

CHAPTER II LITERATURE REVIEW

2.1 Carbon Dioxide (CO₂)

Carbon dioxide is a naturally chemical compound consisted of two oxygen atoms reacted to a single carbon atom in covalently double bonded. It is a gas phase at standard temperature and pressure. CO₂ is a colorless, odorless, non-flammable and slightly acidic liquefied gas. CO₂ is the chief greenhouse gas that results from human activities and causes global warming and climate change.

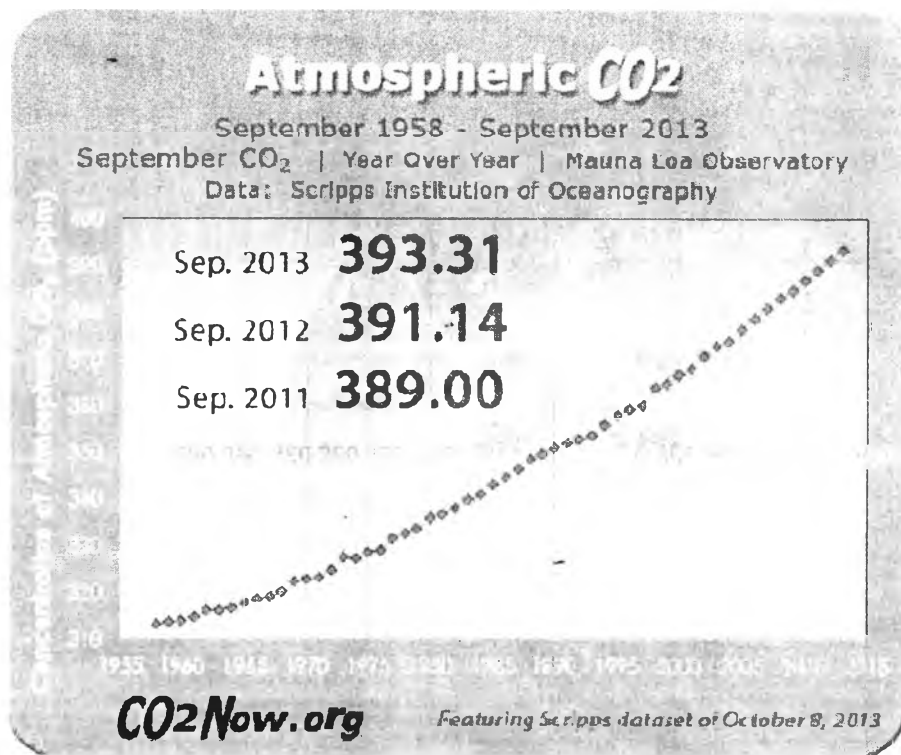


Figure 2.1 Yearly average concentration of atmospheric CO₂ at Mauna Loa (<http://co2now.org/>).

From the past, global concentration of CO₂ in the atmosphere was increasing rapidly and now is around 393.31 ppm followed by Figure 2.1. The main sources of CO₂ emissions are power generation, industrial processes, transportation, residential and commercial buildings. The main application of CO₂ capture is currently ex-

pected to be in power generation and large energy-consuming industries, particularly oil and gas processing and cement, iron and steel and chemicals production. From the growing of CO₂ emission, the strategies such as Carbon Capture and Storage (CCS) are required to reduce them.

2.2 Carbon Capture and Storage (CCS)

Carbon Capture and Storage (CCS) is a "process consisting of the separation of CO₂ from industrial and energy-related sources, transport to a storage location and long-term isolation from the atmosphere" (IPCC, 2005). CCS has three basic stages consists of CO₂ separation, transportation and storage. Three main methods can be envisaged for the capture of CO₂ with these three systems (Figure 2.2).

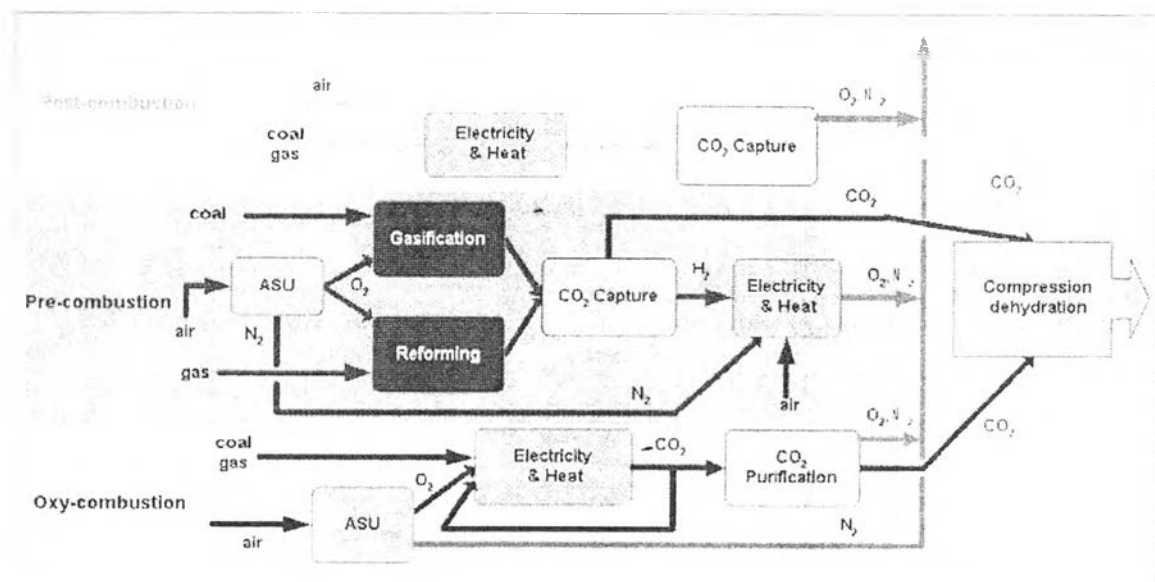


Figure 2.2 The three CO₂ capture processes (Kanniche *et al.*, 2010).

2.2.1 Post-combustion Capture

The post combustion capture is based on removing CO₂ from flue gas after combustion. Instead of being discharged directly to the atmosphere, flue gas is passed through equipment which captures most of the CO₂. Post-combustion capture offers some advantages as existing combustion technologies can still be used without radical changes on them. This makes post-combustion capture easier to apply as an

effective way compared to the other two options (Songolzadeh *et al.*, 2012). There are many post combustion capture technologies such as absorption, cryogenic separation, membrane separation, micro algal biofixation and adsorption. Adsorption is a separation technology, potential to reduce the cost and energy of post-combustion capture compared to other technologies. Adsorption processes for gas separation via selective adsorption on solid media are also well-known, and it can produce high purity streams with low energy consumption.

2.2.2 Pre-combustion Capture

The fossil fuel is reacted with air or oxygen and is partially oxidized to form CO and H₂ (syngas). Then in a gasification reactor, it is reacted with steam to produce a mixture of CO₂ and more H₂. CO₂ is then separated, and resulting in a hydrogen-rich fuel which can be used in many applications. (Songolzadeh *et al.*, 2012)

2.2.3 Oxy-combustion Capture

Oxy-combustion is when oxygen is used for combustion instead of air, which results in a flue gas that consists mainly of pure CO₂ and is potentially suitable for storage. (Songolzadeh *et al.*, 2012)

2.3 Adsorption

Adsorption is the process through which atoms, ions, or molecules from a gas or liquid, originally present in one phase, adhere to a solid surface based on significant intermolecular forces between gas or liquid and the surfaces of certain solid material. Depending on the temperature, partial pressures, surface forces and adsorbent pore sizes, single or multiple layers of gases may be adsorbed and the adsorption may be selective. This process creates a film of the adsorbate on the surface of the adsorbent. Figure 2.3 shows the behavior of adsorption.

