

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Global Warming

Global warming is the rise in the average temperature of Earth's atmosphere and oceans since the late 19th century. Since the early 20th century, Earth's mean surface temperature has increased by about 0.8 °C (1.4 °F), with about two-thirds of the increase occurring since 1980 (Board on Atmospheric Sciences and Climate, 2011). Warming of the climate system is unequivocal, and scientists are more than 90% certain that it is primarily caused by increasing concentrations of greenhouse gases.

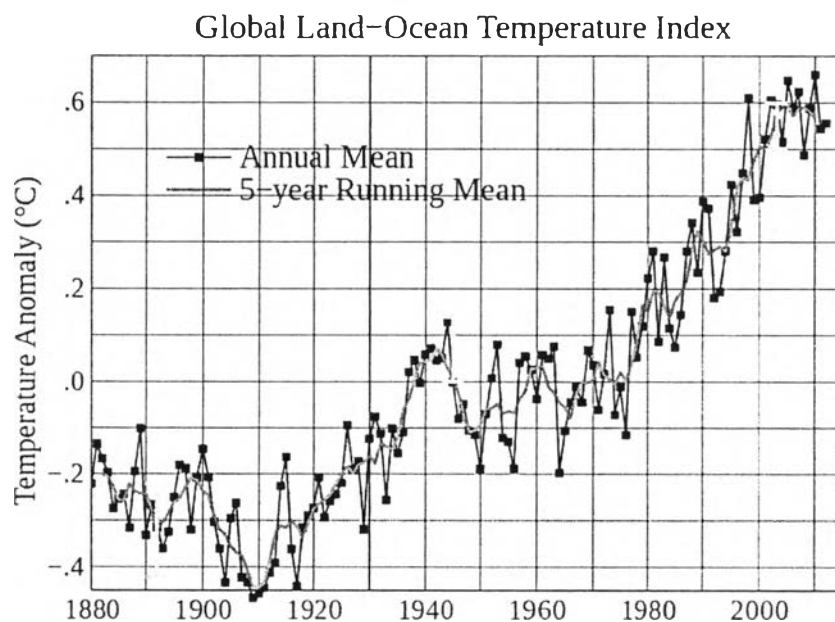


Figure 2.1 Global temperature anomaly 1880-2012 (data.giss.nasa.gov).

A greenhouse gas (GHGs) is a gas in an atmosphere that absorbs and emits radiation within the thermal infrared range. This process is the fundamental cause of the greenhouse effect. The primary greenhouse gases in the Earth's atmosphere are water vapor, carbon dioxide, methane, nitrous oxide, and ozone. Greenhouse gases greatly affect the temperature of the Earth (en.wikipedia.org).

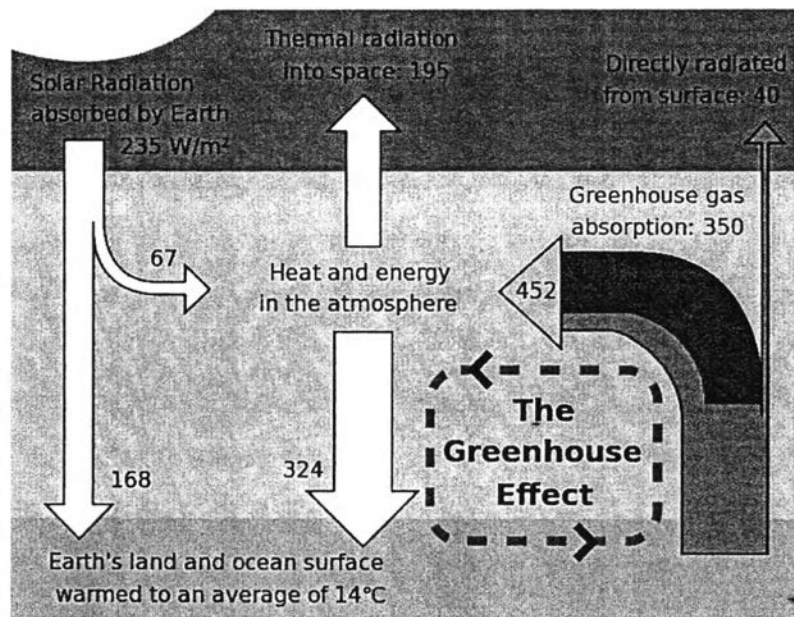


Figure 2.2 Representation of the exchanges of energy between the Sun, the surface, the atmosphere, and the ultimate sink outer space (www.globalwarmingart.com).

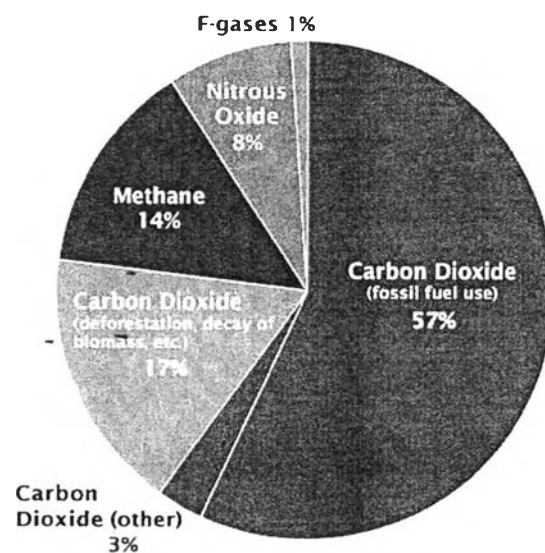


Figure 2.3 Global greenhouse gas emissions by gas (www.ipcc.ch).

The Intergovernmental Panel of Climate Change (IPCC) developed the Global Warming Potential (GWP) to compare the ability to trap heat or potential of GHGs that affects the greenhouse effect. Carbon dioxide (CO₂) is a major cause of global warming. Although the global warming potential (GWP) of CO₂ is low but the large amount of CO₂ emission is the problem (www.ipcc.ch).

