CHAPTER II
THEORETICAL BACKGROUND

2.1 A Review of Carbon Dioxide Emission

Carbon dioxide (CO_2) is the most important greenhouse gas produced by human activities, mainly from the combustion of fossil fuels. Its concentration in the Earth's atmosphere has risen by more than 30% since the industrial revolution (Rojey and Torp, 2005). Options for cutting CO_2 emissions to the atmosphere can be: (i) to reduce energy consumption by increasing efficiency, (ii) to switch to less carbon intensive fuels, (iii) to increase the use of renewable energy sources or nuclear energy, (iv) to capture CO_2 by enhancing the biological absorption capacity of forests and soils, and (v) to capture and store CO_2 chemically or physically (Plaza *et al.*, 2007). One of the interesting technologies that can reduce this problem is CO_2 capture by using solid adsorbents to adsorb CO2 at the end of the combustion process. The major advantages of this process are that it does not need any chemical, no corrosion and no hazard waste. There are three technological pathways to reduce CO_2 emission (Thiruvenkatachari *et al.*, 2009).

2.1.1 Post-Combustion Capture

Post- combustion capture, which is a removal of CO2 at the end of combustion process, is most widely process used to capture CO_2 from flue gas containing CO_2 mixed with other gasses (Strube and Manfrida, 2011). A schematic is shown in Figure 2.1.

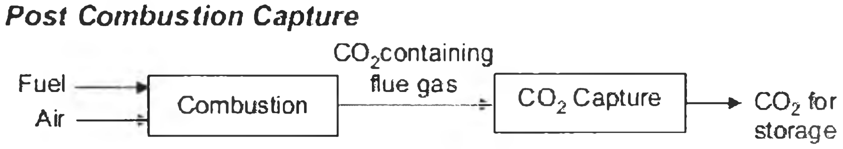


Figure 2.1 Post-combustion capture (Thiruvenkatachari *et al.*, 2009).

2.1.2 Oxy-Fuel Combustion

Oxy-fuel combustion is a modified post-combustion process (Fig 2.2). In the process, fuel is combusted in almost pure oxygen instead of air, which results in high concentration of CO_2 in flue gases. When fuel is burnt in pure oxygen, the flame temperature is excessively high, so some CO_2-rich flue gas would be recycled to the combustor to make the flame temperature similar to that in normal air-blown combustor (Olajire, 2010).

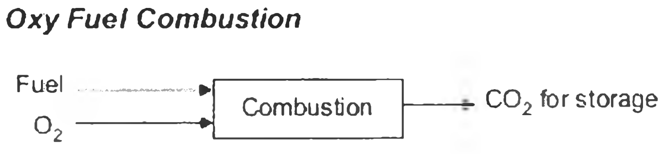


Figure 2.2 Oxy-fuel combustion (Thiruvenkatachari *et al.*, 2009).

2.1.3 Pre-Combustion Capture

In pre-combustion capture, CO_2 is recovered from the fuel before the fuel is burned by being reacted with oxygen or air, and in some cases steam, to give mainly carbon monoxide and hydrogen. This process is known as gasification, partial oxidation or reforming. The mixture of mainly CO and H_2 is passed through a catalytic reactor, called a shift converter, where the CO reacts with steam to give CO_2 and more H_2. The CO_2 is separated and the H_2 is used as fuel in a gas turbine combined-cycle plant. A schematic of pre-combustion is shown in Figure 2.3. This technology is usually used for internal gasification combined cycle (IGCC), however it could be applied to liquid and gaseous fuel (Olajire, 2010).

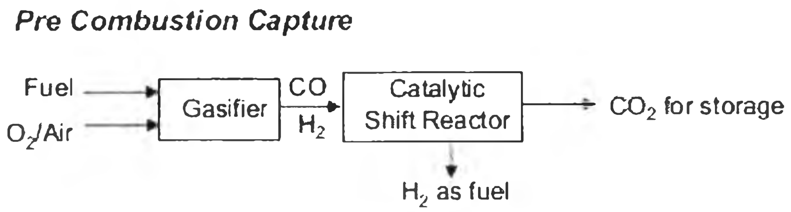


Figure 2.3 Pre-combustion capture (Thiruvenkatachari *et al.*, 2009).

The conditions for CO_2 separation in pre-combustion capture processes will be quite different from those in post-combustion capture. For example, in a coal IGCC process modified for capture, the CO_2 concentration would be about 35-40% at a pressure of 20 bars or more. Therefore, amine solutions or absorbents can be used them with lower reactivity and less corrosion. The comparison between advantages and disadvantages of each process are shown in Table 2.1 (Olajire, 2010).

Table 2.1 Compare the advantages and disadvantages of each capturing process (Olajire, 2010)

Capturing process	Advantages	Disadvantages
Post-combustion	- The most well known technology - Can easily be added to existing CO_2 emissions sources	- Large equipment sizes and high capital costs - Regeneration requires large amount of energy - Powerful chemical solvents have to be used - Solvent degradation
Oxy-fuel combustion	- Flue gas has a CO_2 concentration of over 80%, so only simple CO_2 purification is required - NOx formation is suppressed - Avoid the use of any reagent and/or solvents	- Large quantity of oxygen is required - Expensive, both in terms of capital cost and energy consumption - Need to recycle large quantities of flue gas to avoid excessively high combustion temperatures
Pre-combustion	- Carbonless fuel - The CO_2 concentration and pressure are higher than post combustion - Equipment is much smaller and different solvents can be used - Lower energy is required for regeneration	- The process is endothermic and needs temperatures from 700 °C to 850 °C - Total capital costs of the generating facility are very high - Extensive supporting systems requirements

2.2 Post-Combustion Capture

To date, there are several post combustion gas separation and capture technologies being investigated namely; (a) absorption, (b) adsorption, (c) cryogenic and (d) membrane separation. Figure 2.4 summarizes various technology options for post combustion CO2 capture (Olajire, 2010).