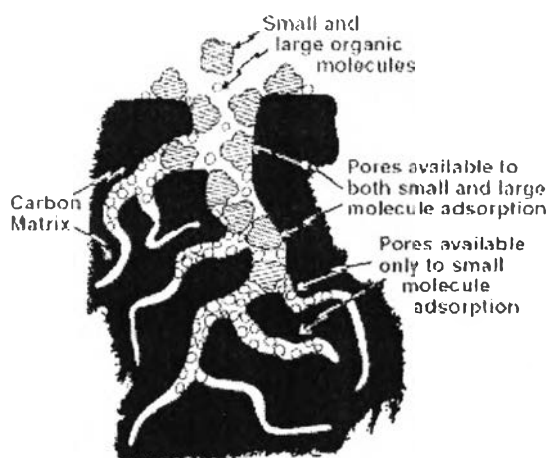


Figure 2.3 Adsorption of organic molecules on the activated charcoal
 - (www.chemistryland.com).

This process must be distinguished from absorption by which a fluid (absorbate) is dissolved by a liquid or solid (absorbent). Figure 2.4 reveals that the adsorption is a surface-based process while absorption involves the whole volume of the materials.

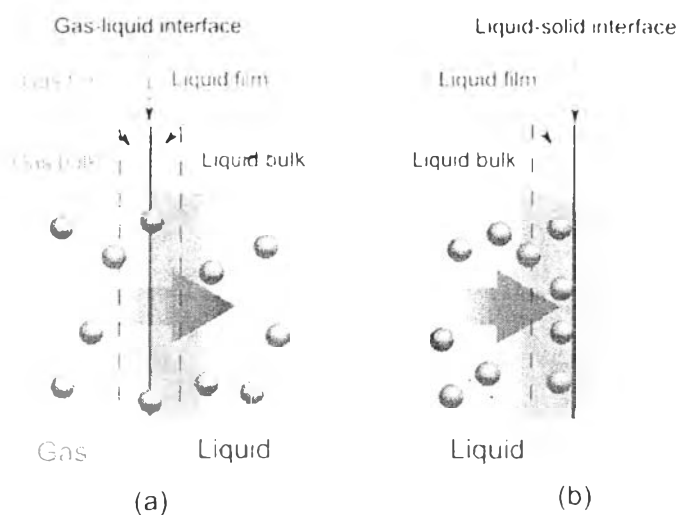


Figure 2.4 Gas-liquid absorption (a) and liquid-solid adsorption (b) mechanism
 (en.wikipedia.org).

Adsorption is present in many kinds of systems, natural physical, biological, and chemical, and is widely used in industrial applications. The most common industrial adsorbents are activated carbon, silica gel, alumina, and zeolite.

Adsorption process is generally classified into two types: physisorption and chemisorption. Physisorption is caused by weak intermolecular van der Waals forces between the adsorbing molecules and the exposed surface of solid material (Hibbitts *et al.*, 2007). Even though the interaction energy is very weak (~ 10 – 100 meV), physisorption plays an important role in nature. Chemisorption means that the adsorbate-substrate interactions form strong bonds similar to ordinary bonds found in molecules. The products resulting from chemisorption look like chemical moieties. Their structure and reactivity should be explained from consideration of the local structure around an 'active surface site' with the help of an appropriate electron count. Chemisorption may concern different kinds of substrates such as metals, metal oxides, semi-conductors and zeolites (Minot *et al.*, 1998). An important example of chemisorption is in heterogeneous catalysis which involves molecules reacting with each other via the formation of chemisorbed intermediates. After the chemisorbed species combine (by forming bonds with each other) the product desorbs from the surface. The difference between physisorption and chemisorption is shown as below.

Table 2.1 Difference between physisorption and chemisorption

Physisorption (Vander Waal's adsorption)	Chemisorption (Langmuir adsorption)
Low heat of adsorption usually in range of 20-40 kJ/mol	High heat of adsorption in the range of 50-400 kJ/mol
Forces of attraction are Vander Waal's forces.	Forces of attraction are chemical bond forces.
It is reversible	It is irreversible
It is usually takes place at low temperature and decreases with increasing temperature.	It takes place at high temperature.

Table 2.1 Difference between physisorption and chemisorption (cont'd)

Physisorption (Vander Waal's adsorption)	Chemisorption (Langmuir adsorption)
It is related to the case of liquefaction of the gas.	It is not related.
It forms multi-molecular layers.	It forms monomolecular layers.
High pressure is favorable. Decrease of pressure causes desorption.	High pressure is favorable. Decrease of pressure does not cause desorption.
It is not very specific.	It is highly specific.

2.4 Porous Materials

Porous materials are the materials containing pores (voids). The skeletal portion of the material is often called the "matrix" or "frame". The pores are typically filled with a fluid (liquid or gas). The skeletal material is usually a solid, but structures like foams are often also usefully analyzed using concept of porous media. Porous materials are most often characterized by their porosity. Porous materials have been used in a wide range of applications such as adsorption, filtration, aerospace applications, biology and biophysics. According to the IUPAC classification, porous materials have been categorized into three groups based on pore size regimes, as follows.

- Microporous materials: refer to porous materials having pores with internal width smaller than 2 nm. Pore size comparable to the molecules. Movement in micropores is by activated diffusion.

- Mesoporous materials: refer to porous materials having pores with internal width between 2 and 50 nm. Flow through mesopores is described by Knudsen diffusion and surface diffusion, multilayer adsorption and capillary condensation are contributed.

- Macroporous materials: refer to porous materials having pores with internal width greater than 50 nm. Flow through macropores is described by bulk diffusion and viscous flow.

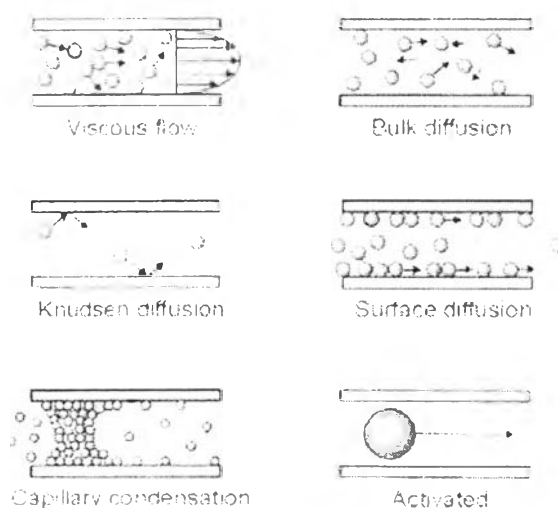


Figure 2.5 Transport mechanisms through pores (Schubert, 2012).

Nowadays, the term of nanoporous materials is widely used for both micro and mesoporous materials.

In CO₂ adsorption, pore size of adsorbent adsorbents play an important role in adsorption process. Since the diameter of CO₂ is around 0.33 nm (Armenta *et al.*, 2001, Qian *et al.*, 2013), suitable pore sizes for CO₂ molecules to be able to access the pores are in the ranges of micro and mesopores.

Heydari-Gorji *et al.* (2011) investigated the effect of the pore length of amine-modified mesoporous silicas. They used pore-expanded MCM-41 (11.4 nm), conventional SBA-15 with different pore diameters (7.2 (SBA-15SP) and 10.5 nm (SBA-15LP)), and SBA-15 with platelet morphology (SBA-15PLT) (13.6 nm) as the supports. The pore lengths were 25, 1.5 and 0.2 μm , respectively. In impregnation, they used polyethylenimine (PEI) and designated by the name of the support followed by (x), where x is the PEI loading in weight percent. The results showed that the size of the pores cannot affect the adsorption performance when the pores of the adsorbent are completely filled. Larger pore size or pore volume supports contain larger quantities of amine, but the accessibility of amine sites and the diffusion pathway are also important factors in the adsorption performance. The shorter the pore length, the higher CO₂ adsorption capacity at all temperatures because the shorter

diffusion pathway allowed higher amine accessibility with diminished diffusion resistance.

Maroto-Valer *et al.*, (2005) studied about micropore range of activated anthracites and reported that the molecular size of gas less than pores size about 5 times are effective for gas adsorption at atmospheric pressure. This result was confirmed by mathematical simulation using grand canonical Monte Carlo (GCMC) and the nonlocal density functional theory (NLDFE). Since the molecular size of CO₂ is 0.209 nm, pores size of activated anthracites about 1.0 nm are effective towards CO₂ capture at atmospheric pressure.