Table 2.1 Global warming potentials (GWP) and atmospheric lifetimes (Years) used in the inventory (www.ipcc.ch)

Gas	Atmospheric Lifetime	100-year GWP	20-year GWP	500-year GWP
Carbon dioxide	50-200	1	1	1
Methane	12 ±3	21	56	6.5
Nitrous oxide	120	310	280	170
HFC-23	264	11,700	9,100	9,800
HFC-125	32.6	2,800	4,600	920
HFC-134a	14.6	1,300	3,400	420
HFC-143a	48.3	3,800	5,000	1,400
HFC-152a	1.5	140	460	42
HFC-227ea	36.5	2,900	4,300	950
HFC-236fa	209	6,300	5,100	4,700
HFC-4310mee	17.1	1,300	3,000	400
CF ₄	50,000	6,500	4,400	10,000
C ₂ F ₆	10,000	9,200	6,200	14,000
C ₄ F ₁₀	2,600	7,000	4,800	10,100
C ₆ F ₁₄	3,200	7,400	5,000	10,700
SF ₆	3,200	23,900	16,300	34,900

2.2 Carbon Dioxide

Carbon dioxide (CO₂) is the primary greenhouse gas emitted through human activities. In 2010, CO₂ accounted for about 84% of all U.S. greenhouse gas emissions from human activities. Carbon dioxide is naturally present in the atmosphere as part of the Earth's carbon cycle (the natural circulation of carbon among the atmosphere, oceans, soil, plants, and animals). Human activities are altering the carbon cycle-both by adding more CO₂ to the atmosphere and by influencing the ability of natural sinks, like forests, to remove CO₂ from the atmosphere. While CO₂ emissions

come from a variety of natural sources, human-related emissions are responsible for the increase that has occurred in the atmosphere since the industrial revolution (National Research Council, 2010).

Since the beginning of the Industrial Revolution, the burning of fossil fuels has contributed to a 40% increase in the concentration of carbon dioxide in the atmosphere from 280 ppm to 397 ppm. Anthropogenic carbon dioxide (CO₂) emissions come from combustion of carbon based fuels, principally wood, coal, oil, and natural gas (Lindeburgh, 2006).

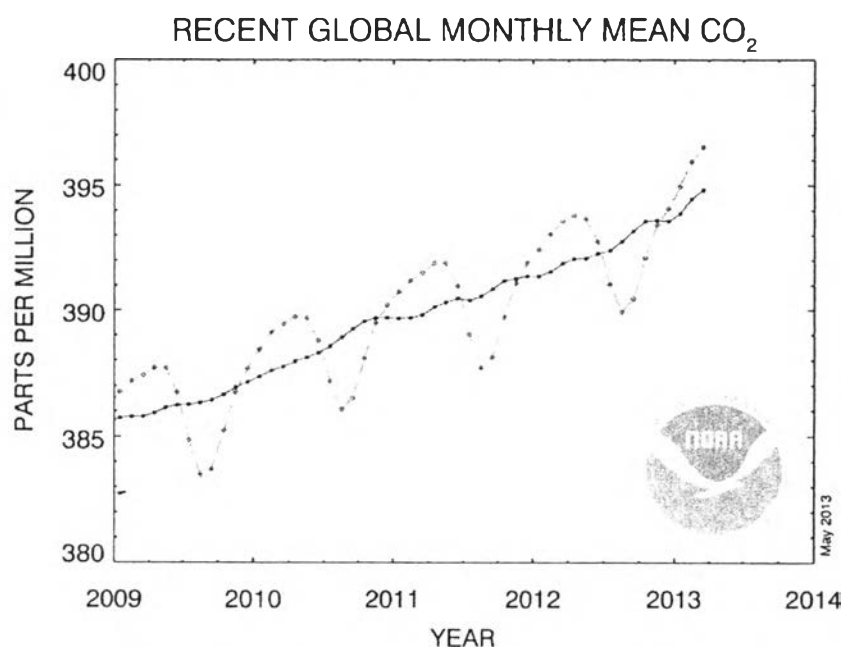


Figure 2.4 Recent monthly mean carbon dioxide globally averaged over marine surface sites (www.esrl.noaa.gov).

Consequently, the only three remaining options of reducing total CO₂ emission into the atmosphere are: (1) reducing energy intensity; (2) reducing carbon intensity, i.e. use of carbon-free fuel; and (3) enhancing the sequestration of CO₂. The first option requires efficient use of energy. The second option requires switching to using non-fossil fuels such as hydrogen and renewable energy. The third option involves the development of technologies to capture and sequester more CO₂. It is

clear that implementation of all the above-mentioned options will be necessary if CO₂ emission abatement becomes a serious global priority (Olajire, 2010).

2.3 Carbon Capture Technologies

There is growing concern that anthropogenic carbon dioxide (CO₂) emissions are contributing to global climate change. Therefore, it is critical to develop technologies to mitigate this problem. Irons *et al.* (2007) show that CO₂ emissions can be reduced for power generation by three capture technologies: pre-combustion, oxyfuel combustion and post-combustion.

2.3.1 Pre-combustion Capture

In pre-combustion capture, fuel is reacted with oxygen to give mainly carbon monoxide and hydrogen. This process is known as partial oxidation. The mixture of mainly CO and H₂ is passed through a catalytic reactor, called a shift converter, where the CO reacts with steam to give CO₂ and more H₂. CO₂ is separated, and H₂ is used as fuel in a gas turbine combined-cycle plant. The primary disadvantage of pre-combustion capture is that total capital costs of the generating facility are very high (Olajire, 2010).

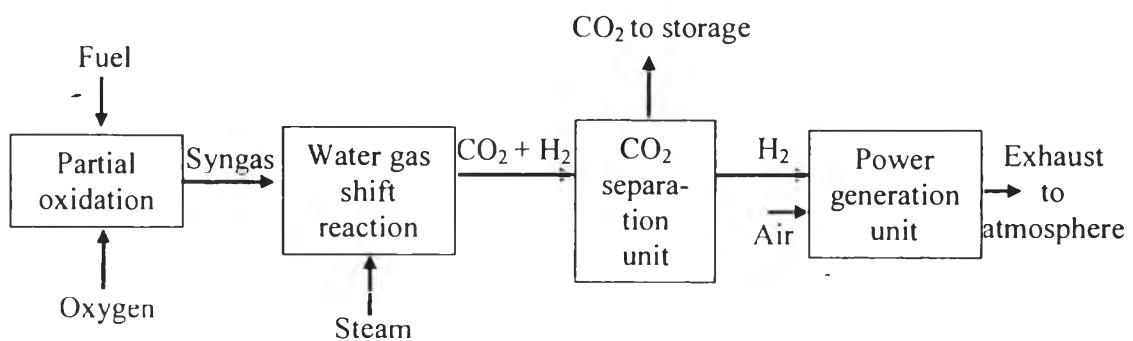


Figure 2.5 Principle of pre-combustion CO₂ capture (Mondal *et al.*, 2012).

2.3.2 Oxyfuel Combustion Capture

Oxyfuel combustion systems are being developed as an alternative to post-combustion CO₂ capture for conventional coal fired power plants. Here, pure oxygen rather than air is used for combustion. This eliminates the large amount of nitrogen in the

flue gas stream. The flue gas consists only of water vapor and CO_2 . The water vapor is easily removed by cooling and compressing the flue gas. Additional removal of air pollutants leaves a nearly-pure CO_2 stream that can be sent directly to storage (Rubin *et al.*, 2012). The main disadvantage of oxyfuel combustion is that a large quantity of oxygen is required, which is expensive, both in terms of capital cost and energy consumption (Olajire., 2010).

