model that accounts for chemical reactions and transport effects with the eddy diffusivity theory. They compare the CO_2 capture effect of PZ/MDEA blend with DEA/MDEA and MEA/MDEA blends that calculated in the work of Glasscock *et al.*,(1991). The result showed that PZ/MDEA blend increase the performance of MDEA by a factor of 50 at low loading (<0.14mol CO_2/mole amine). And the PZ/MDEA blend enhances its performance up to a factor of 5 that is more than 50%MDEA as shown in Figure 2.4.
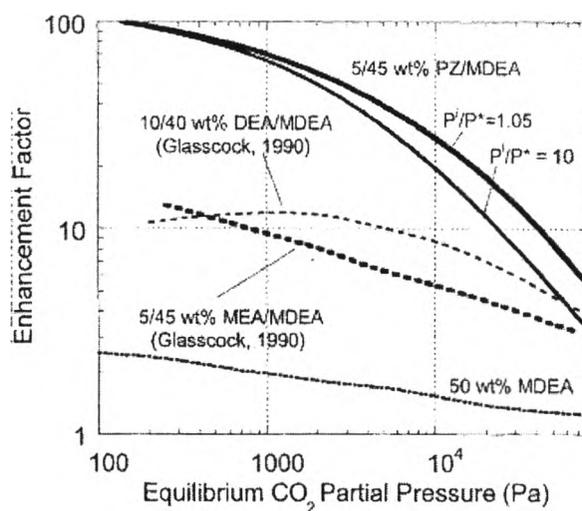

Figure 2.4 Comparison of PZ/MDEA blends to conventional blends (Predictions at 40°C, $k° = 1.0E-4$ m/s. $P'/P^* = 1.05$ unless specified (Bishnoi and Rochelle, 2002)).

Cullinane and Rochelle (2006) compared overall rate constants of several amines at 1.0 M and 25 °C as shown in Table 2.3. 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 compared this characteristic with other diamine,such as ethylenediamine(EDA) and heterocycles such as piperidine and morphorine.

Dugas and Rochelle (2009) studies absorption and desorption rates of carbon dioxide with 7, 9, 11, and 13 m monoethanolamine and 2, 5, 8, and 12 m piperazine at 40 and 60°C. The result showed that CO_2 capacity of 8 m PZ is about a 75% greater than the CO_2 capacity of 7 m MEA. At equivalent CO_2 partial pressure, CO_2 absorption and desorption rate is 2–3 times faster with PZ than with MEA. The CO_2 flux for both MEA and PZ is practically independent of temperature and amine concentration over the range of these experiments when represented as a function of the equilibrium partial pressure at 40°C.

Table 2.3 Overall rates constants for 1.0 M amine at 25 °C (Cullinane and Rochelle, 2006)

amine	Structure	pKa	Rate constant $(s^{-1} \times 10^3)$	$\triangle Ha$ (kJ/mol)	Source (rate/pKa)
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 6.7	39.4 40.1	Alper *et al.*, *1990*; Littel*et al.*, *1990* Al-Juaied*etal.*, *2004;*Littel*et al.*, *1990*
Ethylenediamine		9.91	15.1		Jensen *et al.*, *1995;* Christensen *et al.*, 1969
Piperidine		11.12	93.3 60.3		Sharma *et al.*,1969; Christensen *et al.*, 1969 Jensen *et al.*, 1969; Christensen *et al.*, 1969
Morpholine		8.94	20.6 20.0 22.3	23.3	Alper *et al.*, *1990* ; Christensen *et al.*, 1969 Sharma *et al.*, 1965; Christensen *et al.*, 1969 Al-Juaied*etal.*, *2004*; Christensen *et al.*, 1969
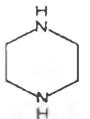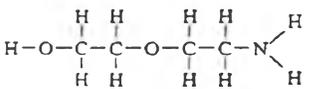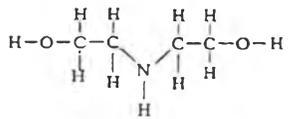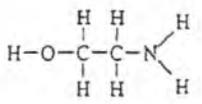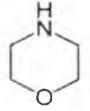
Freeman *et al.* (2010) investigated carbon dioxide capture with concentrated, aqueous piperazine (PZ). Rate of CO_2 absorption is considered in term of the normalized flux, k'_g. It is found that the rate of CO_2 absorption into 8 m PZ is 1.5-3 times that of 7 m MEA in a range of 40-100 °C as demonstrated in Figure 2.5. The CO_2 capacity of 8 M PZ is double that of 7 m MEA at 0.90 mole of CO_2 per kg (PZ+H_2O) compared to 0.43 mole CO_2 per kg (MEA+H_2O). Initial system modeling suggests that 8 m PZ will be approximately 10-20 % less energy than 7 m MEA. Moreover they studied thermal degradation and oxidative degradation of concentrated, aqueous piperazine (PZ). The thermal degradation of concentrated, aqueous piperazine (PZ) is negligible up to 150 °C showing on advantage over MEA system. Oxidative degradation of concentrated PZ was found to be 4 times slower than MEA in presence of stainless steel metal (Fe^{+2}, Cr^{3+}, Ni^{2+}) and low concentration of Vanadium (V^{5+}).
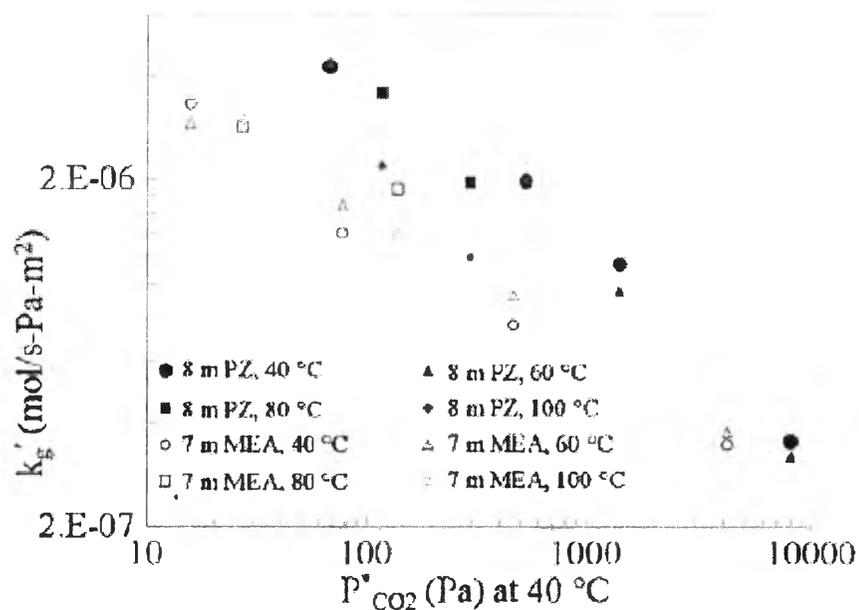