Son *et al.*, (2008) studied a series of mesoporous silica materials including MCM-41, MCM-48, SBA-15, SBA-16, and KIT-6, by impregnating with 50wt% polyethyleneimine (PEI) and evaluated the CO₂ adsorption performance at 75 °C. The results showed that for a pure support material, pore size varied in the descending order of KIT-6 (6.0 nm) > SBA-15 (5.5 nm) > SBA-16 (4.1 nm) > MCM-48 (3.1 nm) > MCM-41 (2.8 nm). KIT-6 also had the largest pore volume among the prepared samples. In impregnation, the pore volume and pore size decreased with increasing PEI loading into the pores. After CO₂ measurement, the CO₂ adsorption capacities of the series of adsorbent with PEI loading of 50wt% were in a range of 110–135 mg/g-adsorbent and followed the order of KIT-6 (135 mg/g) > SBA-16 (129 mg/g) ≈ SBA-15 (127 mg/g) > MCM-48 (119 mg/g) > MCM-41 (111 mg/g). Pore diameter of the support material was the most important variable with respect to controlling the adsorption kinetics. PEI can be introduced into the pore easier as the pore diameter of the adsorbent increased. Besides, more efficient contact between CO₂ gas and the impregnated PEI is achieved when a small space is still left inside the pores of the adsorbent after PEI loading.

Yan *et al.*, (2011) studied the effect of pore structure on the performance of CO₂ capture for SBA-15 modified with polyethyleneimine (PEI) by wet impregnation. They prepared different pore size and pore volume of SBA-15 by using different hydrothermal treatment time and denoted as S-x, where x represented the time of the hydrothermal treatment process. The treatment time was varied at 6, 24 and 48 hr. The properties of S-6 had the lowest total pore volume (0.71 cm³/g) and pore size (6.9 nm). S-24 had the total pore volume of 1.06 cm³/g and pore size of 8.5 nm. S-48

had the total pore volume of $1.14 \text{ cm}^3/\text{g}$ and pore size of 8.6 nm and S-3D had the largest pore size (9.4 nm) among the four samples with a pore volume of $0.99 \text{ cm}^3/\text{g}$. After impregnation of 50wt% PEI loading, the total volume and pore size of all adsorbent was decreased. For S-24/P material, the pore volume was only $0.07 \text{ cm}^3/\text{g}$ with the pore size of 3.7 nm. Similar to S-24/P, the pore volumes of S-48/P and S-3D/P decreased to $0.11 \text{ cm}^3/\text{g}$ and $0.07 \text{ cm}^3/\text{g}$, and pore sizes decreased to 4.9 and 3.3 nm, respectively. However, the loading amount of PEI in S-6/P was in excess of its maximum adsorption capacity, because PEI was coated on the external surfaces. After CO_2 adsorption at $75 \text{ }^\circ\text{C}$, the CO_2 adsorption capacity were in a range of 80-110 mg/g of adsorbent and the order of adsorption of different samples was as follows: S-48/P > S-24/P > S-3D/P > S-6/P. The result was dependent on the total pore volume of the adsorbent and the pore size.

Zelenak *et al.*, (2008) studied the effect of pore size on CO_2 adsorption by using three mesoporous silica materials with different pore sizes (33 Å for small pore size MCM-41; 38 Å for SBA-12; 71 Å for large pore size SBA-15) and pore connectivity (2D for MCM-41 and SBA-15-type materials; 3D for SBA-12 material) were prepared and functionalized with aminopropyl (AP) ligands by grafting. The CO_2 sorption capacity was measured by microbalances at $25 \text{ }^\circ\text{C}$. The total amount of sorbed CO_2 was 0.57 mmol/g for MCM-41/AP, 1.04 mmol/g for SBA-12/AP and 1.54 mmol/g for SBA-15/AP. The results showed that different sorption capacities were observed for MCM-41/AP and SBA-12/AP samples although both of them have similar amine surface densities (1.1 and 1.2 group/ nm^2 , respectively). This suggests that the amine surface density is not the only parameter influencing the carbon dioxide sorption in these materials. Another parameter influencing the sorption capacity is pore size. On the other hand, three-dimensional accessibility of amine sites inside the pores of SBA-12 silica resulted in a faster response to CO_2 uptake in comparison with MCM-41 and SBA-15 molecular sieves.

2.5 Adsorbent

An adsorbent is the material that uses to catch an adsorbate in the adsorption process. The suitable adsorbent for CO_2 capture from flue gas should combine sever-

al attributes, including high adsorption capacity, high selectivity, fast kinetic, high mechanical strength of adsorbent particles, high chemical stability, easy regeneration and low cost (Samanta *et al.*, 2011, Sayari *et al.*, 2011). The important characteristic of adsorbent is porosity. In addition to porosity, the physical characteristics for the proper adsorbent include surface area, pore size, pore volume and pore distribution. Adsorbents are used usually in the forms of spherical pellets, rods, moldings, or monoliths with hydrodynamic diameters between 0.5 and 10 mm. Moreover, adsorbents must have high abrasion resistance, high thermal stability and small pore diameters, which enable higher exposed surface area and hence high surface capacity for adsorption. The adsorbents must also have a distinct pore structure that enables fast transport of the gaseous vapors.

Nowadays, for industrial adsorbents, there are three classes of adsorbents:

- Oxygen-containing compounds: typically hydrophilic and polar, including silica gel and zeolites.
- Carbon-based compounds: typically hydrophobic and non-polar, including activated carbon and graphite.
- Polymer-based compounds: polar or non-polar functional groups in a porous polymer matrix.

2.5.1 Silica

Silica or silicon dioxide is a chemical compound that is an oxide of silicon with the chemical formula SiO_2 . It has been known since ancient times. Silica is most commonly found in nature as sand or quartz, as well as in the cell walls of diatoms (frustule). Silica is manufactured in several forms including fused quartz, crystal, fumed silica (or pyrogenic silica), colloidal silica, silica gel, and aerogel.

In order to improve properties of the adsorbent for CO_2 capture, considerable synthetic effort to develop pore sizes of adsorbent, one of the well-developed silica is modified in mesoporous materials forms. The most common types of mesoporous materials are MCM-41 and SBA-15.

In the study of Zelenak *et al.*, (2008), it showed that SBA-15/AP sample had the largest adsorption capacity, as well as the highest amine surface density among all materials studied (2.4 group/nm^2). The chemical reaction (chemisorption) between amine active sites and carbon dioxide is the driving force for the sorption of

carbon dioxide by amine-modified silica materials, yielding carbamate in anhydrous conditions.



Since the reaction involves two nitrogen atoms of the amine groups, two nitrogen atoms in close proximity are required on the surface.

Kamarudin and Alias, (2013) investigated CO₂ adsorption performance on solid adsorbent in a pressure swing adsorption (PSA) system at a pressure of 1.5 bar and temperature of 25 °C and its regeneration performance. They used MCM-41 for adsorbent and modified it by using MEA (primary amine) and DEA (secondary amine) to enhance the adsorption of CO₂ with wet impregnation method. They varied 10, 15 and 25wt% of MEA and 25wt% of DEA and compared them to the parent sample. The results showed the BET surface area reduced from 750 m²/g to 589 m²/g after MEA was impregnated into MCM-41. In comparison, after the modification using DEA, the surface area of modified MCM-41 was reduced to 651 m²/g. Based on the rapid pore filling theory, the smaller size molecule (MEA) can rapidly fill into the pore; thus it creates pore blockage and resulted in the lowering of the BET surface area. The results showed that the presence of amines has increased the amount of CO₂ removed from the gas streams since it has the ability to form the strong interaction between amine and CO₂ by forming surface ammonium carbamates. In the comparison of MEA and DEA impregnation, the performance of 25wt%-MEA-MCM-41 is higher than the performance of 25wt% DEA-MCM-41 indicates that a higher surface area does not necessarily lead to a higher adsorption capacity. These results also further validate the theory of synergetic effect of MCM-41. In principle, the amount of CO₂ adsorbed increased with the increase of the straight alkyl chain in the amine. However, as the secondary amine had a larger molecular size, it had lower CO₂ adsorption as compared to MEA due to steric hindrance. In regeneration, it was found that modified MCM-41 using 25wt% MEA-MCM-41 had high CO₂ removal even after the 10 cycles of operation.