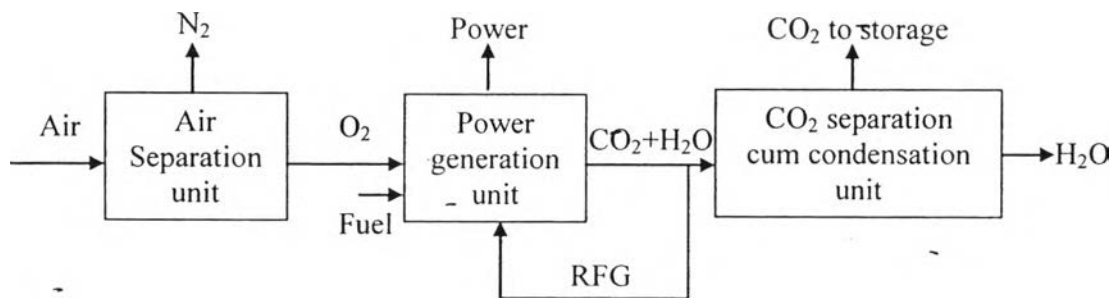


Figure 2.6 Principle of oxyfuel combustion CO_2 capture (Mondal *et al.*, 2012).

2.3.3 Post-combustion Capture

Post-combustion capture involves the removal of CO_2 from the flue gas produced by combustion. Existing power plants use air, which is almost four-fifths nitrogen, for combustion and generate a flue gas that is at atmospheric pressure and typically has a CO_2 concentration of less than 15% (Figuerola *et al.*, 2008). The low concentration of CO_2 in power-plant flue gas means that a large volume of gas has to be handled, which results in large equipment sizes and high capital costs. Post-combustion capture offers a significant design challenge due to the relatively low partial pressure of CO_2 in the flue gas (Olajire., 2010).

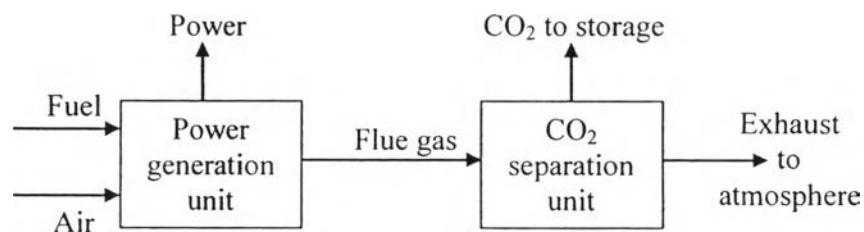


Figure 2.7 Principle of post-combustion CO_2 capture (Mondal *et al.*, 2012).

2.4 CO₂ Separation Techniques

There are several technologies available to capture CO₂ from fossil fuel power plant. These include mainly absorption, adsorption, cryogenic, and membrane processes.

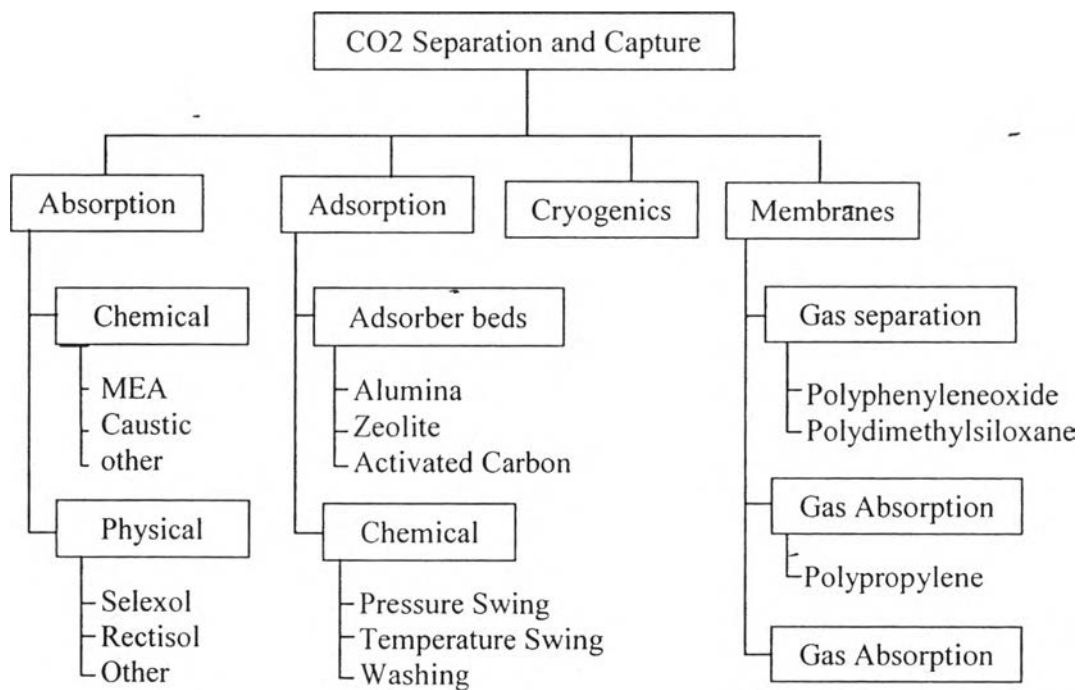


Figure 2.8 Technology options for CO₂ separation (Rubin *et al.*, 2012).

2.4.1 Absorption

Chemical or physical absorption processes are widely used in the petroleum, natural gas, and coal fired power plants as well as chemical industries for separation of CO₂. It is based on the reaction between CO₂ and chemical solvent such as aqueous solution of mono-, di- and tri-amine, di-isopropanol amine, etc. (Choi *et al.*, 2009). In this method, absorber and regenerator are working continuously. Flue gas stream containing CO₂ is introduced at the bottom of the absorber. Absorbent is introduced from top of the column that leads counter current contact between flue gas and solvent and a selective absorption of CO₂ takes place. Then, CO₂ rich stream is fed to the regenerator, where desorption of CO₂ occurs, and regenerated solvent is recycled for further use. Desorbed CO₂ is

compressed and sent to storage. Available literature reveals that the chemical absorption holds good result in terms of removal efficiency and can be used for low concentration flue gases (Rao *et al.*, 2002). Amine-based solvents have been enhanced over the years, such that primary (monoethanolamine (MEA) & diglycolamine (DGA)), secondary (diethanolamine (DEA) & diisopropanolamine (DIPA)) and tertiary (methyldiethanolamine (MDEA) & triethanolamine (TEA)) variants are available through different suppliers, many of which include special proprietary additives to improve performance and other characteristics. The choice of a particular alkanolamine is primarily dictated by the requirements of the specific application. With the exception of a few, these amines have a maximum sorption capacity of 1 mole of CO₂ to two moles of amines. Liquid tertiary amines and amidines have shown a higher sorption capacity with a ratio of 1:1 molar, thereby reducing the volume of amine, but the reaction rate is much slower. Amine blends have been used to compensate for this difference in order to reduce regeneration and recirculation costs and increase CO₂ loading capacity (Benamor *et al.*, 2012).