Figure 2.5 Comparison of mass transfer coefficients in 8 m PZ (filled shapes) and 7 m MEA (open shapes) from 40 to 100 °C (Freeman *et al.*, 2010).

2.3.2 Membrane Technology

Membranes have been widely used in various industrial separations for the last two decades. Membrane is a semi-permeable barrier able to separate substance by various mechanisms such as solution/diffusion, adsorption/diffusion, molecular sieve and ionic transport (Olajire, 2010). Membranes are available in different material types, which can be either organic (polymeric) or inorganic (carbon, zeolite, ceramic or metallic) and can be porous to non-porous. Membranes can separate carbon dioxide from a gas stream by size exclusion or by chemical affinity. Chemical affinity membranes are often impregnated with a scrubbing solution or chemical functional group (e.g. amine) selective for carbon dioxide (Granite and O'Brien, 2005). Moreover, membranes have to have two characteristics in indicating membrane performance: permeability and selectivity. A membrane separation process requires less expenditure for maintenance and energy than absorption process and is simple modular system that does not have waste steam. However, membranes have several drawbacks. For example, the high temperature of flue gases will rapidly destroy the membrane, so the gases need to be cooled to below 100°C prior to membrane separation. The membranes need to be chemically resistant to the harsh chemicals contained within flue gases, or these chemicals need to be removed prior to the membrane separation. Additionally, creating a pressure difference across the membrane will require significant amounts of power. (Yang *et al.*, 2008)

2.3.3 Cryogenic Processes

Cryogenic separation processes of gas mixtures are the physical process needed to compress and cool the gas mixtures in several stages to induce phase changes in CO_2 and other mixture components. The advantage of cryogenic processes is that, the CO_2 feed is properly conditioned so that high recovery of CO_2 and other feed constituents is possible. This may also facilitate the final use (Meisen and Shuai, 1997).

2.3.4 Adsorption

Adsorption is considered as one of the most promising technology in commercial and industrial application for separating CO_2 from gas mixture due to its low energy requirement, ease of operation and low maintenance (Xu*et al.*, 2009). Adsorption is the process which the surface of a solid adsorbent has the tendency to attract and retain the molecules of the adsorbate. These molecules of the adsorbate remain only at the surface of the adsorbent and do not go deeper into the bulk. Adsorption is a consequence of surface energy. In a bulk material, the bonding requirements (ionic, covalent or metallic) of the constituent atoms of the material are filled. But atoms on the (clean) surface experience a bond deficiency, because they are not wholly surrounded by other atoms. Thus it is energetically favorable for them to bond with whatever happens to be available. The exact nature of the bonding depends on the details of the species involved, but the adsorbed material is generally classified as exhibiting physisorption or chemisorption.

Physisorption (Physical Adsorption) the force of attraction between the adsorbate and adsorbent are Van der Waals forces (induced dipole-induced dipole) and electrostatic forces. Since the adsorption process is exothermic, the physical adsorption occurs readily at low temperature and the interaction is very weak, therefore this type of adsorption can be easily reversed by heating or by decreasing the pressure. Physical adsorption takes place with formation of multilayer of adsorbate on adsorbent. The increasing of adsorption increases with the increase of surface area of the adsorbent. Thus, finely divided metals and porous substances having large surface areas are good adsorbents in many research of adsorption. Moreover, it has quite low enthalpy of adsorption (Ramanathan, 2006).

Chemisorption (Chemcal Adsorption) : The force of attraction between the adsorbate and adsorbent may be covalent or ionic in nature. It involves a high energy of activation and is, therefore, often referred to as activated adsorption. Chemisorption is also an exothermic process but the process is very slow at low temperatures on account of high energy of activation. Adsorption often increases with rise of temperature and high pressure. Enthalpy of chemisorption is high (80-240 kJ mol^{-1}) as it involves chemical bond formation. The increasing of the surface of adsorbent and the attraction between adsorbate and adsorbent give the higher

adsorption capacity. For the CO_2 adsorption, the adsorbent was improved the selectivity and ability to operate at the high temperature. The modification with the amine deivertives on the surface of adsorbent is mostly used in many researches because the amine groups form covalent bond with CO_2 molecules that help to increase adsorption capacity (Ramanathan, 2006).

2.3.4.1 Adsorbents for CO₂ Adsorption

The capture of carbon dioxide by adsorptive process is mainly based on preferential adsorption of the adsorbate on a porous adsorbent, so that researcher have developed properties of adsorbent with high adsorption capacity, high selectivity and high adsorption rate (Zhao *et al.*, 2009). The temperature, partial pressures, surface forces and adsorbent pore sizes, single or multiple layers of gases are significant parameters that help the adsorption to be selective (Meisen and Shuai, 1997). Solid adsorption such as activated carbon, zeolites and mesoporoussilicates, alumina, metal oxides has been extensively used for gas separation.