2.5.2 Activated Carbon

Activated carbon is a porous carbon based material with small and low-volume pores that increase the surface area available for substance adsorption or

chemical reactions. Activated carbon is made from carbonaceous matters such as nutshells, coconut husk, wood, peat, coals, petroleum coke, and coir. It can be produced by two methods:

- Physical activation: The carbon material is generated into activated carbons by using hot gases. Normally, it use one or combination of the following processes:

- Carbonization: The carbon material is pyrolyzed at high temperatures about 600–900 °C, usually using argon or nitrogen

- Activation/Oxidation: The carbon material is oxidized in oxidizing atmospheres, e.g. carbon dioxide, oxygen, or steam, at temperatures above 250 °C, usually around 600–1200 °C.

- Chemical activation: The carbon material is impregnated with some chemicals liked an acid, strong base, or a salt. Then, it is carbonized at lower temperatures (450–900 °C). Chemical activation is preferred over physical activation because of the lower temperatures and shorter time required for activation.

Drage *et al.*, (2007) studied the chemical activation of urea-formaldehyde and melamine formaldehyde resin for CO₂ adsorbent based on assumption that all of urea and melamine are converted to resins and used K₂CO₃ impregnated by vary activation temperature. The result showed that carbons prepared by chemical activation was higher in CO₂ adsorption performance compared to the one prepared by physical activation with CO₂. At 500 °C activation temperature is the highest adsorption capacity for both types of resins (8.19wt% of urea-formaldehyde and 4.53wt% of melamine-formaldehyde). At higher activation temperature (over 600 °C), the CO₂ adsorption capacity decreased because the basic sites suitable for the adsorption of CO₂ are destroyed. However higher activation temperatures seem to generate more favorable textural properties for adsorption.

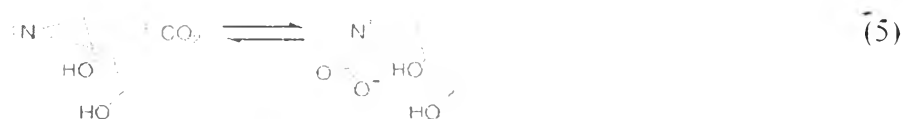
The modified adsorbent to improve the performance of CO₂ adsorption can be done by using chemical modification on the surface of adsorbent. Since carbon dioxide is an acidic gas, the organic groups (amine), hydroxyl groups and inorganic metal oxide (alkali metal or alkali-earth metal) are remarkable to investigate. The interaction between the CO₂ molecules and the modified active sites on the surface facilitates CO₂ adsorption via the formation of covalent bonding. Amine-based

adsorbents have widely been studied and exhibited the advantage as low heat of regeneration over amines due to the low heat capacity of solid supports. Recently, the amine-based adsorbents improvement was proposed by the preparation of supports with high amine loading and the type of impregnated with nitrogen content.

From Xu *et al.* (2003), they suggested the CO₂ chemical adsorption mechanism of the amine groups with CO₂. The formation of carbamate is favored in the manner shown in Eqns. (2) - (4). Two moles of amine groups react with one mol of CO₂ molecule.



In the system with hydroxyl groups, the formation of carbamate that called zwitterions is stabilized in a manner as shown in Eqn. (5) Only one mole of amine group reacts with one mole of CO₂ molecule. Consequently, the adsorption capacity increased with the same amine group.



Even though PEG (Figure 2.6) cannot adsorb CO₂, the chemical adsorption mechanism also influenced by the presence of OH groups that help promote and stabilize the carbamate type zwitterions.



Figure 2.6 Polyethylene glycol (PEG) structure (http://en.wikipedia.org/wiki/Polyethylene_glycol).

Maroto-Valer *et al.*, (2008) focused on the development of activated fly ash derived sorbents for CO₂ capture. Using de-ashed fly ash activated on one step method at 850 °C because previous work has shown that high surface area materials can be generated at this temperature and varied time of activation. Then one sample was chosen and impregnated with amine groups solutions. MEA (Figure 2.7), MDEA (Figure 2.7) and DEA (Figure 2.7), to enhance CO₂ adsorption capacity in the desired temperature (30 °C, 70 °C, 100 °C, and 120 °C) in 100 ml/min pure N₂ flow. The results showed that at 120 min of activation temperature, the one-step activation process increased the surface area and total pore volume up to 1075 m²/g and 0.774 ml/g, respectively. The longer of activation time, the higher burn-off levels. For instance, after 30 min activation, the burn-off was 11% compared to 67% after 120 min activation. The suitable sample chosen for impregnation experiment was at 90 min of activation. The impregnation process with MDEA, DEA, MEA, and MDEA + MEA, resulted in a decrease of the micropore and mesopore volumes followed by the pore filling effects. The highest adsorption capacity at 30 °C, and 70 °C for the amine impregnated activated carbon (68.6 mg CO₂/g sorbent of MEA impregnated) was due to a combination of physical adsorption and chemical adsorption of the amine groups loading. Hence, the contribution from physical adsorption decreased quickly and probably offsets any gain in the chemical adsorption enhanced by the increase in temperature. Besides, the decrease in CO₂ adsorption capacities at higher temperatures may also be related to the amines volatilization.

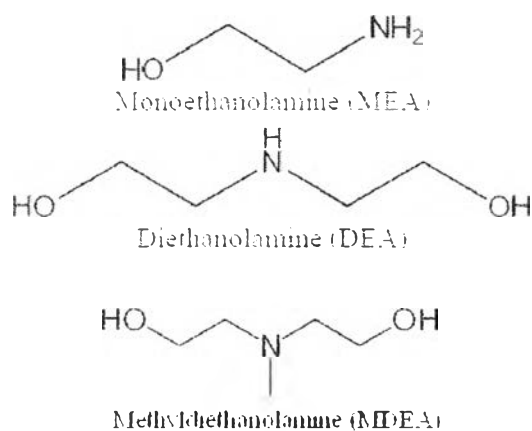


Figure 2.7 MEA, DEA and MDEA structures (Yu *et al.*, 2012).

Plaza *et al.*, (2007) evaluated a potential source of basic sites for CO₂ capture by using different alkylamines for impregnation and used commercial activated carbon as a support. A series of sorbents were obtained by filling in activated carbon with different amine group compounds: diethylenetriamine, pentaethylenhexamine, and polyethylenimine, which will be referred to as DETA, PEHA, and PEI, respectively (Figure 2.8), by a wet impregnation method. The fact that the raw carbon presented the highest CO₂ capture capacity at room temperature was due to the higher contribution of physisorption, which was limited in the case of the modified sorbents due to the pores being blocked by the amine film. However, at medium temperatures (70–90 °C), the contribution of chemisorption associated to the incorporated amino groups may improve the performance of the carbon. The impregnated carbons presented the less decreasing CO₂ adsorption capacity with higher temperature than raw activated carbon, due to the stronger interactions between the acidic gaseous CO₂ and the basic amine groups. This effect was obviously revealed in the case of impregnated activated carbon with DETA, which has the highest nitrogen content.

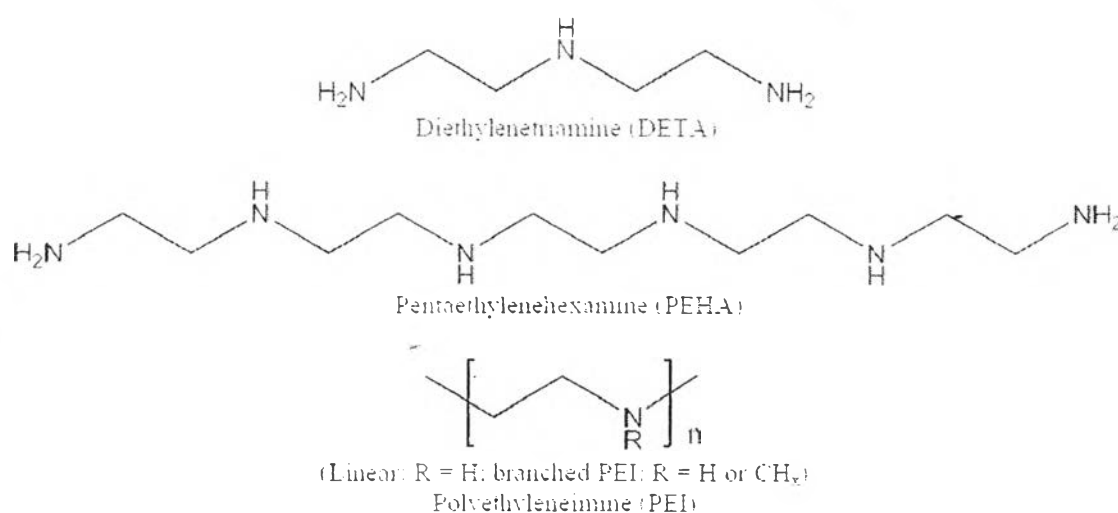


Figure 2.8 DETA, PEHA and PEI structures (Yu *et al.*, 2012).