The use piperazine as an activator in conventional amine systems for acidic gases removal has increasingly been reported in the literature. This is, because of its high absorption capacity, high selectivity, and low regeneration energy. Rochelle *et al.* (2011) studied a new process that uses piperazine (40 wt% PZ) with regeneration at 150 °C by a two-stage flash as a substitute to the conventional 30 wt % MEA scrubbing process. They claimed that piperazine can be used up to 150 °C without significant thermal degradation, it is resistant to oxidative degradation and has less volatility than MEA, and it is not corrosive to stainless steel. Blended solvents provide an enhancement in overall efficiency than individual solvent. However, several limitations to absorption process such as, solvent degradation, corrosion, solvent regeneration efficiency, etc affect the efficiency of CO₂ removal (Mondal *et al.*, 2012).

2.4.2 Adsorption

Adsorption is a process for removal of one or more components of a mixture with the help of a solid surface. The adsorption processes are based on significant intermolecular forces between gases (including CO₂) and the surfaces of certain solid materials (such as molecular sieves and activated carbons). This attachment can be either physical (physisorption) or chemical (chemisorption) depending on the temperature, partial pressure, sur-

face force and adsorbent pore sizes, single or multiple layers of gases can be adsorbed (Olajire, 2010; Axel and Xiaoshan, 1997). In CO₂ capture by adsorption technology, a packed column is mainly filled by spherical adsorbent, and CO₂ bearing stream is passed through the column. CO₂ is attracted towards the adsorbent and adheres on the surface of adsorbent, followed by regeneration (desorption), which can be achieved either by reducing pressure (Pressure-Swing Adsorption or PSA), or by increasing temperature (Temperature Swing Adsorption, or TSA) or by passing an electric current through the adsorbent (Electrical Swing Adsorption, or ESA) or process hybrids (PTSA) or washing (Mondal *et al.*, 2012).

Solid adsorbents such as activated carbons, zeolites, mesoporous silicates, alumina, and metal oxide have been extensively used for gas separation (Thiruvengatchari *et al.*, 2009). Adsorption of CO₂ from a gas stream is a dry process; hence, it has no by-product such as wastewater in conventional absorption process. Moreover, it requires low energy compared to that of cryogenic and absorption processes. But there are some limitations that make this process less effective such as low selectivity and capacity of available adsorbent for CO₂, lower removal efficiency compared to other technologies (absorption and cryogenic) and regeneration and reusability of adsorbent (Choi *et al.*, 2009). In these reasons, much attention is required for developing the new adsorbents or modification on surface chemistry of existing adsorbents so that the adsorbents can operate at higher temperatures in the presence of steam with increased capacity and improved selectivity (Mondal *et al.*, 2012).

2.4.3 Cryogenics

The cryogenic method of purification involves the separation of the gas mixtures by fractional condensation and distillation at low temperature. Low temperature distillation (cryogenic separation) is a commercial process commonly used to liquefy and purify CO₂ from relatively high purity (> 90%) sources. It involves cooling the gases to a very low temperature (lower than -73.3 °C) so that CO₂ can freeze out/liquefied and separated. The process has the advantage that it allows recovery of pure CO₂ in the form of a liquid, which can be transported conveniently or pumped to the injection site for enhanced oil recovery (EOR) or enhanced coal-bed methane (ECBM) (Olajire, 2010).

Cryogenic process is inherently difficult to apply for CO₂ capture, because most CO₂ occurs in conjunction with other gases (SO_x, NO_x, H₂O), which severely inter-

fere with cooling and cause corrosion, fouling, and plugging. There is a need to remove all trace water from feed, which leads to increase the CO₂ capture cost. Furthermore, the phase behavior of CO₂ is complex, and it easily leads to the formation of solids, which plug equipment and severely reduce heat transfer rates resulting in the reduction of process efficiency (Axel *et al.*, 1997). In light of these limitations and high cost of refrigeration, this process can be used only for special circumstances as an adjunct to other processes (Mondal *et al.*, 2012).

2.4.4 Membrane

A relatively novel capture concept is the use of selective membranes to separate certain components from a gas stream, which can be CO₂ from flue gas (post-combustion system), CO₂ from natural gas (natural gas processing), and CO₂ from hydrogen (pre-combustion systems) or oxygen from nitrogen (in oxyfuel combustion system). Membranes are semi-permeable barriers able to separate substances by various mechanisms (solution/diffusion, adsorption/diffusion, molecular sieve, and ionic transport). They 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 act as filters to separate one or more gases from a feed mixture and generate a specific gas rich permeate as shown in Figure 2.9 below. Two characteristics dictate membrane performance; permeability, that is the flux of a specific gas through the membrane, and selectivity, the membrane's preference to pass one gas species over the other (Olajire, 2010).

In membrane technology for CO₂ separation, the required energy per unit mass of CO₂ captured is in the range of 0.5-6 MJ/kg of CO₂ compared to other existing technologies. But low removal efficiency and low purity of CO₂ make this process ineffective. Also its feasibility is decreased when concentration of CO₂ in the feed stream is below 20%. Since the membrane cannot usually achieve high degree of separation, it cannot be optimized for large volume of gas separation. So, multiple stages and/or recycle of one of the streams are necessary. Membranes are sensitive to sulfur compounds and other traces (Abass and Olajire, 2010).