Gargiulo *et al.* (2007) studies preparation and characterization of polyethylene-modified mesoporoussilicas (MCM-48 and SBA-15) as CO_2 sorbent by using impregnation technique, and these were tested as media for CO_2 adsorption. Increasing PEI loading effect to decrease surface area and pore size of the adsorbents. Non-functionalized MCM-48 mesoporous silica did not adsorb CO_2 while Non-functionalized SBA-15 mesoporous silica absorbed 1% of the mass increase of the adsorbent (10 mg CO_2/g). PEI loading improves CO_2 adsorption capacity as function of actual PEI content of samples. The maximum measured adsorption capacity for PEI-modified MCM-48 and PEI-modified SBA-15 are about 6% of the mass increase of the adsorbent(60 mg CO_2/g) and adsorption capacity of PEI-modified SBA-15 was a little higher than that of MCM-48 samples. Adsorption and desorption curves of PEI loaded SBA-15 samples and MCM-48 are almost perfectly coincident, but the modified MCM-48 samples show slight hysteresis phenomena, with desorption curves constantly lower than the adsorption curves. This means that the desorption capacity is close to 100% for all the functionalized samples and therefore they are fully renewable under vacuum

Plaza *et al.,* (2007) studies CO_2 adsorption of immobilized amines on activated carbon Norit (mesoporous carbon) adsorbent. The adsorbent was

prepared by impregnation method using diethylentriamine (DETA), pentaethylenehexamine (PEHA), and polyethylenimine(PEI). Two different approaches were studied: temperature programmed adsorption (TPA) and vacuum swing adsorption (VSA) cycle. Sorbent performance was monitored by mass increase of sample when exposed CO_2 and expressed as weight percentage. The result showed that the highest capacity occurred at room temperature. The CO_2 adsorption capacity decreased when temperature was increased. It was expected due to exothermic character of physisorption in case of raw materialand also to the contribution of exothermic CO_2 sorption reaction in case of impregnated sample. The CO_2 capture capacity curve of impregnated activated carbon Norit is lower than the raw material when temperature was increased. That result was interpreted due to the interaction between the acid gas CO_2 and basic amine group on impregnated carbon surface is very strong and impregnation in activated carbon blocked the mesoporous texture according to decreasing of surface area of impregnated sample. From VSA cycle, Norit reached the plateau of maximum capture capacity in 20 min and continued upward tendency for 30 min of capture. Actually the CO_2 capture capacity of cycle 2 and 3 was slightly decreased than that of fresh adsorbent

      Maroto-Valer *et al.*, (2008) focus on the development of activated fly ash derived sorbent (AC) for CO_2 capture by using one step stream activation process at 850 °C and impregnation process with MEA, MDEA, DEA and MDEA+MEEA (AC-MEA, AC-MDEA, AC-DEA, AC-MM). It was found that the one- step activation process significantly increase the surface area and total pore volume up to 1075 m^2/g and 0.774 mL/g, respectively. Increasing the activation time helped to promote the formation of mesopores due to the removal of pore wall and enlargement of micropores. The CO_2 adsorption capacity of parent and activated fly ash is decreasing when temperature is increasing from 30 to 75 °C. For impregnation process with MEA, MDEA, DEA and MDEA+MEEA, The impregnation reduced the micropore and mesopore volume, resulting pore filling, due to the different molecular size and shape of amines. MEA is very specific toward filling/or blocking micropore and does not accumulate in mesopore, but MDEA may build up in mesopore and block off the micropore. Furthermore the impregnation can improve

the performance of CO_2 adsorption for the activated fly ash. The CO_2 adsorption of the activated and de-ashed samples at 30 C and 70 C is the highest for amine impregnated activated carbon. It was probably due to combination of physical adsorption from the parent sample and chemical adsorption of the amine groups.

Chang *et al.* (2009) prepared solid adsorbents by modified mesoporous silica including MCM-41, SBA-15 and pore expanded MCM-41 using mono-, di-, tri- aminosilane. The monoamine-loaded mesoporous silicas denoted as 1N/MCM-41, 1N/SBA-15, and 1N/PE-SBA-15. The calcined mesoporous silica SBA-15 was functionalized by reacting with three primary and secondary aminosilanes are APS, AEAPS, and TA under two grafting methods to give mono- (1N), di- (2N) and tri-amine (3N) grafted SBA-15s. They proposed the adsorption mechanism of primary and secondary amine grafted on APS, AEAPS and TA/SBA under anhydrous CO_2 which proceeded through carbamate intermediate mechanism as shown in the Figure 2.6. Furthermore, the CO_2 adsorption capacity is shown that SBA-15 was better support than MCM-41 and poreexpanded MCM-41. The tri-amine graft SBA-15(TA/SBA-15) has CO_2 adsorption capacity about 2.41 mmol/kg under CO_2 flow and 2.72 mmol/kg under CO_2 flow with relative humidity (RH) of 78% at 333K. For CO_2 adsorption in different CO_2 content in gas stream, the result showed that the more CO_2 could be adsorbed as the partial pressure of CO_2 increased and decrease temperature.
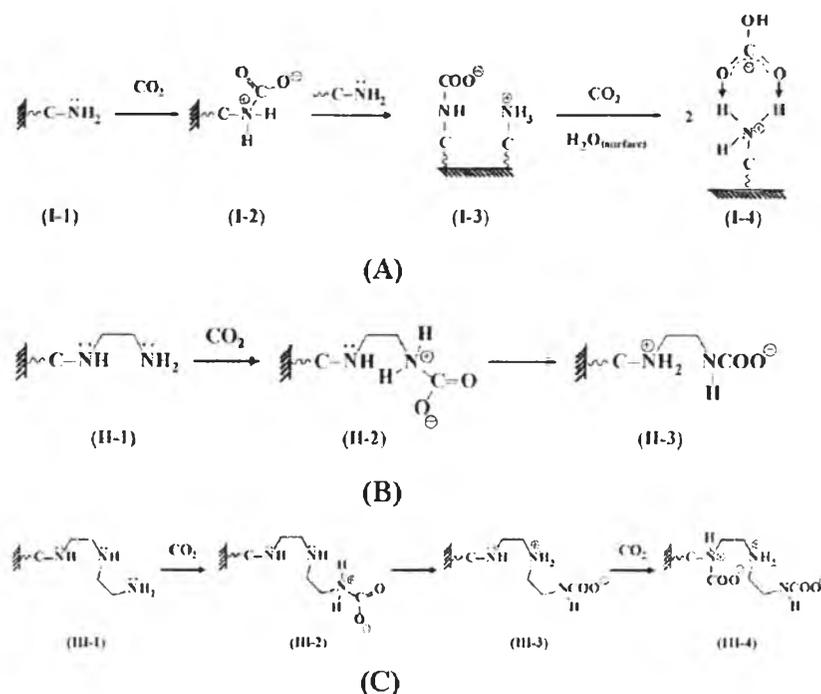
Figure 2.6 CO_2 reaction pathway with (A) monoamine- (B) di-amine- and (C) tri-amine -grafted on mesoporous silica (Chang *et al.*, 2009).