Sarmah *et al.*, (2013) investigated the effect of structure of impregnated amines on the adsorbent surface. Fly ash was used as base adsorbent and impregnated by the combination of two classes of amine, FAA₁₃ from primary and tertiary

amines (MEA/DMA) and FAA₂₃ from secondary and tertiary amines (DEA/DMA). The results showed that the CO₂ adsorption capacity was 0.065 mmol/g for the pure fly ash. The maximum CO₂ sorption capacities for FAA₁₃ and FAA₂₃ composites were found to be 6.89 mmol/g and 5.99 mmol/g under one hour constant flow of CO₂ gas. Furthermore, a high CO₂ adsorption may be enhanced by the higher density of MEA (1.014–1.016 g/L) than that of DEA (0.703–0.705 g/L). Compared to the solid raw FA/MEA and FA/DEA composites, they showed maximum CO₂ adsorptions of 0.0715 mmol/g and 0.0747 mmol/g, respectively. The addition of tertiary amine increases the reactivity of the composite by increasing its stability of the composites.

Somy *et al.*, (2009) studied the effect of impregnation of activated carbon with Cr₂O and Fe₂O₃ and promoted by Zn²⁺ on its adsorptive properties of CO₂ by using a volumetric adsorption method at ambient condition. Two impregnation methods were employed: slurry and solution. The adsorption system was operated at room temperature and the CO₂ pressures were in the range of 30–110 ± 0.1 kPa. The results showed that the slurry impregnation method could better improve the CO₂ adsorption capacity of the activated carbons than the conventional solution impregnation. This was because the dipping of activated carbon in a solution may cause pore blocking in the structure of activated carbon, and, consequently, cause the decrease in adsorption capacity. Deposition of metallic cations on the activated carbon surface from the aqueous solution generally depends on chemical properties of the carbon surface and the nature of metal cations in the solution. Although it can be suggested that the distribution of impregnating species on activated carbon may be better in slurry method from the results of BET surface area (814 m²/g in slurry method and 795 m²/g in solution method). The decrease in surface area may happen when the impregnating species are distributed in the pores of adsorbent. Samples impregnated with Fe₂O₃ showed more decrease in adsorption capacity. The reason can be related to a large molecular size of Fe₂O₃ that leads to improper distribution of Fe₂O₃ agent on the activated carbon surface. It also may cause blocking of micropores which can result in decreasing the adsorption capacity. Adding only one type of metal oxide as impregnating agent has caused a decrease in adsorption amount on the raw activated carbon for both Fe₂O₃ (25, Slurry) and Cr₂O (25, Slurry) samples. The results also showed that the CO₂ adsorbed amount has been increased

about 15% on the samples which were washed after impregnation in comparison with the unwashed samples. The reason can be interpreted as a result of pore blocking in unwashed impregnated samples which may be caused by physically adsorbed impregnating species. It also can be observed that an increase in adsorption amount was obtained when the mixture of metallic species, Zn-Cr₂O, was used as impregnating agents.

The other ways for modified adsorbent to improve the performance of CO₂ adsorption can be done by the carbonization and activation, carbonization is the process of taking a carbon-rich piece of material and converting it to pure carbon through heating. Very dense carbonaceous material is used in the beginning and then it was generated pore size and pore volume. in the end, it needs to be extra-porous for activated carbon purposes. Pore diameter is quite big and has very little attraction force. As it cannot be used as an adsorptive agent, it gets activated to add more adsorption properties.

Hayashi *et al.*, (2000) studied the preparation of activated carbon from lignin by chemical activation. They mixed lignin with the six activating reagents (K₂CO₃, Na₂CO₃, KOH, NaOH, ZnCl₂, and H₃PO₄) and water then it was heated up to the carbonization temperature under N₂ flow at the rate of 10 °C /min and was held for 1 h at that temperature. The carbonization temperature was varied from 500-900 °C. The result showed that the surface areas obtained at the carbonization temperature of all activation were larger than the commercial activated carbons.

Milenkovic *et al.*, (2013) investigated the removal of 4-dodecylbenzene sulfonate (DBS) ions from aqueous solutions by ultrasound-assisted adsorption onto the carbonized corn cob. The corn cob was carbonized and activated with CO₂ in an oven at 880 °C for 2 h. The result showed specific surface area of the obtained carbonized material, 431 m²/g, is of the same order as those of similar materials.

Wang *et al.*, (2010) used corn cob as the reactant for synthesized activated carbon and studied the adsorption properties. The sample was heated to the carbonization temperature, 450 °C, at a rate of 5 °C/min and then held at 450 °C under N₂ atmosphere for 0.5 h. The carbonization samples were activated at 800 °C for 1 h in N₂ (40 mL/min) at a heating rate of 10 °C/min. The result showed The S_{BET}

and V_T are 2789 m²/g, and 1.55 cm³/g, respectively. The maximum adsorption capacity of H₂, CH₄, and CO₂ on activated carbon was 12.76 (77 K), 7.66 (213 K), and 3.56 (301 K) mmol/g, respectively at 0.1 MPa.

2.5.3 Polymer-based Compounds

A polymer is a chemical compound or mixture of compounds consisting of repeating structural units created through a process of polymerization. The term derives from the ancient Greek word refers to a molecule whose structure is composed of multiple repeating units, from which originates a characteristic of high relative molecular mass and attendant properties. Most commonly, the continuously linked backbone of a polymer used for the preparation of plastics consists mainly of carbon atoms. Polymer properties are broadly divided into several classes based on the scale at which the property is defined as well as upon its physical basis. The most basic property of a polymer is the identity of its constituent monomers. A second set of properties, known as microstructure, essentially describe the arrangement of these monomers within the polymer at the scale of a single chain. These basic structural properties play a major role in determining bulk physical properties of the polymer, which describe how the polymer behaves as a continuous macroscopic material. Chemical properties, at the nano-scale, describe how the chains interact through various physical forces. At the macro-scale, they describe how the bulk polymer interacts with other chemicals and solvents.

For the CO₂ adsorption, many researchers have developed many kinds of polymers because their properties, such as large surface area, high chemical stability, narrow pore size distribution, low skeleton density and much more functional groups that effect to increase CO₂ adsorption performance.

Chaikittisilp *et al.*, (2011) studied a CO₂ adsorption by using low-molecular-weight poly(allylamine) (Figure 2.9), which was prepared via free-radical polymerization for wet impregnation method into mesocellular silica foams. Poly(allylamine) (PAA) contains all of its amine sites on the side chain of the hydrocarbon backbone so all the amine sites are primary amines. The PAA impregnated and poly(ethyleneimine) (PEI) (Figure 2.9) impregnated at different amine loadings were used to capture CO₂ from flue gas (10% CO₂) or from ambient air (400 ppm CO₂). The results showed that the adsorbents with low PAA loadings were shown to

be of similar utility to branched PEI-containing adsorbents, which are currently the benchmark adsorbents for CO₂ capture from ambient air and are among the most promising adsorbents for flue gas applications. At higher loadings of PAA, the amine sites did not seem to be as accessible, as the CO₂ capacities and amine efficiencies decreased. It was hypothesized that this difference in behavior was from their different backbone structures, with PAA being a linear polymer with a hydrocarbon backbone. In the comparison with linear PEI, PAA and branched PEI, PAA and branched PEI are much more efficient under the simulated ambient air conditions.