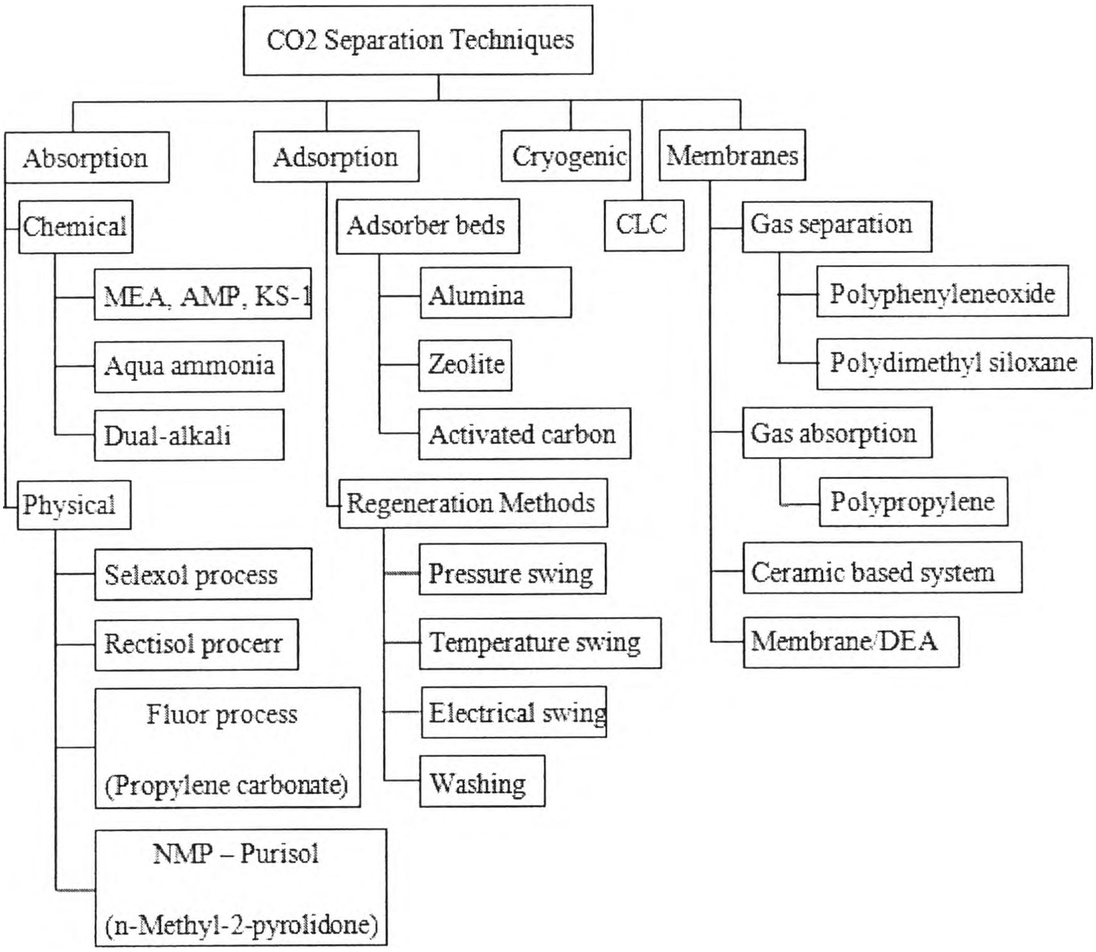


Figure 2.4 Technology options for CO_2 separation (Olajire, 2010).

2.2.1 Absorption

Chemical absorption separate CO_2 from exhaust gases. The separation process of carbon dioxide by chemical absorption consists of two steps: absorption of CO_2 by chemical solvents at a low temperature (40-65°C) and recovery of CO_2 from the chemical solvents by using low-grade heat (a temperature in the range of 100-150 °C).

Chemical absorption with amines is used for over 95% of all gas sweetening in the United States, while other methods such as carbonate processes, solid bed adsorbents and physical absorption account for the remaining 5% (Plaza *et al.*, 2007). Amine scrubbing technology was established more than 60 years ago in the oil and chemical industries for H_2S and CO_2 removal from gas streams. Commercially, it is the most well established of the techniques available for CO_2 capture. There are several facilities in which amines are used to capture CO_2 from flue gas streams today. Monoethanolamine (MEA) is a type of amine which is widely used for CO_2 capture. The reaction of CO_2 with primary and secondary alkanolamines can be described (Zhang *et al.*, 2008).

$$CO_2 + RNH_2 \rightleftharpoons RNH_2^+COO^- \quad (2.1)$$

$$RNH_2^+COO^- + B \rightleftharpoons RNHCOO^- + BH^+ \quad (2.2)$$

(Where B stands for bicarbonate)

On the basis of this mechanism, amine, water, and hydroxyl ion lead to deprotonate the solutions.

$$RNH_2^+COO^- + RNH_2 \rightleftharpoons RNHCOO^- + RNH^+_3 \quad (2.3)$$

$$RNH_2^+COO^- + H_2O \rightleftharpoons RNHCOO^- + H_3O^+ \quad (2.4)$$

$$RNH_2^+COO^- + OH^- \rightleftharpoons RNHCOO^- + H_2O \quad (2.5)$$

The mechanism is also used in model CO_2 absorption with sterically hindered amines.