Chatti *et al.* (2009) synthesized immobilized amines, monoethalnolamine (MEA) and and isopropanol amine (IPA) on Zeolite 13X. The breakthrough curves of CO_2 adsorption on amine loaded zeolite is higher approximately 20-30% than bare zeolite matrix at 75°C because of the decreasing of surface area and pore volume as compared with the bare zeolite matrix. The adsorption process was explained, divided into two categories: physical adsorption (physisorption) and chemical adsorption (chemisorption). The physical adsorption is dominant over chemical adsorption, in which the surface area of the adsorbent holds a vital key to adsorption, while the chemical adsorption process is dominant process due to the incorporation of amine group in zeolite at elevated temperature so that the adsorption capacity increased when temperature was increased because of increasing of chemisorption. The possible reaction mechanism the same as reaction between the liquid amine and gaseous CO_2 as illustrated in reaction (2.1) and (2.2). Thus, this process has a hybrid mechanism of adsorption and absorption taking place in the in pore of zeolite 13X.

$$2RNH_2 \quad + \quad CO_2 \rightarrow \quad RNHCOO^- \quad + \quad RNH_3^+ \qquad (2.1)$$

$$RNHCOO^- + H_2O \quad \rightarrow \quad RNH_2 + HCO_3^- \qquad (2.2)$$
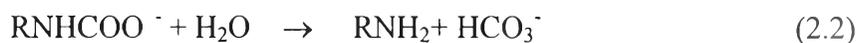
Amino-functionalized mesoporoussilicas (AFMS) are ideal candidates for capturing CO_2 from combustion flue gas due to the reversible formation of ammonium carbamates and/or carbonates during CO_2 adsorption, as well as due to uniform, large pores, and high surface area. Hao *et al.*, (2010) synthesized an amino-functionalized silica nanospheres with centrosymmetric radial mesopores using the anionic surfactant N-lauroylsarcosine sodium (Sar-Na) as template and 3-aminopropyltrimethoxysilane (APMS) as co-structure directing agent and study CO_2 adsorption. It was found that as-synthesized sample extracted with a solution of MEA in ethanol is better CO_2 adsorption than the sample extracted with a solution of acetonitrile, calcium and HCl. The adsorbed amount of CO_2 on the as-synthesized sample extracted with a solution of MEA in ethanol was 1.30 mol/kg that is higher than 1.25 mol /kg on the amine-grafted MCM-41 , 0.40 mol/ kg on the PEI surface modified MCM-48 , 0.80 mol /kg on the APS surface-modified MCM-48 , and 1.12 mol /kg1 on the APS surface-modified silica xerogel.

Yan *et al.*, (2011) prepare dmesocellular silica foam (MCF) material with different window sizes and functionalized with polyethyleneiemine (PEI) for use as CO_2 adsorbents. For the same window size, the CO_2 adsorption capacity of hybrid material increased with amount of PEI impregnated due to the shape of the pores having windows which PEI has difficulty of getting inside every cells because the windows are narrow in MCF. The PEI-MCF at 50% loading of PEI is highest CO_2 uptake capacity (115.9 mg/g adsorbent). The CO_2 uptake, it found that CO_2 uptake increased with temperature and the highest CO_2 uptake (124 mg/g adsorbent) occurred at 100°C for PEI-MCF at 50% loading of PEI. In case of different window sizes, the CO_2 adsorption capacity increase with the window size of MCF substrates because increasing of window size could be easily introduce PEI to cell of MCF. The largest window size MCF adsorbent which have NH_4/Si molar ratio equal 6% exhibited the largest CO_2 uptake of 152.0 mg/g adsorbent with 50% loading of PEI under the 15.1%v/v CO_2 in N_2 at 75°C and atmospheric pressure.

Repeated adsorption/desorption cycles revealed that the MCF modified by PEI was a good adsorbent for good cyclic stability.

Lu *et al.* (2009) studied thermodynamics and regeneration of CO_2 adsorption on mesoporous spherical-silica particles (MSPs) that modified with N-[3-(trimethoxysilyl) propyl]ethylenediamine (EDA) solution. The thermodynamic analysis gave low isosteric heats of adsorption. The adsorption process is endothermic in the temperature range of 20-60°C but is exothermic in the temperature range of 60-150°C which are physical adsorption. The cyclic adsorption via MSP (EDA) showed that the adsorbed CO_2 desorbed via thermal treatment and via vacuum suction at 120 °C for 25 min and at 120 °C and 0.145 bar, subsequently. The adsorption time of spent MSP (EDA) was shortened to 7.5 min via the combination of thermal treatment and vacuum suction at 120 °C and 0.145 bar and thus reduced the amount of energy penalty. The adsorption performance of MSP (EDA) can be stable in the prolonged cyclic adsorption (15 cycles of adsorption and regeneration).