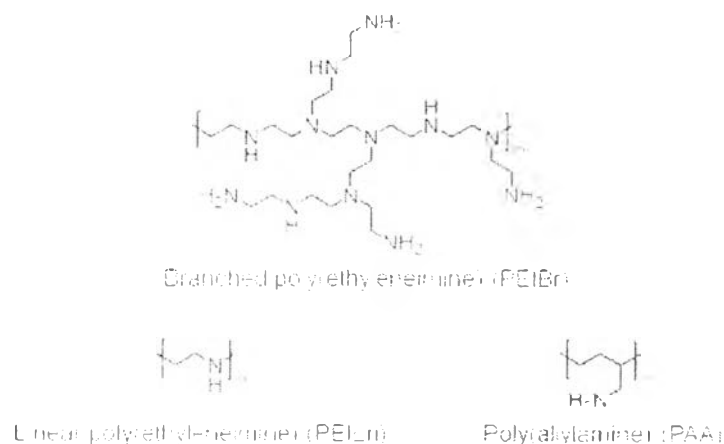


Figure 2.9 PAA and PEI chemical structures used (Chaikittisilp *et al.*, 2011).

Liu *et al.*, (2013) synthesized the microporous polymelamine network for CO₂ adsorption from a mixture of melamine (1.25 g, 9.9 mmol) and 1, 3, 5-benzenetricarboxaldehyde (0.80 g, 4.9 mmol) in drydimethyl sulfoxide (50 mL) under Argon bubbles for 30 min. Then, the resulting mixture was stirred at 180 °C under Argon for another 72 h. After cooling down to room temperature, the solvent was removed under vacuum and the residue was thoroughly washed with water, acetone and dichloromethane. A final white powder product with 64% yield was obtained after the Soxhlet extraction of the crude product with methanol and tetrahydrofuran. In order to investigate the gas adsorption selectivity of the microporous polymer network, CO₂, N₂, and CH₄ sorption properties were evaluated by volumetric methods at the same conditions. The synthesized microporous polymelamine network exhibited high selectivity towards CO₂ over N₂ and CH₄. The CO₂/N₂ selectivity at 273

K was about 3:1 (v/v) at 0.05 bar and 7:1 (v/v) at 1.0 bar, and the CO₂/CH₄ selectivity was about 265:1 (v/v) at 0.05 bar and 123:1 (v/v) at 1.0 bar.

Qian *et al.*, (2013) studied the microporous polyamide networks for CO₂ capture. They synthesized by the interfacial polymerization of piperazine and acyl chloride monomers containing tetrahedral carbon and silicon cores with a yield of 90-92%. The resulting polyamide networks exhibited selectivity in adsorption of CO₂ over N₂ up to 51. There were two main differences between N₂ and CO₂ adsorption measurements. Firstly, the kinetic diameter for CO₂ at 3.3 Å is smaller than that of N₂ at 3.64 Å, hence the CO₂ molecules are able to access the narrow micropores where N₂ has difficulty to access. Secondly, the higher temperature used for CO₂ adsorption imparts a significant kinetic energy to the molecules, enabling them to enter into the narrow pores. The uptake value of CO₂ at 1 bar and 273 K was 2.23 and 1.95 mmol/g for tetraphenylmethane-chloride/piperazine (TPMC/PIP) and tetraphenylsilane-chloride/piperazine (TPSC/PIP), respectively, and the corresponding BET surface area was 584 and 488 m²/g. The enhanced CO₂ adsorption capacities of TPMC/PIP and TPSC/PIP derived from the presence of polar acrylamide groups in their backbones, terminal amine groups, as well as tetrahedral cores. Thus, the CO₂ uptake in these networks at low pressure was not entirely due to their BET surface area, showing the potential for application in the area of carbon capture and storage.

For the polymeric materials improvement, many researchers studied and developed many kinds of polymeric materials to improve the polymer properties such as surface area, pore volume, pore size, and selectivity that used for many applications. The carbonization and activation were the methods to enhance those performances.

Kocirik *et al.*, (2001) synthesized bead-shape polymers for adsorption and in composite membranes. The polymer was immersed into a solution of strong acid ion exchangers then was pretreated in a thin layer at 190 °C, 200 °C or 275 °C for 48 h in a drying oven under air. Heating to 770 °C, or 1000 °C, for 1, 5, 4 and 8 h under nitrogen or carbon dioxide atmosphere were employed to carbonize the polymer. Styrene-divinylbenzene cation exchangers and acrylonitrile-DVB copolymers were found as the best starting materials for polymeric molecular sieves which large surface area (1140 m²/g). Because of the high content of micropores the resulting

products can be characterized as good quality adsorbents for the separation of small molecules.

Kumar *et al.*, (2011) studied the removal of fluoride and arsenic (V) from wastewater by development of polymeric adsorbents. The adsorbents were prepared by suspension polymerization. Fe and Al were incorporated during a polymerization step. The polymeric beads were carbonized then physically activated using steam in a horizontal tubular furnace. The beads were carbonized at 1050 °C for 1 h under N₂ atmosphere. Prior to the carbonization, the beads were pre-heated from room temperature to the carbonization temperature at a heating rate of 5 °C/min. Subsequent to the carbonization, the activation was performed for 1 h by steam at 900 °C. The synthesized adsorbents which large surface area (~760 m²/g) were shown to possess significant loadings of fluoride (~100 mg/g) and arsenic (V) (~40 mg/g) ions.

Sevilla and Fuertes (2013) studied macro/mesoporous carbon monoliths with a graphitic framework by carbonizing polymeric monoliths of poly(benzoxazine-co-resol). The sample was dried under vacuum at 55 °C for 6 h and heat-treated under a nitrogen flow up to a temperature in the 800–1000 °C range for 1 h (heating rate: 5 °C/min). The result showed that they have a dual porosity made up of macropores and mesopores (~2–10 nm), with a BET surface area and pore volume being, respectively, in the 280–400 m²/g range and ~0.4 cm³/g.

Vázquez-Santos *et al.*, (2008) prepared activated carbon fibers from poly (p-phenylene benzobisoxazole) (PBO) by carbon dioxide activation. PBO chopped fibers were first carbonized in a U-shaped reactor made from quartz by heating to 1123 K under argon (flow, 50 STP cm³/min). Once this temperature was reached, the material was cooled down to 1073 K under Ar flow and kept at that temperature and gas flow for 10 min. Then, the gas was switched to carbon dioxide (flow, 50 STP cm³/min) and kept for different periods of time to attain different burn-off (BO) degrees. The result showed the surface area and pore volume of the materials gradually increase following the duration of CO₂ activation. N₂ and CO₂ physisorption results agreed in indicating that the obtained adsorbents are principally supermicroporous with a certain contribution from narrow mesopores.

In this work, polybenzoxazine is chosen for the new polymer for impregnating species and as carbonaceous adsorbents.

2.5.3.1 Polybenzoxazine

Polybenzoxazine is a new developed type of phenolic resins. It is a molecule where an oxazine ring (a heterocyclic six-membered ring with oxygen and nitrogen atom) is attached to a benzene ring. It has excellent molecular design flexibility that allows the properties of the cured materials to be controlled for various applications. Polybenzoxazine has many advantage characteristics compared to the traditional phenolic resins.

Basic chemistry

The basic chemistry of benzoxazine resins is described as follows. These resins can be readily synthesized by a combination of a phenolic derivative, formaldehyde, and a primary amine (Figure 2.10) where X and R^{*} are substituents. R^{*} includes a group such as CH₃, C₂H₅, and benzene. Two examples of bifunctional benzoxazine resins are shown in Figure 2.11 where R is a group, such as CH₃ and other aliphatic groups, or substituted benzene rings, and X is a group, such as -, CH₂, C(CH₃)₂, C(CF₃)₂, C=O, SO₂. Any combination of a bifunctional phenol and primary amine can be used. In a similar manner, any combination of a bifunctional amine and mono-functional phenol can also be used as shown in Class B example, though the structure of the cross-linked polymer is somewhat different. Naturally, multifunctional amines or phenolic derivatives can also be used to synthesize multifunctional benzoxazines.