$$CO_2 + RNH_2 + H_2O \rightleftharpoons RNH_3^+ + HCO_3^- \quad (2.6)$$

The absorption products, or carbamates, can be decomposed to release CO_2 by steam stripping before recycling the alkanolamine solutions to the absorber.

$$RNHCOO^- + H_2O \rightleftharpoons RNH_2\,CO_2 + OH^- \qquad (2.7)$$

$$HCO_3^- \rightleftharpoons CO_2 + OH^- \qquad (2.8)$$

$$CO_3^{2-} + H_2O \rightleftharpoons CO_2 + 2OH^- \qquad (2.9)$$

Reaction (2.7) demonstrates the carbamate ($RNHCOO^-$) transforms into CO_2 and amine. CO_2 recovery rates of 98% and product purity in excess of 99% can be achieved. However, there are some questions about its degradation rate in the oxidizing environment of a flue gas and the amount of energy required for regeneration. Improved solvents can reduce energy requirements by as much as 40% compared to conventional MEA solvents. Sterically-hindered amine is considered as an interesting chemical in the use of amines, which are claimed to have good absorption and desorption characteristics (CO_2 Capture Project, 2008).

2.2.2 Adsorption

Adsorption is considered to be one of the most promising techniques for the capture of CO_2 from flue gases which can be applied to post-combustion capture at both pressures close to ambient and for high pressure pre-combustion capture applications (Brandt *et al.,* 1993).

2.2.3 Cryogenic

The cryogenic CO_2 capture (CCC) process (Fig 2.5) flue gas from existing systems is dried and cooled to a temperature slightly above the point where CO_2 forms a solid, then the gas is expanded to further cool it, until CO_2 precipitates. Then solid CO_2 is removed from flue gas and reheated (Tuiniera *et al*., 2010).

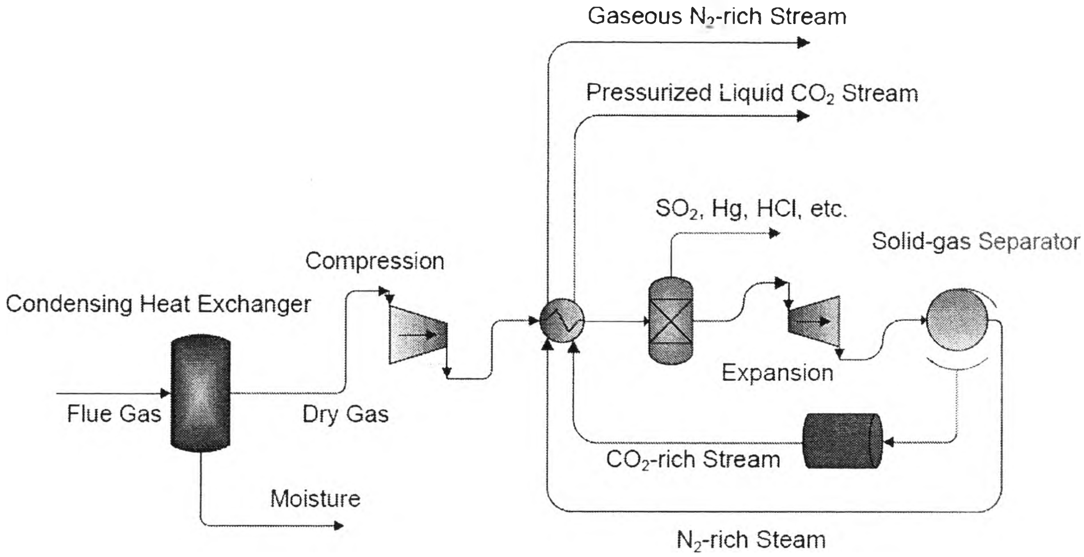


Figure 2.5 Simple schematic diagram of the cryogenic carbon capture (CCC) process (Burt *et al.*, 2010).

2.2.4 Membrane

Gas separation membranes allow one component in a gas stream to pass through faster than the others. Membranes act as filters to separate one or more gases from a feed mixture and generate a specific gas rich permeate, as shown in Fig 2.6. 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 and not another.The application of membrane gas separation to CO_2 capture from a coal gasification process is one potential solution to reduce green house gas emissions (Scholes *et al.,* 2008 and 2010). Each separation process has a lot of advantages and disadvantages, Table 2.2 summarizes and compares the advantages and disadvantages of each for post combustion CO_2 capture.

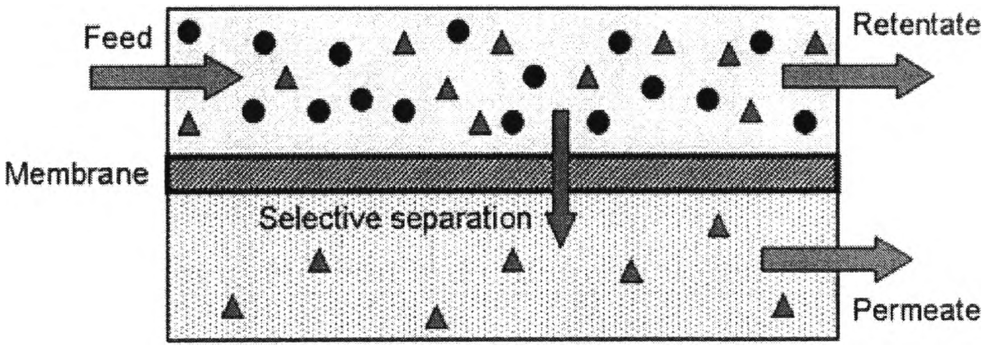


Figure 2.6 Schematic of membrane gas separation (Scholes *et al.*, 2008).