Facilitated transport membrane, mixed matrix membrane etc. are good enhancement in membrane technology. Also the membrane process in combination with other existing processes may increase the overall efficiency of the process, e.g. membrane with cryogenic and membrane with absorption process (Mondal *et al.*, 2012)

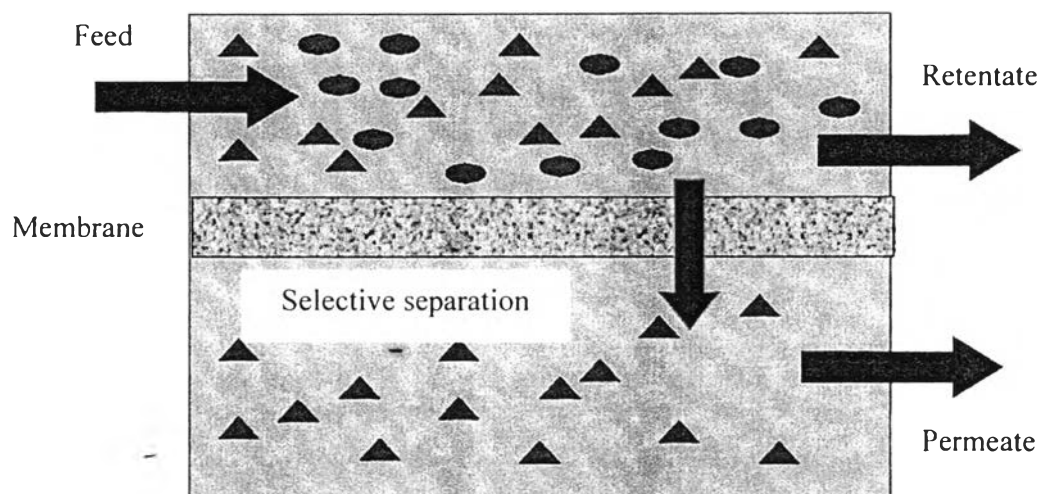


Figure 2.9 Schematic of gas-separation membrane (Olajire, 2010).

2.5 Adsorbents

Several different sorbents, e.g. carbonaceous material, zeolites, ordered mesoporous silica, metal-organic frameworks, and amine-base materials, have been used for physical and chemical adsorption of CO_2 . The potential adsorbents must have: (1) high selectivity and adsorption capacity for CO_2 ; (2) adequate adsorption/desorption kinetics; (3) stable cyclic adsorption capacity; (4) mechanical durability to maintain reasonable performance after extended cyclic exposure to high pressure or high temperature; and (5) low energy needs for regeneration of pure CO_2 (Kwon *et al.*, 2011).

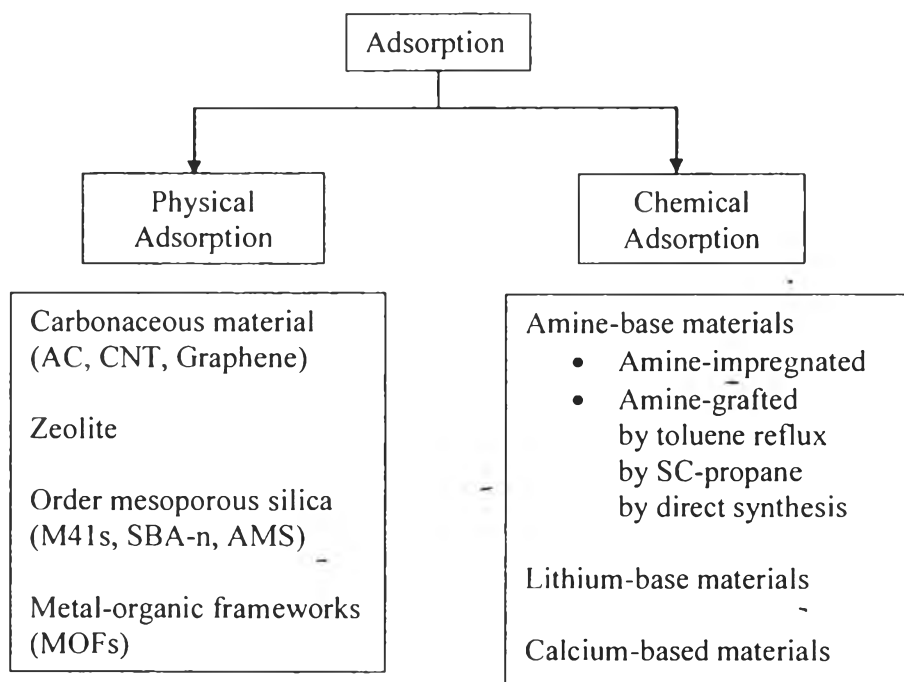


Figure 2.10 Flow diagram for CO₂ capture by adsorption (Yu *et al.*, 2012).

2.5.1 Physical Adsorbents

Physical adsorbents can be classified into :

- Carbonaceous material
- Zeolite
- Ordered mesoporous silica
- Metal-organic frameworks (MOFs)

2.5.1.1 Carbonaceous material

Because of their wide availability, low cost, and high thermal stability, it is largely established that activated carbons have advantages over other CO₂ adsorbents. Among the carbon based adsorbents reported in the literature, activated carbons (ACs) and carbon nanotubes (CNTs) are the most investigated materials. CO₂ adsorption on ACs have been studied experimentally and theoretically for a long time and have found commercial applications. There is a wide range of ACs with a large variety of microporous and mesoporous structures. Activated carbons may be produced from many raw materials such as coal, coke pitch, wood or biomass sources (e.g., saw dust, coconut shells, olive stones), often via two steps: carbonization and activation (Lozano-Castello *et al.*, 2002). Carbon molecular sieves (CMS), which are a sub-class of activat-

ed carbon with narrow pore size distribution (PSD), are kinetic-based adsorbents. They have been commercialized mainly for the separation of air and the production of high purity N_2 (Coe, 1995). However, at low CO_2 partial pressure, ACs exhibit 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 (Filipe *et al.*, 2009).

Carbonaceous materials seem to be interesting only for CO_2 removal at high pressure and low (e.g., room) temperature. These limitations may not be suitable for low pressure CO_2 capture from flue gas treatment. However, as discussed later, the strategy to increase the strength of CO_2 interactions with such materials at low partial pressure via surface modification may hold promise (Sayari *et al.*, 2011).

2.5.1.2 Zeolite

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, there are 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 (Yu *et al.*, 2012).

2.5.1.3 Ordered mesoporous silica

Ordered mesoporous silica may be a candidate because of its high surface area, high pore volume, tunable pore size, and good thermal and mechanical stability. So far mesoporous silicas including the families of M41S, Santa Barbara Amorphous type material (SBA-n), anionic surfactant- templated mesoporous silica (AMS), etc., have been reported. However, the CO_2 adsorption capacities are not high enough, especially, at atmospheric pressure, to allow their practicability (Yu *et al.*, 2012).

The liquid amine absorption process inspired researchers to use amine-modified solid materials as adsorbents for CO₂ capture. As far as flue gas treatment is concerned, it was anticipated that supported amines will maintain a high selectivity toward CO₂ with a negligible uptake of other components, particularly N₂, but without the aforementioned drawbacks associated with aqueous amine solutions.