Hsu *et al.* (2009) prepared multiwalled carbon nanotubes (CNTs) that modified by 3-aminopropyl –triethoxysilane (APTS) solutions in order to study thermodynamics and regeneration of CO_2 adsorption from gas streams. CO_2 can be efficiently adsorbed on CNTs and CNT(APTS) with capture efficiencies more than 97%. The breakthrough time appears longer at low temperature, indicates exothermic nature of adsorption process, or after the APTS modification. The thermodynamic analysis gave low isosteric heats of adsorption. The cyclic adsorption showed that the adsorbed CO_2 desorbed via thermal treatment and via vacuum suction at 120 °C for 25 min and at 120 °C and 0.145 atm subsequently. The regeneration time was shortened to 5 min via thermal/vacuum desorption and thus reduced an 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. CO_2 adsorptions from literatures are summarized in Table 2.4.

Table 2.4 Summary of amine adsorbent

Amine Adsorbents	mmol CO_2/g	Reference
amino-functionalized silica nanospheres	1.03	Hao *et al.*, (2010)
amine-grafted MCM-41	1.25	
APS surface-modified MCM-48	0.80	
APS surface-modified silica xerogel	1.12	
Monoamine/MCM-41	0.39	Chang *et al.*, (2009)
Monoamine/SBA-15	0.45	
Monoamine/PE-SEA-15)	0.15	
APS/ SBA-15 (method I and II)	1.06,0.43	
AEA/ SBA-15(method I and II)	1.73,2.09	
TA/ SBA-15(method I and II)	2.41,1.50	
Zeolite 13X	0.36	Chatti *et al.*, (2009)
Zeolite 13X/MEA	0.45	
Zeolite 13X/IPA	0.51	
Activated fly ash (AC)	0.42	Maroto-Valer *et al.*, (2008)
AC-MDEA	0.69	
AC - DEA	0.84	
AC – MEA	1.13	
AC -MEA+MDEA	0.81	
PEI-modified SBA-15	1.36	Gargiulo *et al.*, (2007)
PEI-modified MCM-48	1.36	
Activated carbon Norit (N)	1.65	Plazz*et al.*, (2007)
N-DETA	0.91	
N-PEHA	1.09	
N-PEI	1.11	
MFC (Mesoculluar silica foam)	0.33	Yan *et al.*, (2011)
MFC-50%PEI loading	2.63	
MFC-60% PEI loading	2.51	
MFC-70% PEI loading	2.46	
MFC3*- MFC-50%PEI loading	3.37	
MFC6**- MFC-50%PEI loading	3.45	

*percentage of NH4/Si molar ratio in MCF =3

** percentage of NH4/Si molar

2.3.4.2 Regeneration

The adsorbent is generally adsorbed amount of the molecules that is the impurity of the gas mixture or the separated gases; it will reach the equilibrium of the adsorption. After this point, the molecules can't adsorb to the surface of the adsorbent. In the industry, the adsorbent is always regenerated in order to remove the absorbed molecules in the desorption cycle of adsorption process. There are four basic methods that used to release absorbed molecules from the adsorbent.

Thermal swing adsorption (TSA): the adsorbent is regeneration by heating. The stream of hot gas is heated to the desorption temperature. The adsorbed species are desorbed from the adsorbent to the fluid steam. The temperature of desorption is much higher than the adsorption temperature.

Pressure swing adsorption (PSA): the desorption process is operated by reducing pressure at essentially constant high temperature of the flue gas source and then purging the bed at low pressure. The operation is restricted to gaseous system. This application is for bulk separations with high concentration of contaminants.

Purging gas stripping: The adsorbate is purged with a nonadsorbing inert gas in elution chromatograph at the constant pressure and temperature. This method is applied only when the adsorbed molecules are weak bond.

Displacement desorption: The adsorbate is purged with stream containing a competively adsorbed molecules as in displacement chromatograph. This method is applied to both liquid and gas system.

2.4 Biopolymer and Modified Biopolymer

Biopolymer is non-toxic and renewable. Biopolymer is employed in industries, including packaging, electronics, automotive, and agricultural purposes, and medical applications such as in medical devices, tissue engineering, and drug delivery applications (Dash *et al.*, 2011).

Biopolymers are distinguished according to the chemical structure. A polynucleotide molecule is a biopolymer composed of 13 or more nucleotide monomers covalently bonded in a chain. DNA (deoxyribonucleic acid) and RNA (ribonucleic acid) are examples of polynucleotides with distinct biological function. Polypeptides are short polymers of amino acids linked by peptide bonds. They have the same peptide bonds as those in proteins, but are commonly shorter in length. And Polysaccharides are polymeric carbohydrate structures, formed of repeating units joined together by glycosidic bonds. Starch, glycogen cellulose, chitin are examples of polysaccharide.

Cellulose is naturally occurring material found in wood, cotton hemp and another plants-based material. The primary use of cellulose is wrapping film. It has also found in the treatment of renal failure, as well as in a variety of more recent and evolving clinical application such as scaffolds in tissue engineering, temporary skin substitute, a haemostatic agent, post-operative adhesion barrier and as a culture material for hepatocytes (Hoenich, 2006).