Table 2.2 Compare the advantages and disadvantages of each post combustion process

Capturing method	Advantages	Disadvantages
Cryogenic (Tuinier *et al.*, 2011)	- H_2O and CO_2 can be captured simultaneously while producing a very pure CO_2 stream - Avoiding expensive pre- or post-treatment - No plugging occurred - An effective separation between H_2O and CO_2 was obtained - Enables direct production of liquid CO_2	- The allowed water content in the flue gas is limited due to the heat required for evaporation of the condensed H_2O in the recovery cycle - The mixture needs to be flashed to remove most H_2O - The amount of energy required to provide the refrigeration necessary for the process - Normally only be applied to high concentration, high pressure gases

Table 2.2 (Cont.) Compare the advantages and disadvantages of each post combustion process

Capturing method	Advantages	Disadvantages
Adsorption (Olajire, 2010), (CO_2 Capture Project, 2008)	- Reasonable capital and operating cost - Small footprint - Flexibility - No corrosion	- Capacity and CO_2 selectivity of available adsorbents is low
Absorption (Olajire, 2010)	- The most well known technology - High reactivity	- Capacity is equilibrium limited - Solvent degradation - Corrosion - Heat stable salt
Membrane (Hussain *et al.*, 2011), (CO_2 Capture Project, 2008)	- Versatility - Adaptability - Environmentally friendly - Easy to operate - Suitable for space and weight restrictions (i.e. offshore)	- Membranes are expensive. - Operating pressures over 450 psig - Cannot usually achieve high degrees of separation , so multiple stages and/or recycle of one of the streams is necessary

2.3 Adsorption Process

The adsorption process is the technology using porous solid adsorbents and chemical or physical reactions between the adsorbent and CO_2 may occur during the separation process (Liang *et al.*, 2003 and Xiaoliang *et al.*, 2009).

Adsorption is the adhesion of atoms, ions, bi-molecules or molecules of gas, liquid, or dissolved solids to a surface. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. It is a *surface phenomenon* (Brandt *et al.*, 1993). Adsorption is caused by a type of Van der Waals Force which exists between molecules. These forces are extremely short ranged and therefore sensitive to the distance between the adsorbent surface and the adsorbate molecule. In general, the adsorbability of a compound increases with: increasing molecular weight, a higher number of functional groups such as double bonds or halogen compounds and increasing polarizability of the molecule.

2.3.1 Adsorbent

Most industrial adsorbents can be categorized into:

- *Oxygen-Containing Compounds* – typically hydrophilic and polar, materials such as silica gel and zeolites.
- *Carbon-Based Compounds* – typically hydrophobic and non-polar, materials such as activated carbon and graphite.
- *Polymer-Based Compounds* - polar or non-polar functional groups in a porous polymer matrix.

Adsorbents are used usually in the form of spherical pellets, rods, moldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm. They must have high abrasion resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and hence high surface capacity for adsorption. The adsorbents must also have a distinct porous structure which enables fast transport of targeted molecules. The applications of each adsorption are shown in Table 2.3.

2.3.2 Types of Desorption (Cavalcante Jr., 2000)

To date, there are several desorption methods which have many advantages and disadvantages. Table 2.4 summarizes the advantages and disadvantages of each regeneration methods to desorb CO_2.

Thermal Swing Adsorption (TSA): The CO_2 desorption is occurred by an increase in temperature. This is energy intensive and slow since the entire mass of adsorbent must be heated.

Pressure Swing Adsorption (PSA): The CO_2 desorption is occurred by a decrease in pressure, usually from an elevated level to near atmospheric pressure.

Inert Purge: The CO_2 desorption is occurred by using inert gas to purge CO2 out of the adsorbent.

Desorbent Displacement: The CO_2 desorption is occurred by sorbate displacement with a third compound (desorbent) that may also be preferentially adsorbed.

Table 2.3 Typical applications of commercial adsorbents (Yang, 2003)

Adsorbent	Applications
Silica Gel	Drying of gases, refrigerants. organic solvents, transformer oils Desiccant in packings and double glazing Dew point control of natural gas
Activated Alumina	Drying of gases, organic solvents, transformer oils Removal of HCl from hydrogen Removal of fluorine in alkylation process
Carbons	Nitrogen from air Hydrogen from syngas Vinyl chloride monomer (VCM) from air Removal of odours from gases Recovery of solvent vapours Removal of SOX and NOX Purification of helium
Polymers & Resins	Water purification Recovery and purification of steroids, amino acids Separation of fatty acids from water and toluene Separation of aromatics from aliphatics Recovery of proteins and enzymes Removal of colours from syrups Removal of organics from Hydrogen peroxide
Clay	Treatment of edible oils Removal of organic pigments Refining of mineral oils Removal of polychlorinated biphenyls (PCBs)

Table 2.3 (Cont.) Typical applications of commercial adsorbents (Yang, 2003)

Adsorbent	**Applications**
Zeolites	Oxygen from air Drying of gasses Removing water from azeotropes Sweetening sour gases and liquids Purification of hydrogen Separation of ammonia and hydrogen Recovery of carbon dioxide Separation of oxygen and argon Removal of acetylene, propane and butane from air Separation of xylenes and ethyl benzene Separation of normal from branched paraffins Separation of olefins and aromatics from paraffins Recovery of carbon monoxide from methane and hydrogen Drying of refrigerants and organic liquids Pollution control, including removal of Hg, NOX and SOX Recovery of fructose from corn syrup