The following sections are organized according to the type of interactions between amine groups and the support, namely (i) amine-impregnated materials where mostly weak interactions occur, and (ii) covalently bonded amine-containing species, obtained typically via surface-grafting of aminosilanes. The grafted materials offer comparatively higher rate of adsorption than amine-impregnated adsorbents (Serna-Guerrero and Sayari, 2001) and, in some cases even higher than commercial adsorbents such as 13X (Harlick and Sayari, 2007). However, the organic content of amine-grafted adsorbents depends on the surface density of hydroxyl groups, needed to anchor the aminosilane. As for impregnated amines, higher loadings may be achieved, but often accompanied by increasingly strong diffusion limitations (Sayari *et al.*, 2011).

2.5.2.2 Amine-impregnated Adsorbent

Xu *et al.* (2002) reported the effects of polyethylenimine (PEI) loading, gas conditions, temperature, moisture, and supports on CO₂ adsorption capacity for the PEI-impregnated mesoporous silica and carbonaceous materials. A higher PEI loading significantly enhanced CO₂ adsorption capacity together with the decrease in the surface area, pore size, and pore volume of the PEI impregnated supports. The highest CO₂ 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 CO₂ at 75 °C, while the highest amine efficiency (CO₂/N₂ molar ratio) occurred at 50 wt% PEI loading and was reduced with an increase in the PEI loading. In general, the amine loading is not directly related to the amines for CO₂ adsorption because the formation of the aggregated amine on supports would reduce the amine accessible to CO₂. When the PEI/MCM-41 with 50 wt% PEI loading was used to treat an anhydrous gas containing 15% CO₂ in N₂ at 75 °C, the adsorption capacity was found to reduce to 2.03 mmol/g. When the temperature was decreased from 75 to 25 °C, the CO₂ adsorption capacity was found to decrease as well. It is known that CO₂ adsorption is an exothermic process. The increasing temperature is unfavorable for CO₂ adsorption capacity. However, the formation of bulk-like PEI inside the pore at low temperature leads to CO₂ adsorption as

a diffusion-limited process (Sayari *et al.*, 2011). At high temperature, the high CO₂ adsorption capacity is possibly due to the high diffusion rate of CO₂ into bulk like PEI and the increasing reaction rate of CO₂ with PEI (Yu *et al.*, 2012).

Xu *et al.* (2005b) further studied the effect of moisture on CO₂ capture using the PEI/MCM-41 and showed that the CO₂ adsorption capacity was increased from 2.03 mmol/g for an anhydrous flow containing 15% of CO₂ to 2.84 mmol/g for a flow containing 10% of moisture and 13% of CO₂. The improvement of CO₂ adsorption capacity was interpreted in terms of adsorption mechanisms, i.e., the formation of carbamate and bicarbonate under anhydrous and hydrous conditions, respectively. The positive effect of moisture was only observed for the molar concentration of moisture not higher than that of CO₂. Concerned with structure of support, Wang and Song (2012) also prepared the PEI-impregnated SBA-15 with a PEI loading of 50 wt% and found a higher CO₂ adsorption capacity as 3.18 mmol/g, which was about 1.5 times higher than the PEI/MCM-41 for an anhydrous flow containing 15% CO₂ at 75 °C. Son *et al.* (2008) also reported the effect of support and demonstrated that CO₂ adsorption capacity and kinetics were mainly influenced by pore size and followed an order of hexagonal mesoporous silica (HMS) > KIT-6 > SBA-16 ≈ SBA-15 > MCM-48 > MCM-41.

Plaza *et al.* (2007, 2008) studied CO₂ capture using activated carbon and alumina impregnated with various types of amines including primary and secondary alkylamines such as diethylenetriamine (DETA), pentaethylenhexamine (PEHA) and PEI, alkanolamines such as diisopropanolamine (DIPA), sterically hindered 2-amino-2-methyl-1,3-propanediol (AMPD), and triethanolamine (TEA). Their results indicated that the DETA-impregnated alumina exhibited the highest CO₂ adsorption capacity throughout the tested temperature range. The decrease in the CO₂ adsorption capacity for impregnation of amine-impregnated activated carbon was mainly due to reduction of microporous volume responsible for physical adsorption of CO₂. They further studied the carbon-based supports derived from sewage sludge and air-oxidized olive stones impregnated with PEI and found that the increase of CO₂ adsorption capacity depended on the textural properties of the support and the surface modification methodology (Yu *et al.*, 2012).

Quanmin *et al.* (2012) studied CO₂ capture using silica gels impregnated with methyldiethylamine (MDEA) activated with piperazine (PZ). Their results indicated

that surface coating with a mixture of MDEA and PZ considerably increased the selectivity and capacity of silica gel for CO₂ adsorption.

In addition to mesoporous materials, zeolites have also been used as supports. Jadhav *et al.* (2007) dispersed MEA on 13X zeolite producing materials with different loadings. Quite interestingly, the adsorbent with the highest capacity at low temperature (i.e., 35 °C), with 1.96 mmol/g for 15% CO₂ in N₂, contained only 2.9 wt% MEA, while the best capacity at 75 °C (i.e., 0.45 mmol/g) was obtained on a sample with the highest loading (i.e., 25 wt%). The capacity was comparatively higher than unmodified 13X, which adsorbed 0.64 and 0.36 mmol/g at 35 and 75 °C, respectively. An interesting advantage of amine-containing 13X was a significant improvement in its tolerance to moisture. While it is generally accepted that preferential adsorption of water on 13X resulted in a drastic reduction of CO₂ uptake, the adsorption capacity in the presence of 100% RH decreased by only ca. 13% with respect to dry conditions (Sayari *et al.*, 2011).

It seems to be more appropriate to use supports with large pore size and pore volume to impregnate amine. However, the decreases in adsorption rate, amine efficiency (CO₂/N₂ ratio), and cyclic performance were observed accompanied by high amine loading. Thus, how to overcome these drawbacks in order to promote the performance of amine-impregnated adsorbent needs further studies (Yu *et al.*, 2012).

2.5.2.3 Amine-grafted Adsorbent

Though high CO₂ adsorption capacity was observed in amine-impregnated materials, the lack of thermal stability in desorption was also reported (D'Alessandro *et al.*, 2010). To overcome this limitation, aminosilanes were proposed to be covalently grafted onto the intrachannel surface of the mesoporous silicas through silylation. Generally, there are two preparation methods, post modification and direct synthesis (also called co-condensation). Several studies have been reported for synthesis of amine grafted silicas for CO₂ capture using aminosilanes such as (3-aminopropyl) triethoxysilane (APS), *N*-[(3-trimethoxysilyl)propyl] ethylenediamine (2N-APS) and *N*-[(3-trimethoxysilyl)propyl]diethylenetriamine (3N-APS). Leal *et al.* (1995) firstly published the work on APS grafted silica gel for CO₂ capture and proposed the CO₂ adsorption via the formation of ammonium carbamate under anhydrous condition and the formation of ammonium bicarbonate in the presence of moisture leading to one amino group reacted with one molecular CO₂.