Chitosan is biopolymer of semi-synthetically derived amino polysaccharides having unique structures, multidimensional properties, highly sophisticated functionality and a wide range of applications in biomedical and other industrial areas. They have become interesting, not only because they are made from an abundant renewable resource, but also they are very compatible and effective biomaterials 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 (Figure 2.7). It is obtained by deacetylation of its parent polymer chitin, a polysaccharide widely distributed in nature (e.g. crustaceans, insects and certain fungi) (Dash *et al.*, 2011).
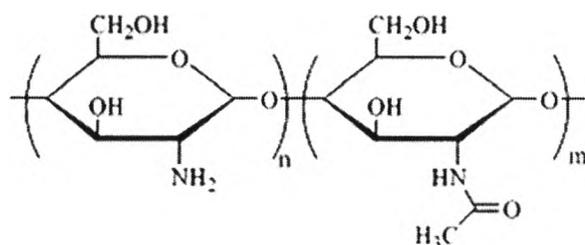
Figure 2.7 Structure of biopolymer.

Quaternary ammonium derivatives of chitosan are interestingly water-soluble, since most of the unique properties of chitosan are attributable to its cationic nature. Holappa *et al.* (2006) synthesized the novel quaternary piperizine derivatives of chitosan either by coupling a quaternary piperazinium acetic acid into chitosan or attaching a tertiary 1,4-dimethylpiperazine into N-chloroacetyl-6-O-triphenylmethylchitosan as starting material for quaternization reaction. The different quaternary piperazine derivatives of chitosan of monoquaternary N-[1-carboxymethyl-2-(1,4-dimethylpiperazinium)]chitosan chloride, monoquaternary N-[1-carboxymethyl-2-(4,4-dimethylpiperazinium)]chitosan chloride and diquaternary N-[1-carboxymethyl-2-(1,4,4-trimethylpiperazi-1,4-dium)]chitosan dichloride, were prepared through quaternization reaction as shown in Figure 2.8. The end products with less degrees of substitution were lower molecular weight and intrinsic viscosity than that of the starting chitosan because of the differences in the positioning of the quaternary nitrogen that affect on the activity of the chitosan derivatives.
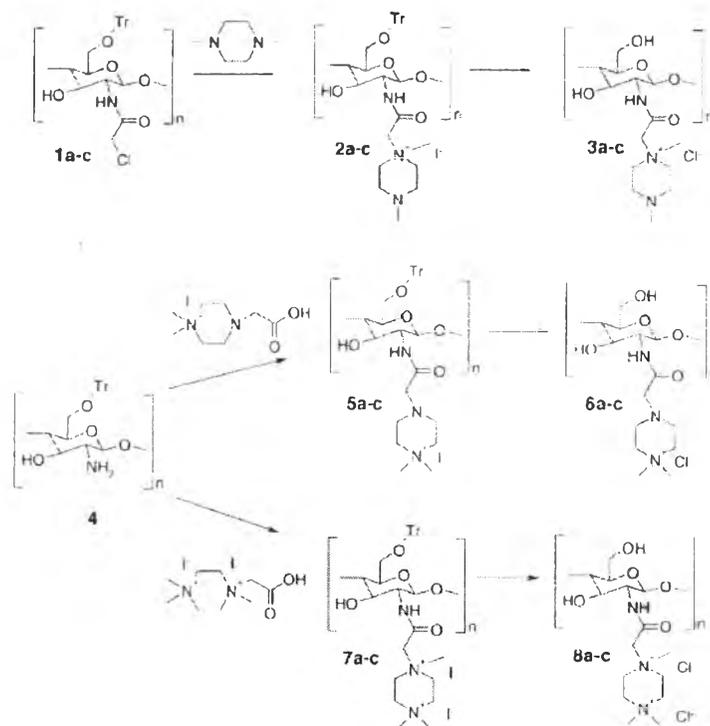
Figure 2.8 Synthetic route for the preparation of quaternary piperazine derivatives of chitosan. 2) 1,4-dimethylpiperazine, KI, NMP, 60 8C; 3) Aq. HCl, RT; 5) 4-carboxymethyl- 1,1-dimethylpiperazinium iodide, DCC, HOBt, NMP, RT; 6) Aq. HCl, RT; 7) 1- carboxymethyl-1,4,4-trimethylpiperazi-1,4-dium diiodide, DCC, HOBt, NMP, RT; 8)Aq. HCl, RT. (Holappa *et al.*, 2006).

Some literatures proposed the route of synthesis chitosan through chloroacetylation of deacetyled chitosan before adding some functional group for many applications. Jekins and Hudson (2001) studied the heterogeneous chloroacetylation of chitosan powder in the presence of sodium bicarbonate, which is widely ranged of possible end uses for chitosan. Effect of the acylating reagent (chloroacetyl chloride and chloroacetic anhydride), the solvent (methylene chloride (MeCl$_2$) and N,N-dimethylformamide (DMF)), and the temperature (0 or 44 °C) were studied to determine the optimal condition. The result found that the use of chloroacetic anhydride provided higher N-acylation and O- acylation yields than the use of chloroacetyl chloride. This could be due to the softer character of the

carboxylate anion leaving group relative to the chloride. For the solvent, the reactions in MeCl₂ consistently yielded higher degrees of acylation than reactions in DMF because the leaving group is charged. It appears that DMF, having a higher dielectric constant than MeCl₂, should promote better leaving group solubilization. Higher temperatures (44 and 0°C) proved more successful in chloroacetylating the chitosan powders because of the uncertainty of the IR molar absorptivities of the *N*-acyl and *O*-acyl groups, comparisons between these yields obtained for a given reaction will not be made.