Table 2.4 Compare the advantages and disadvantages of each regeneration methods (Ruthven, 1988)

Method	Advantages	Disadvantages
TSA	- Good for strongly adsorbed species; small change in T gives large change in q - Desorbate may be recovered at high concentration - Gases and liquids	- Thermal aging of adsorbent - Heat loss means inefficiency in energy usage - Unsuitable for rapid cycling so adsorbent cannot be used with maximum efficiency - In liquid streams high latent heat of interstitial - liquid must be added
PSA	- Good where weakly adsorbed species is required in high purity - Rapid cycling-efficient use of adsorbent.	- Very low P may be required - Mechanical energy more expensive than heat - Desorbate recovered at low purity
Inert Purge	- Operation at constant T and P	- Large purge volume required
Desorbent displacement	- Good for strongly held species - Avoids risk of cracking reactions during regeneration - Avoids thermal aging of adsorbent.	- Product separation and recovery needed (choice of desorbent is crucial)

2.4 LITERATURE REVIEW

2.4.1 Polymer from High Internal Phase Emulsion (HIPE)

High internal phase emulsions (HIPE) have been known for many years. In 1974, Lissant classified high internal phase emulsions, or HIPE, as emulsions containing greater than 70% internal phase volume, although a more precise definition would be those with an internal phase volume above 74.05%. As shown in Figure 2.7 material is highly porous obtained by polymerizing the continuous phase of a high internal phase emulsion (HIPE). These materials can be used as: membranes (Krajnca *et al.*, 2005), absorbents, supports for a variety of heterogeneous catalytic systems (Dizgea *et al., 2009*) and biomaterials (Bokharia *et al.*, 2005 and Hentze and Antonietti, 2002). By far, the most studied PolyHIPE system is the styrene/DVB based material. High internal phase emulsions of an aqueous phase in a mixture of styrene, DVB and non-ionic surfactant are prepared and polymerized by heating in a sealed container, typically for 24 h at 50 °C. This yields a solid, crosslinked, monolithic polymer material with a permanent, macroporous, pen cellular structure (Cetinkaya *et al.*, 2006).

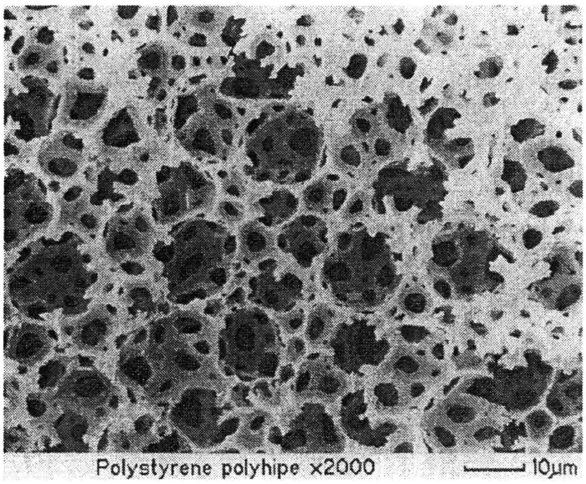


Figure 2.7 Scanning electron micrograph (SEM) of poly(styrene/DVB)PolyHIPE (Cameron and Sherrington, 1996).

2.4.1.1 Polymerization

Emulsion polymerization is a chemical process widely used to produce waterborne resins with various colloidal and physicochemical properties. This heterogeneous *free radical polymerization* process involves emulsification of the relatively hydrophobic monomer in water by an emulsifier, followed by the initiation reaction with either a *water soluble initiator* (e.g. sodium persulfate ($Na_2S_2O_8$)) or an *oil-soluble initiator* (e.g. 2-20-azobisisobutyronitrile (AIBN)). Typical monomers used in emulsion polymerization include butadiene, styrene, acrylonitrile, acrylate ester and methacrylate ester monomers, vinyl acetate, and vinyl chloride. An extremely large oil–water interfacial area is generated as the particle nuclei form and grow in size with the progress of the polymerization. Thus, an effective *stabilizer* such as ionic and non-ionic surfactants and protective colloid (e.g. hydroxyethyl cellulose and polyvinyl alcohol), which can be physically adsorbed or chemically incorporated onto the particle surface, is required to prevent the interactive latex particles from coagulation. Under the circumstances, satisfactory colloidal stability can be achieved via the electrostatic stabilization mechanism, the steric stabilization mechanism or both. The environmentally friendly latex products comprise a large population of polymer particles dispersed in the continuous aqueous phase. These emulsion polymers find a wide range of applications such as synthetic rubbers, coatings, thermoplastics, adhesives, binders, rheological modifiers, plastic pigments, standards for the calibration of instruments, immunodiagnosis tests, polymeric supports for the purification of proteins and drug delivery system, etc. (Chern, 2006).

Smith and Ewart (Smith and Ewart, 1948) and Harkins (Harkins, 1947) explain the distinct features of emulsion polymerization based on their studies of polystyrene. They divided the mechanism of emulsion polymerization into three stages as shown in Figure 2.8. A monomer is dispersed or emulsified in a solution of surfactant and water. Excess surfactant creates micelles in the water. A water-soluble initiator is introduced into the water phase where it reacts with monomer in the micelles. This characteristic differs from suspension polymerization where an oil-soluble initiator dissolves in the monomer, followed by polymer formation in the monomer droplets themselves. This is considered *Smith-Ewart Interval I.* Monomer in the micelle quickly polymerizes and the growing chain terminates. At this point the monomer-swollen micelle has turned into a polymer particle. When both monomer droplets and polymer particles are present in the system, this is considered Smith-Ewart Interval II. More monomer from the droplets diffuses to the growing particle, where more initiators will eventually react.