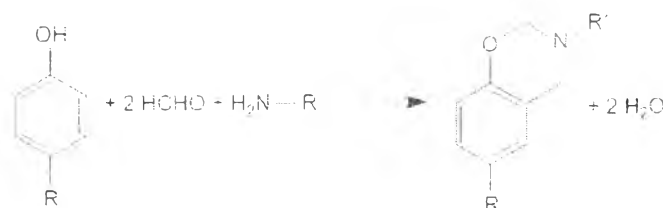


Figure 2.10 Synthesis of benzoxazine resin (Ishida, 2011).

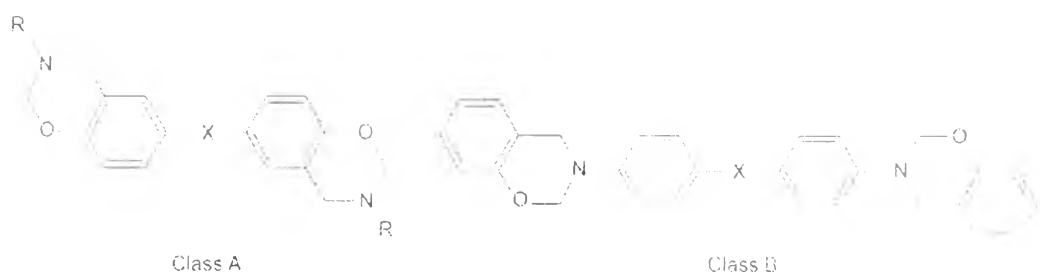


Figure 2.11 Monomeric type bifunctional benzoxazine resins based on bisphenol and monoamine, or diamine and phenol (Ishida, 2011).

A more recent concept of benzoxazine resins involves the use of a bifunctional phenolic compound and a diamine, yielding a linear polymer having oxazine rings in the main chain as in Class C (Figure 2.12) below; however, due to the reactivity of the benzene rings, a small number of branching can take place. The oxazine rings can be used to form crosslinking networks.



Figure 2.12 Main-chain type polybenzoxazine based on bisphenol and diamine. The polymer can further cross-link via the oxazine ring polymerization in the main chain (Ishida, 2011).

Unique properties of benzoxazines and polybenzoxazines

Benzoxazine resins as precursors for cross-linked polybenzoxazines and the resultant cross-linked polymers exhibit a number of unique properties, as described below.

- near-zero volume changes
- high thermal stability
- high mechanical properties
- low water absorption

- glass transition temperature much higher than curing temperatures
- fast physical and mechanical property development
- very high char yield
- excellent electrical properties

These properties will allow the development of unique applications, in addition to providing the opportunity to be the replacement materials for the existing polymers.

Synthesis of benzoxazine and polybenzoxazines

Benzoxazine monomers are typically synthesized using phenol, formaldehyde and the types of amine (aliphatic or aromatic) as initiate materials. Various types of benzoxazine monomer can be synthesized using various phenols and amines with different substitution groups attached (Ghosh *et al.* 2007). In 1944, Holly and Cope first reported the reaction of benzoxazine by using primary amines with formaldehyde and substituted phenols for the synthesis.

Agag *et al.*, (2009) prepared the polymerization of 4, 4'-diaminodiphenyl sulfone-based benzoxazine monomer. They used two methods to synthesize benzoxazine. First method, 4, 4'-diaminodiphenyl sulfone (DDS) and phenol were dissolved in DMSO. Paraformaldehyde was added to the solution followed by heating the mixture at 150 °C in a preheated oil bath. After 60 min, the solution was cooled and poured into 1 L of 1 N aqueous sodium hydroxide solution. The precipitate was collected by filtration, and washed with water several times. The precipitate was finally washed several times with methanol, followed by drying at 50 °C under vacuum to afford pale yellow powder. For the second method, a mixture of DDS, phenol and paraformaldehyde was poured in mixed isomer xylenes. The milky mixture was heated gradually and was kept stirring at 150 °C. After 3 h, the insoluble white color gel coagulated into yellow highly viscous product at the bottom of the flask due to the limited solubility in xylenes. The reaction mixture was stirred for additional 3 h at the same condition. The reaction mixture was cooled to room temperature and then poured into hexane to eliminate xylenes. The rest of the solid product in the flask was washed several times with hexane. The product was dissolved in di-

methylformamide (DMF), precipitated in 1 N aqueous solution of sodium hydroxide to remove any phenolic compounds, washed several times with water and finally with methanol. The product was dried under vacuum at 50 °C for 24 h to afford pale yellow powder.

Allen and Ishida, (2009) studied the effect of phenol substitution on the network structure and properties of linear aliphatic diamine-based benzoxazines. They synthesized benzoxazine monomers by using phenol, paraformaldehyde, and aliphatic diamine. The reactants were dry mixed with the stoichiometric amounts of 2:4:1 in a single neck reaction flask. Approximately 5 ml of chloroform per gram of reactants were added to the flask. The reaction mixture was refluxed with stirring for a time period between 1.5 and 12 h. After cooling to room temperature, the crude reaction products were washed several times with 1 N NaOH solution and then rinsed with distilled water until neutral. The base washed products were dried over sodium sulfate and filtered, followed by solvent removal under vacuum. The material was further purified by rinsing with the alcohol. The purified benzoxazine monomer was dried under vacuum at room temperature for 24 h and refrigerated until the time of use.

Su and Chang, (2003) synthesized benzoxazine monomer. The 0.04 mol 37% formaldehyde aqueous solution and 5 ml dioxane were fed into a three-necked flask equipped with nitrogen flow and an ice bath for 10 min. Then, 0.02 mol 4-(trifluoromethyl)aniline dissolved in 5 ml dioxane was added into the reactor slowly by a dropping funnel. The mixture was stirred continuously for 10 min, and 0.01 mol hexafluorobisphenol A in 20 ml dioxane was added. The reaction temperature was raised to 100 °C, and the mixture was allowed to reflux for 24 h. The solvent was then removed by reducing pressure, and the yellow solid product obtained. The crude product was dissolved in ethyl ether and washed with 1N NaOH and water in sequence for three times. The product solution was dried by magnesium sodium and distilled by reducing pressure, a light yellow solid product was obtained.

2.6 Adsorption Measurement

In recent years, gas adsorption is an apparently straight-forward approach to the study of the interaction between gas molecules and solid surfaces. Industrial applications of gas adsorption such as storage, separation, catalysis, environmental protection etc. are numerous. Reliable and accurate adsorption measurements are critical to the design and characterization of new materials for adsorption. Several methods such as gravimetric, volumetric and temperature programmed desorption (TPD), have been used to determine the gas storage capacity of potential adsorbents.

Gravimetric methods are typically carried out with ca. 1–10 mg of sample in custom built thermo-gravimetric apparatus, with a high pressure balance chamber. Clearly, this technique is sensitive to all gases sorbed and the error can be magnified by the very small sample size used for each experiment, thus adsorption of 0.01 mg impurity in the gas can result in an erroneous reading of 1wt% being observed. (Blackman *et al.*, 2006)

TPD, sometimes referred to as a temperature desorption spectroscopy, determines the gas sorption capacity of a material by observing the desorption profile of a gas loaded material. Typical desorption experiments are carried out with ca. 1–10 mg of sample using a controlled temperature range of 90–970 K under ultra high vacuum (ca. 10^{-6} Pa) and throughout the process the presence of gas is monitored by mass spectrometry from which the amount of hydrogen desorbed can be quantitatively calculated. Even so, like the gravimetric system, TPD uses only a very small amount of sample and is reliant on the mass spectrometry apparatus being capable of accurately quantifying the small amounts of gas being desorbed. (Blackman *et al.*, 2006)

The volumetric method determines the gas storage capacity of a material by measuring the pressure drop resulting from adsorption after exposing the sample to gas at constant volume. Blackman *et al.*, (2006) developed an apparatus by measuring a differential pressure in an attempt to improve the accuracy and reliability of the method. The set-up has two volumetrically balanced limbs each comprising a reservoir and a sample cell. Figure 2.13 shows the schematic of the volumetric differential pressure hydrogen adsorption apparatus.