This APS grafted silica gel exhibited a CO₂ adsorption capacity as 0.41 and 0.89 mmol/g under an anhydrous and hydrous flow with pure CO₂ at 27 °C, respectively.

In previous work, APS, 2N-APS and 3N-APS were grafted onto MCM-41, SBA-15 and pore expanded-SBA-15 (Chang *et al.*, 2009). The experimental results showed that SBA-15 was the most appropriate support because its pore size could accommodate more amines and avoid blocking during CO₂ adsorption. Besides, its high pore surface area providing large amount of silanol group was more beneficial for aminosilane grafting. Among the studied amines, 3N-APS exhibited the highest CO₂ adsorption capacity as 2.74 and 3.06 mmol/g at 40 °C under anhydrous and hydrous (78% RH) flows containing 17% CO₂, respectively, followed by 2N-APS and APS.

The other approach to synthesize amine-grafted adsorbent is the direct synthesis via the co-condensation of siloxane and aminosilane in the presence of an organic template. The direct synthesis can be carried out in acidic or basic media. Kim *et al.* (2008) reported a comparative study for the amine-grafted mesoporous silica using the anhydrous grafting and direct synthesis methods. They used anionic surfactants such as linear alkylbenzene sulfonates (LAS), sodium dodecyl sulfate (SDS), and *N*-lauroylsarcosine sodium salt (LSS) as the templates to synthesize APS-grafted AMS at basic condition. The prepared adsorbents exhibited the amine content up to 3.33 mmol/g and CO₂ adsorption capacity up to 1.25 mmol/g in pure CO₂ at 25 °C (Yu *et al.*, 2012).

2.5.2.4 Alkali Earth metal-based Solid Sorbents

Alkali earth metal, such as CaO can reversibly react with CO₂ to form alkali earth metal carbonate CaCO₃ in the absence of water vapor at high temperature, which is suitable to both pre-combustion and post-combustion applications. For example, the simplified process flow diagram of post-combustion capture using the calcium looping cycle is shown in Figure 2.11. In one vessel (the carbonator), the carbonation reaction between CO₂ and solid CaO separates CO₂ from coal-combustion flue gas at a temperature between 600 °C and 650 °C. The CaCO₃ formed is then passed to another vessel (the calciner), where it is heated to reverse the reaction (900 – 950 °C), releasing the CO₂ suitable for sequestration, and regenerating the CaO-sorbent which is then return to the carbonator. The carbonation process is exothermic, which is matched with the temperature of a steam cycle, allowing recuperation of the heat (Li *et al.*, 2011).

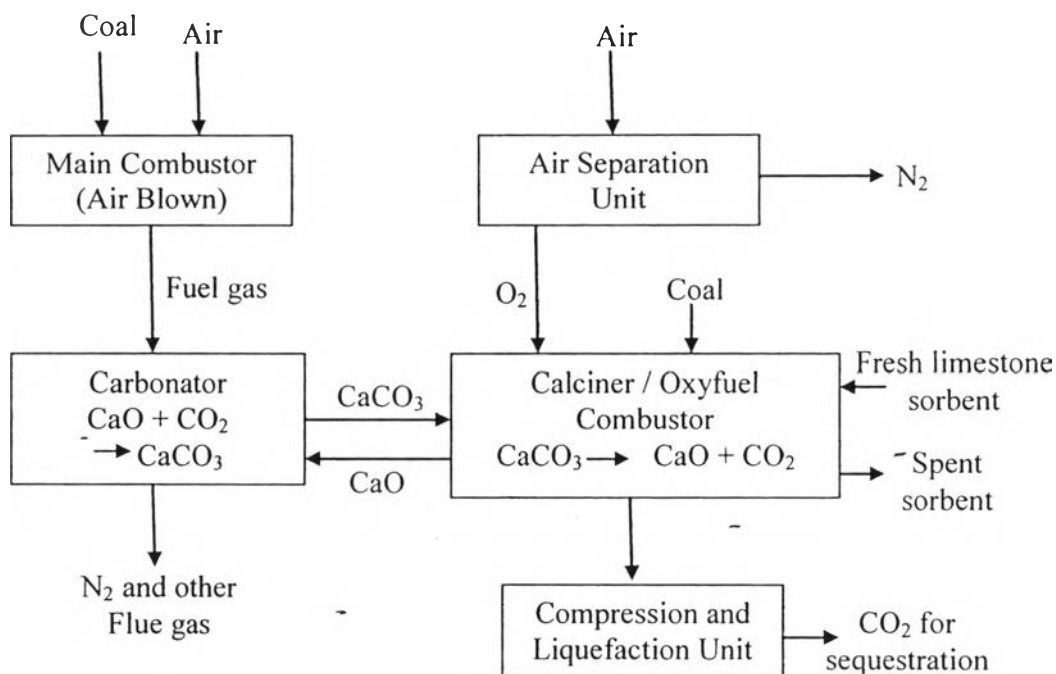


Figure 2.11 The process flow diagram of post-combustion capture using the calcium looping cycle (MacKenzie *et al.*, 2007).

2.5.2.5 Alkali Metal Carbonate Solid Sorbents

Alkali metal carbonate, such as Na_2CO_3 and K_2CO_3 can react with CO_2 and H_2O and transform to alkali metal hydrogen carbonates salt (NaHCO_3 or KHCO_3) at low temperatures. Water vapor is always necessary as the following reaction:



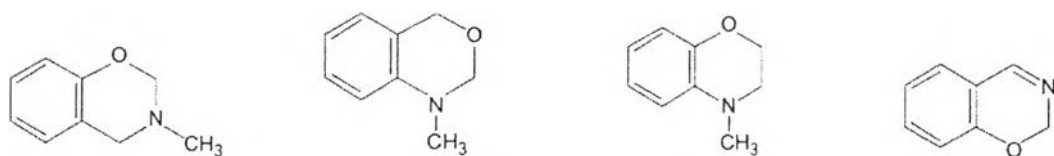
Researchers have tried to develop the K-based sorbents supported on various supports, including activated carbon, MgO , ZrO_2 , SiO_2 , Al_2O_3 , TiO_2 , CaO , and zeolites. The capacity of CO_2 over $\text{K}_2\text{CO}_3/\text{MgO}$ sorbent exhibited excellent characteristics at low temperatures (Lee, 2008). However, the carbonation reaction rate was rather slow. Recently, K_2CO_3 with a hexagonal structure showed excellent CO_2 absorption reaction rate (Zhao *et al.*, 2009).