Eventually the free monomer droplets disappear and all remaining monomer is located in the particles. This is considered Smith-Ewart Interval III. Depending on the particular product and monomer, additional monomer and initiator may be continuously and slowly added to maintain their levels in the system as the particles grow. The final product is a dispersion of polymer particles in water. It can also be known as a polymer colloid, a latex, or commonly and inaccurately as an "emulsion".

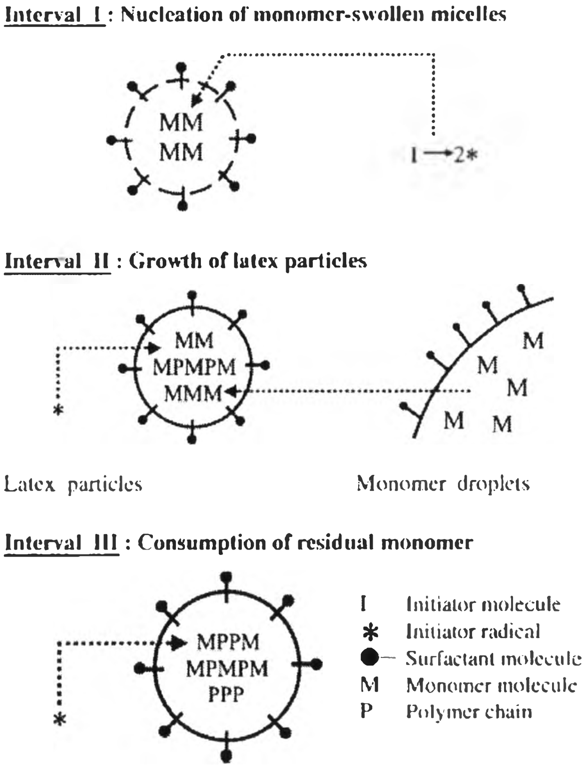


Figure 2.8 Schematic representation of the micelle nucleation model (Chern, 2006).

Advantages of Emulsion Polymerization (Odian, 2004):

- High molecular weight polymers can be made at fast polymerization rates. By contrast, in bulk and solution free radical polymerization, there is a tradeoff between molecular weight and polymerization rate.
- The continuous water phase is an excellent conductor of heat and allows the heat to be removed from the system, allowing many reaction methods to increase their rate.
- Since polymer molecules are contained within the particles, viscosity remains close to that of water and is not dependent on molecular weight.
- The final product can be used as is and does not generally need to be altered or processed.

Disadvantages of Emulsion Polymerization (Odian, 2004):

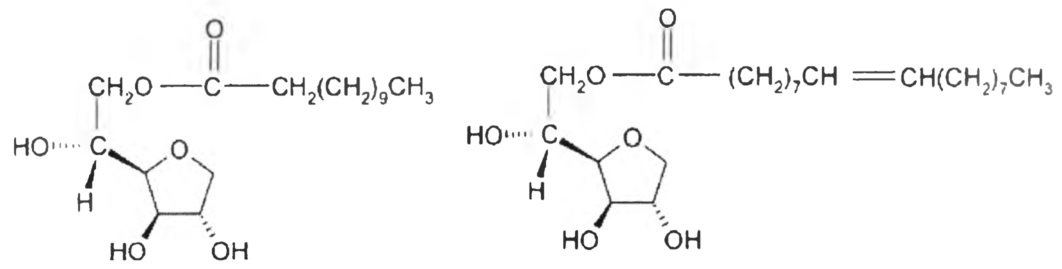
- Surfactants and other polymerization adjuvant remain in the polymer or are difficult to remove.
- For dry (isolated) polymers, water removal is an energy-intensive process.
- Emulsion polymerizations are usually designed to operate at high conversion of monomer to polymer. This can result in significant chain transfer to polymer.
- Cannot be used for condensation, ionic or Ziegler-Natta polymerization, although some exceptions are known.

2.4.1.2 Factors Affecting PolyHIPE Formation

a. Effect of Surfactant

In 2005, Cameron studied the effect of surfactant concentration on the average void diameter. The more surfactant concentration increases, the more decrease in average void diameter due to increase emulsion stability. It was suggested that an increasing surfactant concentration caused thinning of the monomer films separating adjacent emulsion droplets. At a certain critical film thickness, windows between adjacent droplets would be produced on curing. This implied that the cause of window formation is volume contraction on conversion of monomer to polymer.

The types of surfactant also had a crucial effect on surface area of material. In 2004, Barbetta and Cameron changed the surfactant from sorbitan monooleate (Span80) to a 3-component mixture of cetyltrimethylammonium bromide (CTAB), dodecylbenzenesulfonic acid, sodium salt (DDBSS) and sorbitan monolaurate (Span20) as the structure shown in Figure 2.9. When using this surfactant mixture, surface area values were much higher in almost every case than Span80. Mixture of ionic and non-ionic surfactants is known to form a more robust interfacial film around each emulsion droplet, leading to enhance emulsion stability.