Modification of chitosan in many biomedical applications can be done by reacting chitosan only one step which using hydroxyl group and amine group of chitosans. In 1999, Qu *et al.* synthesized the pH- sensitive hydrogels by grafting D,L-lactic acid (LA) without catalyst on the chitosan (CS). The FTIR and X-ray result showed that the dehydration of the CS amino lactate salt occurred to form amine group between the chitosan and D,L-lactic acid by heating solution and the polycondensation of lactic acid occurred at the same time to produce CS–PLA copolymers Methanol is more efficient than chloroform to extract unreacted monomer and oligomer but also salt-bonded LA. Increasing the reaction time and temperature in the amide-forming dehydration step as long as undesirable degradation of the CS–PLA copolymers does not occur can possibly attain a higher degree of substitution. D, L-lactic acid reacts with chitosan in homogeneous solution, the grafting by PLA took place randomly along the chain, giving rise to a random copolymer. This would efficiently destroy the regularity of the packing of the original CS chains, which resulted in the formation of almost amorphous copolymers. In aqueous solutions, an LA-graft-CS copolymer could form a novel pH-sensitive hydrogel due to the aggregation of the hydrophobic side chains. The specific solution content of hydrogels decreased when the pH value and ionic strength were increased. When increasing the salt concentration in the solutions outside the hydrogels, ionic swelling pressure is decreased, which results in a decrease of the gel volume.

Pasanphan *et al.* (2008) synthesized the conjugation of gallic acid onto chitosan for green and watered based antioxidant. The simple conjugation condition occurs in the heterogeneous system. The re-precipited chitosanin the ethanol was

reacted with gallic acid that was initiate the reactive ester group species on the gallic acid by using 1-ethyl-3-(3'-dimetylaminopropyl) carbodiimide (EDC) and N-hydroxysuccinimide (NSH) to induce the necleophilic, therefore the reaction possibly occurred at C-2, C-6 including C-3 of acid and formed the amide and ester linkage with chitosan. The reaction is illustrated in Figure 2.9. The degree of substitution at amino and hydroxyl groups of chitosan is 15.49%, 15.52%, 15.6% and 15.51% at ratio of chitosan: gallic acid: EDC: NHS = 1:1:1:1, 1:2:2:2, 1:3:3:3 and 1:4:4:4, respectively. For the thermal stability, chitosan is degraded before it melts at 290-310 °C. While the degradation temperatures of all derivatives of chitosan are lower than that chitosan in the range of 250-270 °C. It implied the loose of packing structure of chitosan after conjugating with gallic acid. The conjugation of chitosan and gallic acid showed the synergistic antioxidant on the hydroxyl radical scavenging where iron were involved, that is significant antioxidant activity on the free radical.
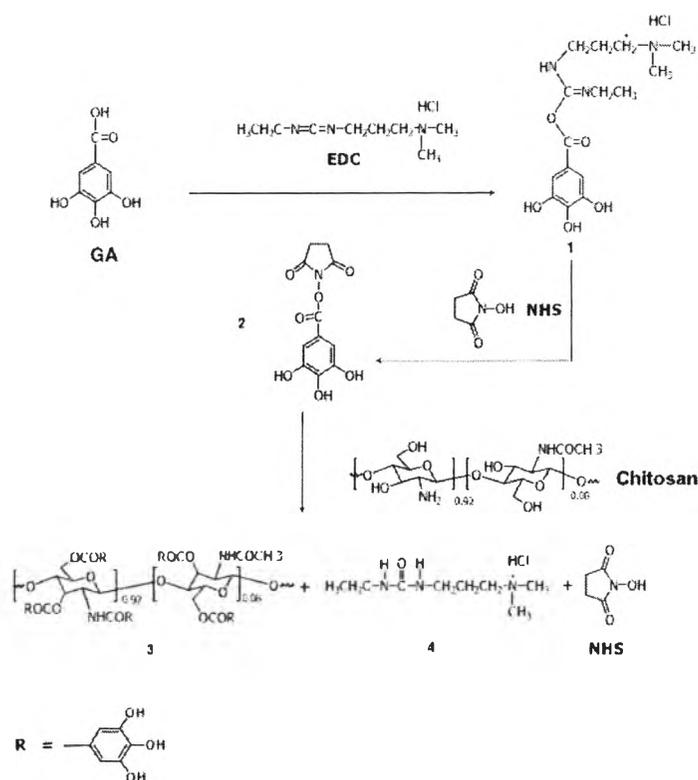
Figure 2.9 Reaction pathway of chitosan conjugated with gallic acid via conjugating agents.

Singh *et al.*, (2009) prepared a novel water-soluble chitosan-L-glutamic acid (CL-GA) aerogel at neutral and basic pH using supercritical carbon dioxide (sc.CO_2) in order to improving its solubility for biomedical application. They synthesized 85% deacetylated chitosan with L-glutamic acid (L-GA) in aqueous AcOH subjected to solvent exchange prior to using sc.CO_2 as a nonsolvent. The FTIR and H-NMR results confirm the formation of amide linkage between amine group (-NH2) of chitosan and carboxylic group (-COOH) of L-glutamic acid under mild condition. The degree of substitution was about 0.36 per glucose unit. The X- ray diffraction prove crystal structure of chitosan was transformed to an amorphous structure into a relatively more crystalline structure in chitosan to CL-GA derivative. It indicated that the structure of chitosan chain has been introduced with the glutamic acid. The decreasing thermal stability of CL-GA is caused by disruption of crystalline structure. The CL-GA is highly water - soluble up to the concentration of 8% (w/v). On the other hand, it was soluble in the acidic and alkali media at the concentrations of 4% and 5% (w/v), respectively. The solubility was increased due to insertion of more hydrophilic L-GA group at a relatively low degree of substitution (~0.36).