In the solid CO_2 sorption process, heat control is important to avoid hot spots generated during the highly exothermic carbonation reaction, and high superficial ve-

locity is also necessary to reduce reactor size. To solve these problems, a fluidized bed is proposed as a proper process to control high volumes of flue gases (Li *et al.*, 2011).

2.6 Benzoxazines

Benzoxazine is a molecule, where an oxazine ring (a heterocyclic six membered ring with oxygen and nitrogen atom) is attached to a benzene ring. There are several benzoxazine structures depending on the position of the heteroatoms, Figure 2.12. For example, the traditional naming of the structure a is a 1,3-benzoxazine (3,4-dihydro-3-methyl-2H-1,3-benzoxazine), whereas structure b is a 3,1-benzoxazine. The numbering is made in such a way that the oxygen position precedes the nitrogen. Thus, structure c is a 1,4-benzoxazine. This is because the benzoxazine was originally the compound with a double bond, such as in structure d. The word, dihydro, indicates the hydrogenated version of benzoxazine d. It is the 1,3-benzoxazines that are the subject of interest for development of polymeric materials as this class of benzoxazines readily polymerizes via cationic ring-opening polymerization (Ishida, 2011).

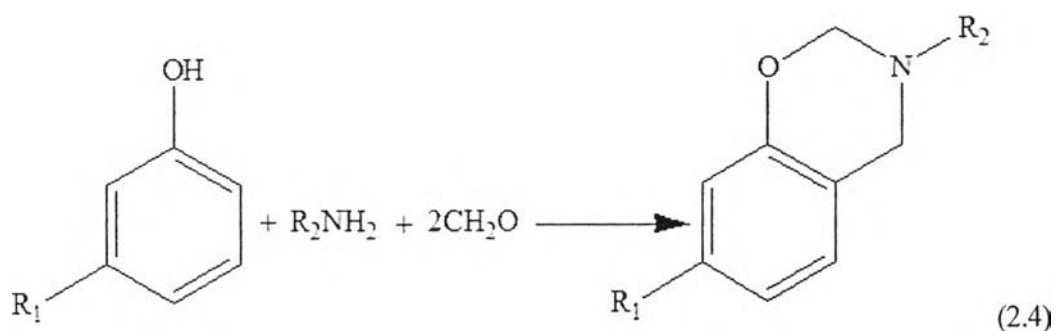


(a) 1, 3-Benzoxazine (b) 3, 1-Benzoxazine (c) 1, 4-Benzoxazine (d) 1, 3-Benzoxazine

Figure 2.12 Various structures of benzoxazine molecules.

2.6.1 Synthesis of Benzoxazine

Benzoxazine monomers are typically synthesized using phenol, formaldehyde, and amine (aliphatic or aromatic) as starting materials either by employing solution or solventless methods. Various types of benzoxazine monomer can be synthesized using various phenols and amines with different substitution groups attached. These substituting groups can provide additional polymerizable sites and also affect the curing process. Consequently, polymeric materials with desired properties may be obtained (Ghosh *et al.*, 2007).



2.6.2 Thermal Polymerization of the Benzoxazine Monomer -

The polymerization process of the benzoxazine monomer through ring-opening reaction of the benzoxazine ring is shown in Figure 2.12. The thermal polymerization of the benzoxazine monomer is initiated by the free phenols from the oligomeric structures. The oxygen atom from the benzoxazine cycle is protonated and then the methylene is linked to the free ortho position from the phenolic structure as depicted in Figure 2.12 (Andronesu *et al.*, 2012).

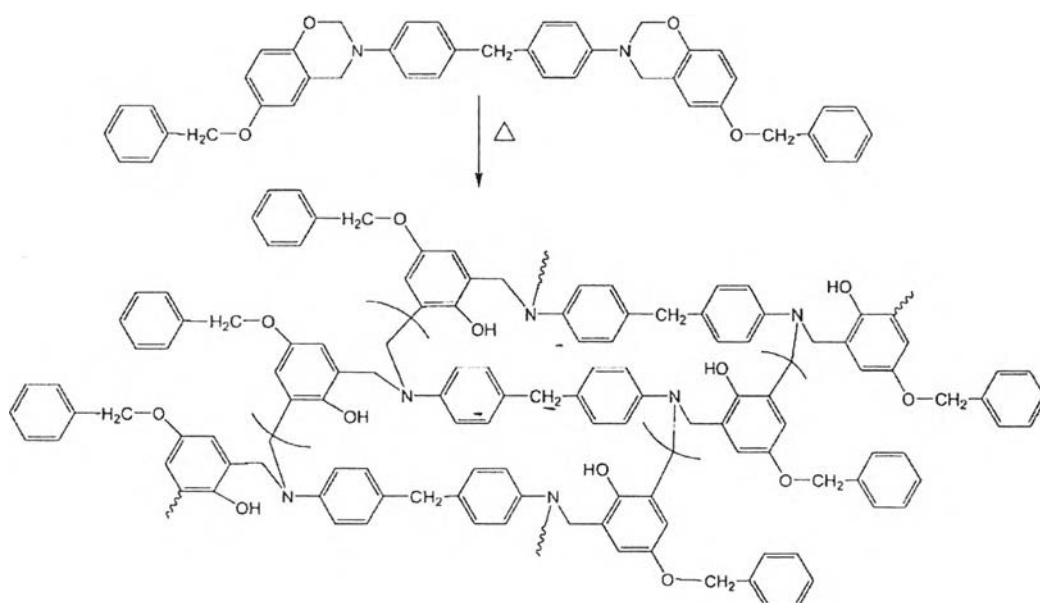


Figure 2.13 Polymerization reaction of the benzoxazine monomer (Andronesu *et al.*, 2012).

Polybenzoxazines are in a class of thermosetting phenolic resins, offering a number of attractive properties such as high glass transition temperature, high

thermal stability, wide molecular design flexibility, good mechanical properties, low absorption of water, high resistance with respect to burning, and low cost. Therefore, they are widely applied in various fields such as protection coatings for circuits in television studios, protection coatings for computer chips, airplane bodies, materials for airplane interiors, curing agents for other synthetic resins, varnishes which form films with a good resistance to water, alkali, and solvents (Garea *et al.*, 2007).

Structure of polybenzoxazines have amine groups that can react with CO₂ molecule. Hao *et al.* (2011) studied CO₂ capture using poly(benzoxazine-co-resol)-based porous carbon monoliths. Their results indicated that the poly(benzoxazine-co-resol)-based carbon sorbents perform well in CO₂ uptakes, selectivity, and regeneration among the commercial and state-of-the-art carbon sorbents reported to date. Moreover, polybenzoxazines have aromatic groups. Torrisi *et al.* (2009) found that the CO₂ molecule have intermolecular interactions with functionalized aromatic molecules.