Sorbitan monolaurate (SPAN 20)

Sorbitan monooleate (SPAN80)

Cetyltrimethylammonium bromide (CTAB)

Dodecylbenzenesulfonic acid, sodium salt (DDBSS)

Figure 2.9 Structures of the surfactants used (Barbetta and Cameron, 2004)

b. Effect of Electrolyte Concentration

In 2005, Cameron found that increasing the concentration of aqueous solution of potassium sulfate (K_2SO_4) caused decrease of void diameter which is related to emulsion stability. The propensity of Ostwald ripening is reduced when increasing electrolyte concentration. This propensity is occurred by large droplets grow at the expense of smaller one due to droplet phase molecules migrating through the continuous phase. The result of Ostwald ripening is progressive coarsening of the emulsion, which leads to coalescence and, eventually, emulsion breakdown. Therefore, preventing or limiting Ostwald ripening leads to a more stable emulsion with a smaller average droplet diameter (Cameron, 2005).

c. Effect of Water Fraction

In 2009, Zhang *et al* studied the effects of water fraction to the stability of HIPEs. Increasing the water volume fraction of the HIPEs will provide materials more open porous structure. With increase of water fraction but the surfactant was kept constant concentration. Therefore the average water droplet size becomes larger, the average void diameter increased steadily and the void diameter distributions become broad.

d. Effect of Porogen

In 2008, Hao *et al.* studied the influences of porogenic type and concentration on the uniformity and specific surface area of microsphere membrane from emulsification and suspension polymerization processes. They found that porogen with low aqueous solubility or relatively high viscosity leads to more uniformity of emulsion, because the polydispersity of emulsion mostly resulted from coalescence and Ostwald degradation of droplets.

It is found that changing the solvent from toluene to chrolobenzene (CB) to 2-chloroethylbenzene (CEB), as the structure are shown in Figure 2.10, provides an increase in BET surface area. This is due to increase in solubility parameter of the solvent. In addition, the mixture of porogenic solvents could lead to high surface area materials. When use 1:1(v:v) mixture of CEB and CB resulted in a material with a high surface area that still retained the expected polyHIPE morphology and substantially more robust than those prepared with CEB alone. High aqueous solubility, on the other hand, causes low yields of polymer microspheres. The concentration of porogens also had a crucial effect on the specific surface area of microspheres (Cameron, 2005).

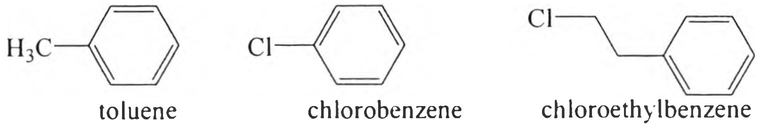


Figure 2.10 Structures of the porogen.

2.4.1.3 Applications of PolyHIPEs

There are several advantages of polyHIPE such as their highly interconnected open-cell structure with porosities that can reach over 90%, voids from 10 to 100 μm, densities down to 0.03 g/cm^3, surface areas up to 700 m^2/g, high permeability, and the ability to adsorb large volumes of liquid (Cameron and Sherrington, 1996). Therefore, polyHIPE can be applied to many applications.

a. Biomaterials

In 2004, Akay *et al.* used polyHIPE modified with hydroxyapatite as a three-dimensional matrix supporting the growth of osteoblasts, the bone forming cells in tissue engineering applications. This material is manufactured through a high internal phase emulsion (HIPE) polymerization route and may be modified with hydroxyapatite. The generic form of the support is known as PolyHIPE Polymer (PHP). By changing the chemical composition of the emulsion and the processing conditions, the pore size can be altered from sub-micron range to a few hundred microns and the porosity varied from 70% to 97%.

b. Adhesives

Highly porous nature of these materials can be used as carriers due to strong forces, which can tightly contain many substances for slow release. Sometime, an accelerator component is also placed into HIPE spheres, retained, and premixed with an adhesive. The two parts are mixed without fear of reaction due to capillary forces preventing viscous liquids from escaping. Later, the reaction is initiated when the beads are crushed or heated to the activation temperature.

c. Catalysis

Any catalytic material can be added to HIPE polymer surface that will have more efficient interaction with reaction due to large voids and interconnected pores. This unique structure allows reactants to flow into spheres, interact with catalysts to form products, and still allows room for product to flow out and away from newly arriving reactants.

In 2009, Dizgea *et al.* studied the biodiesel production by immobilized lipase onto polyglutaraldehyde activated styrene–divinylbenzene (STY–

DVB) copolymer, which is synthesized by using high internal phase emulsion (polyHIPE). The maximum biodiesel yield was 97% at 50 °C in 24 h reaction. The immobilized enzyme retained its activity during the 10 repeated batch reactions.

2.4.2 Polyethyleneimine (PEI)

Polyethyleneimine or PEI is polymer that contains many amino groups in its molecular structure as shown in Figure 2.11. It can be potentially used for capturing CO_2. PEI was first used in CO_2 capture by Satyapal *et al.* in 2001 to improve CO_2 removal in space aircraft applications. To enhance the adsorption capacity of this polymer, Xu *et al.* (2002) developed a ''molecular basket'' system using MCM-41 mesoporous silica support that served as a basket to retain large amounts of PEI. The sterically branched polymer of PEI contains numerous amine sites for CO_2-capturing, was loaded into the large pore volume porous material of mesoporous molecular sieve MCM-41 type to make the ''molecular basket'' adsorbent. The CO_2 adsorption capacity was significantly increased after loading the PEI. The CO_2 ''molecular basket'' adsorbent showed a CO_2 adsorption capacity of 215 mg/g-PEI at 75 °C and pure CO_2 atmosphere, which was 24 times higher than that of the MCM-41 and was two times that of the pure PEI (Xu *et al.*, 2002).

Further works were focused on the CO_2 adsorption capacity as well as the CO_2/O_2 and CO_2/N_2 adsorption selectivity of several materials with PEI polymers (Son *et al.*, 2008). Some studies have been carried out to test the PEI-impregnation in the different types of mesoporous materials to develop different supports such as a glass fiber matrix (Li *et al. 2008*) and a monolith (Chen *et al. 2009*).