Singh and Dutta (2010) prepared biocompatible electrostatic chitosan /pyridine-3,5-di-carboxylic acid (CH-PyCA) complex for biomedical application. The formation of electrostatic complex occurred ionic interaction between protonation (NH_3^+) of chitosan and deprotonation (COO^-) of pyridine-3,5-di carboxylic acid in an acidic medium under mild condition as that was characterized by UV, FTIR, H-NMR. The reaction of formation of electrostatic chitosan /pyridine-3,5-di-carboxylic acid (CH-PyCA) complex is illustrated as Figure 2.10.The crystal structure of chitosan was transformed to an amorphous structure into a relatively more crystalline structure in chitosan to CH-PyCA complex that affect the thermal stability of CH-PyCA complex. It was found that the thermal stability of CH-PyCA complex is lower than chitosan due to the disruption of crystalline structure, especially through the loss of the hydrogen bonding.
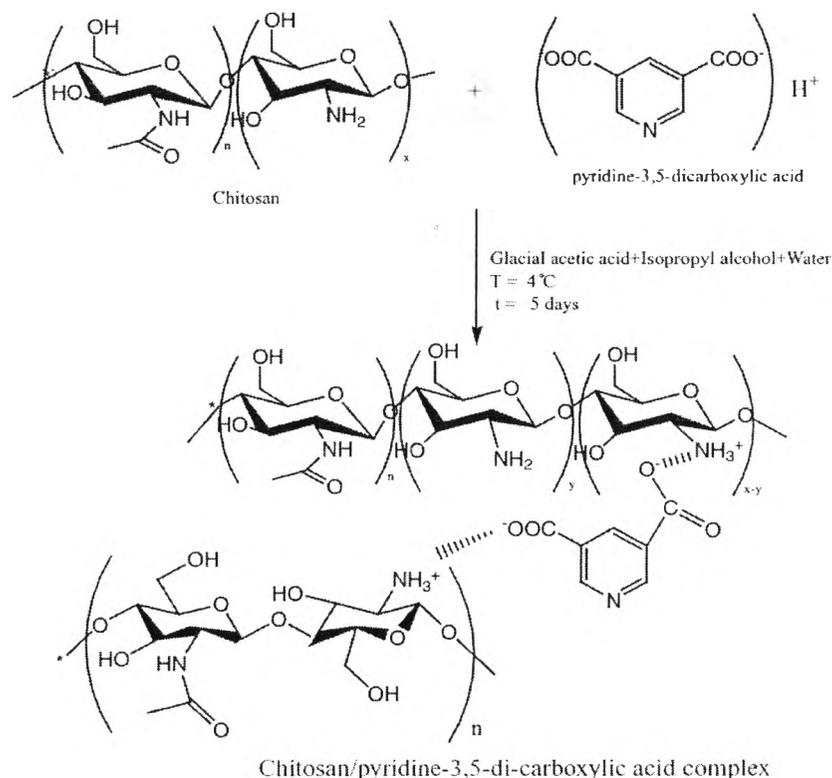
Figure 2.10 Synthesis of CH-PyCA complex.

Yoddee *et al.*, (2011) studied the synthesis of modified chitosan with piperazine in the heterogeneous system for carbon dioxide (CO_2) adsorption. For the synthesis, chitosan was modified by attaching a linkage group (chloroacetyl chloride) and then piperazine containing amino group was functionalized on surface area of purified biopolymer. The modified chitosan or perazylacetyl bipolymer (PABP) was characterized by Fourier transform infrared spectrophotometer (FT-IR) and elemental analysis. In the result of FIIR method, it is shown that the chloroacetyl chloride react with either amino or hydroxyl groups of the purified BP and then piperazine reacted with linkage group (-COC-Cl) instead of chloride group (-Cl) that is shown in Figure 2.11. The degree of piperazine substitution for PABP was 22%. For the CO_2 adsorption, the best adsorption of the modified biopolymer (PABP) was obtained after pretreatment with dry nitrogen at 378 K and had the CO_2 adsorption capacity of 0.2211mmol/g at 298 K under atmospheric pressure. However, the

maximum dynamic CO_2 adsorption capacity of modified chitosan was less than the maximum dynamic CO_2 adsorption capacity of chitosan.

Purified BP   Chloroacetyl chloride   Chloroacetyl biopolymer
                                                          (CABP)

Chloroacetyl biopolymer   Piperazine
(CABP)   (PZ)
                                              Piperazyl acetyl biopolymer
   (PABP)
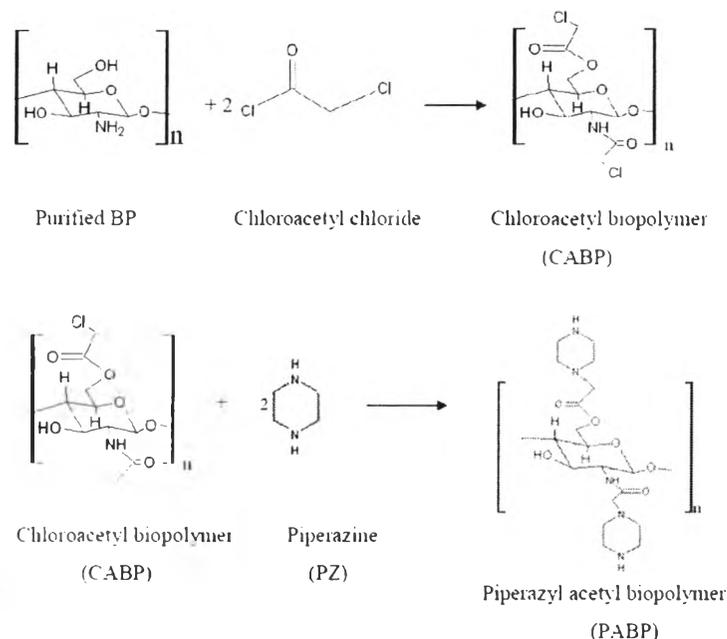
Figure 2.11 The synthesis of modified chitosan with piperazine.

From above literature survey, many attempts have been carried out to improve properties of biopolymer in biomedical and antibacterial applications Biopolymer was modified with different acid compounds such as gallic acid, lactic acid, gulutamic acid, and pyridine-3,5-di-carboxylic acid in order to improve its properties. All reactions occurred at carboxyl group of acid and amine group of biopolymer to form amide linkage or organic interaction. However, there is only one publication which has appeared to focus on the application of CO_2 adsorption. Therefore it is possible to modify biopolymer with piperazine-2-carboxylic acid to improve the CO_2 capacity and selectivity of the biopolymer.