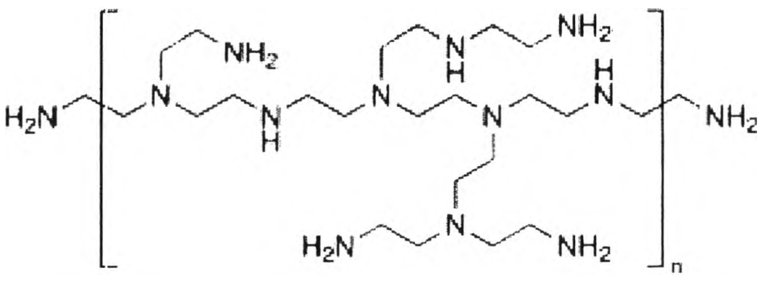


Figure 2.11 PEI structure.

In 2007, Gargiulo *et al.* studied the functionalization of MCM-48 and SBA-15 mesoporous silicas with polyethylenimine (PEI) using the wet impregnation technique for CO_2 adsorption. They found that increasing PEI loading resulted in decreasing of the surface area and pore size of the potential adsorbents. PEI-modified mesoporous systems did not adsorb any N_2 at 77 K. However, both materials were able to adsorb large amounts of CO_2 at 348 K and at very low pressure. At PEI loading of 50 wt% in MCM-48 and 44 wt% in SBA-15 adsorption capacities over 6 wt% were obtained. CO_2 desorption from the mesoporous silica samples under vacuum was close to 100% (Gargiulo *et al.*, 2007).

In 2010, Chen *et al.* synthesized series HMS (hexagonal mesoporous silica), which were employed as a host for supporting PEI (polyethyleneimine) (PEI/HMS) as a CO_2 capturing agent. The HMS alone showed a moderate sorption capacity of 34 mg_{CO2} /$g_{sorbent}$ at 25 °C. The PEI/HMS prepared using a HMS having complementary textural mesopores with a 45 wt% PEI loading exhibited CO_2 sorption capacity of 128 mg CO_2 /gsorbent at 75 °C, whereas a sorption capacity of HMS host with negligible textural mesoporosity were obtained only 94 mg CO_2 /$g_{sorbent}$ under the same loading level. In addition, they were able to increase the PEI loading to 60 wt% without losing the capturing efficiency of the former, and achieved a CO_2 sorption capacity of 184 mg CO_2 /$g_{sorbent}$. PEI/HMS exhibited only a minor drop in CO_2 capture capacity during a 4 repeated cyclic sorption–desorption run at 75 °C (Chen *et al.*, 2010).

In 2011, Subagyono *et al.* tried to load polyethyleneimine (PEI) (*M*w = 2500) and branched PEI (*M*n = 1200) onto SBA-15 and mesocellular siliceous foam (MCF) for CO_2 adsorption. CO_2 adsorption/desorption isotherms under dry CO_2 were obtained at 75, 105 and 115 °C. The CO_2 adsorption/desorption kinetics were improved with temperature, though the CO_2 capacities generally decreased. The adsorption capacity for MCF loaded with branched PEI at 105 and 115 °C were 151 and 133 mg/g adsorbent, respectively (in 50% CO_2/Ar, 20 min adsorption time). These are significantly higher than the adsorption capacity observed for SBA-15 loaded with branched PEI under the same conditions, which were 107 and 83 mg/g adsorbent, respectively. Thus the results indicate that amine modified MCF's are potentially better adsorbents than amine modified SBA-15 for CO_2 capture (Subagyono *et al.*, 2011).

In 2009, Lu *et al.* studied thermodynamics and regeneration of CO_2 adsorption from gas streams on mesoporous spherical-silica particles (MSPs) functionalized by amine (propyl ethylene diamine (EDA)). The thermodynamic analysis indicated that the adsorption process is endothermic in 20–60 °C but is exothermic in 60–150 °C. The cyclic CO_2 adsorption showed that the adsorbed CO_2 can be effectively desorbed at 120 °C for 25 min while the adsorbed CO_2 due to physical interaction can be effectively desorbed at 0.145 bars for 30 min. The desorption time of spent MSP(EDA) can be further shortened to 7.5 min via a combination of thermal treatment and vacuum suction.

Table 2.5 Summary some of porous materials loaded with PEI

Adsorbent	% PEI loading	Adsorption Temperature	CO2 capacity (mg CO2/ g. adsorbent)	References
MCF/x.1200	70 wt%	105 °C	143.9	Subagyono *et al.*, 2011
MCF/y.1200	70 wt%		150.7	
MCF/x.2500	70 wt%		61.5	
MCF/y.2500	70 wt%		59.0	
SBA-15/1200	50 wt%		107.1	
SBA-15/2500	50 wt%		55.6	
HMS (hexagonal mesoporous silica)	45 wt%	75 °C	128	Chen *et al.*, 2010
	60 wt%		184	
HMS with negligible textural mesoporosity	45 wt%		94	

Objectives of my research were to study effect of adding PEI into polyHIPE for adsorption of CO_2 in flue gas from coal fired power plant and to study effect of monomer ratio to the properties of the polyHIPE with and without PEI loading.

Scope of this research covers as follow: (1) Synthesis of PolyHIPEs by using divinylbenzene (DVB) and vinyl benzyl chloride (VBC) as monomers, (2) vary monomer ratio of DVB/VBC from 100/0, 90/10, 80/20, 70/30, 60/40 and 50/50, (3) vary weight% of PEI loading from 0%, 5%, 10%, 15%, 20%, 25% and 30%.