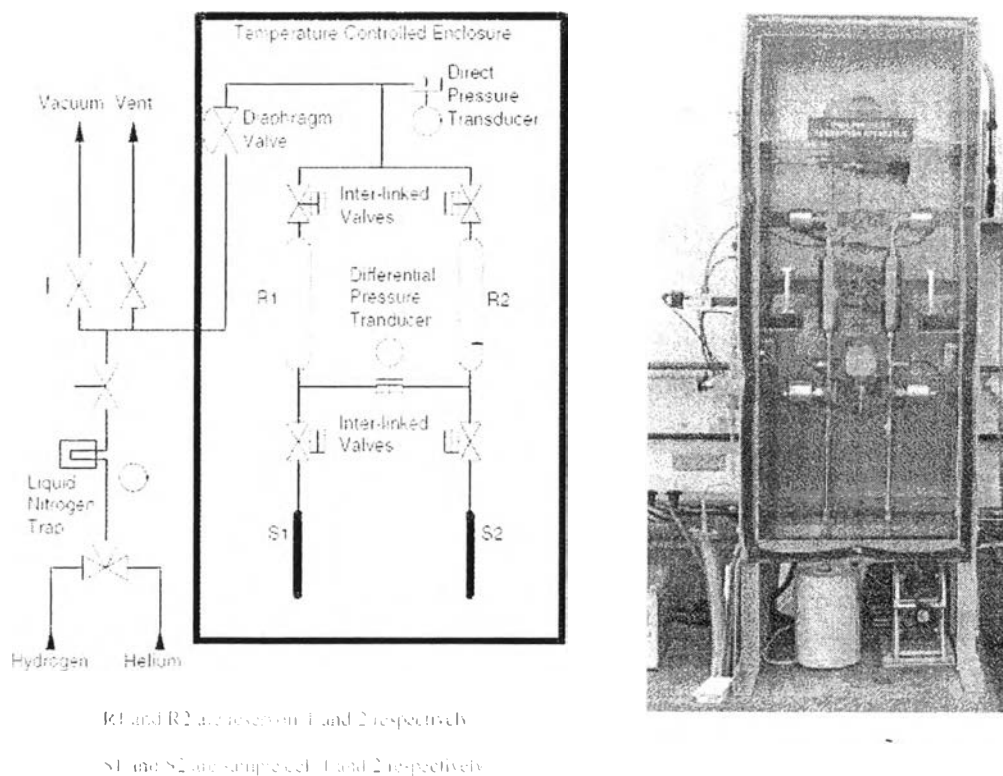


Figure 2.13 Schematic and real apparatus of the volumetric differential pressure hydrogen adsorption apparatus (Blackman *et al.*, 2006).

A series of activated carbons and carbon nanofibers were used as adsorbent. The operating conditions of the apparatus are 10 MPa of pressure. The method had a conservative limit of detection of 0.1wt% and accuracy of 0.05wt%. The temperature of the enclosure was maintained at a constant 30 ± 0.1 °C. The volumes of the reservoirs (R1 and R2) and sample cells are 168.1 ml and 17.3 ml, respectively. This is the proper ratio and the reservoir was used to increase the internal system volume. The hydrogen storage capacity can be determined by using a differential pressure between the reference cell and the sample cell. The results showed that the amount of hydrogen adsorbed was less than 1wt% for all the carbons examined.

Another volumetric method, namely “Pressure-decay” is the original and most popular method for high-pressure sorption measurements. Pressure decay is very simple in concept. An experiment is conducted by isolating a polymer sample and a high-pressure gas in a closed vessel. As the polymer absorbs the gas, the pres-

sure drop in the vessel is monitored as a function of time. An equation of state for the gas is used to convert the pressure into the mass uptake or absorption capacity in the polymer. In the work by Davis *et al.*, (2004), two new sorption techniques were developed to measure diffusion and solubility in polymer-solvent systems as shown in Figure 2.14. There are two techniques for their experiments. The first technique is the Dual-Chamber technique which used a known weight of reservoir capsule to determine the initial density of the gas. The second one is called the extrapolation technique, which used to determine the initial gas density by using data analysis. It consisted of data reduction, diffusion and solubility coefficient and Panayioutou and Vera equation of state. Solubility and diffusion data were collected with both techniques for carbon dioxide, ethylene, and nitrogen in LDPE at 150 °C over a wide range of pressures. The two techniques showed the same result but there is a greater possibility for leaks in the dual-chamber techniques than in the extrapolation technique. The extrapolation techniques might provide more reliable results if leaks are a problem.

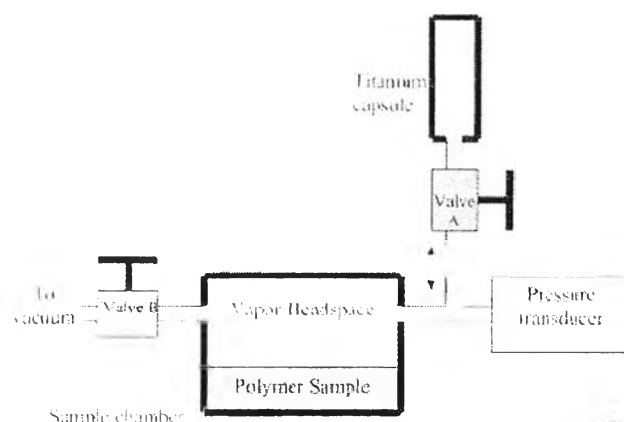


Figure 2.14 Diagram of the dual-chamber variation of the pressure decay experiment (Davis *et al.*, 2004).

In this work, the gravimetric method was used for determining the CO₂ adsorption performance. The CO₂ adsorption capacity was related to many parameters such as pore size distribution, surface chemistry, functional group and structure of the adsorbents. An excellent molecular design flexibility of polybenzoxazine allows the properties of the treated materials to be controlled for CO₂ adsorption. Polyben-

zoxazine synthesized from different amines were employed in two approaches. As impregnating materials in the first approach, polybenzoxazine was impregnated on the activated carbon surface at various loading. The second approach was to carbonize and activate the polybenzoxazine to obtain a suitable porous adsorbent while maintaining their nitrogen functionalities on the surface. It was anticipated that a good understanding of the adsorbent characteristics and properties developed from different structures of amine at various conditions will help determining and suggesting future development of polybenzoxazine-based adsorbent for CO₂ adsorption.

For the objectives of this work, they were followed:

1. To evaluate the proper structure of amine for the synthesis of polybenzoxazine for CO₂ adsorption.
2. To characterize adsorbents developed from polybenzoxazine and to determine CO₂ adsorption capacity.

In the scopes of this research, they covered the following:

Objective 1: To evaluate the proper structure of amine for the synthesis of polybenzoxazine for CO₂ adsorption.

Different structures of amine were varied to prepare benzoxazine suitable for CO₂ adsorption. Two types of amine with different chain length were used in this study including Diethylenetriamine (DETA) and Pentaethylenhexamine (PEHA) as illustrated in Figure 2.15. They were used to evaluate the proper structures of polybenzoxazine for CO₂ adsorption. The two structures of polybenzoxazine with different amine are shown in Figure 2.16.

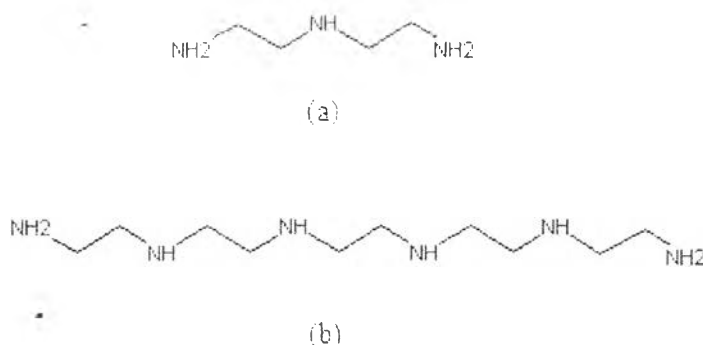


Figure 2.15 Types of amine structure a) Diethylenetriamine (DETA) and b) Pentaethylenhexamine (PEHA).

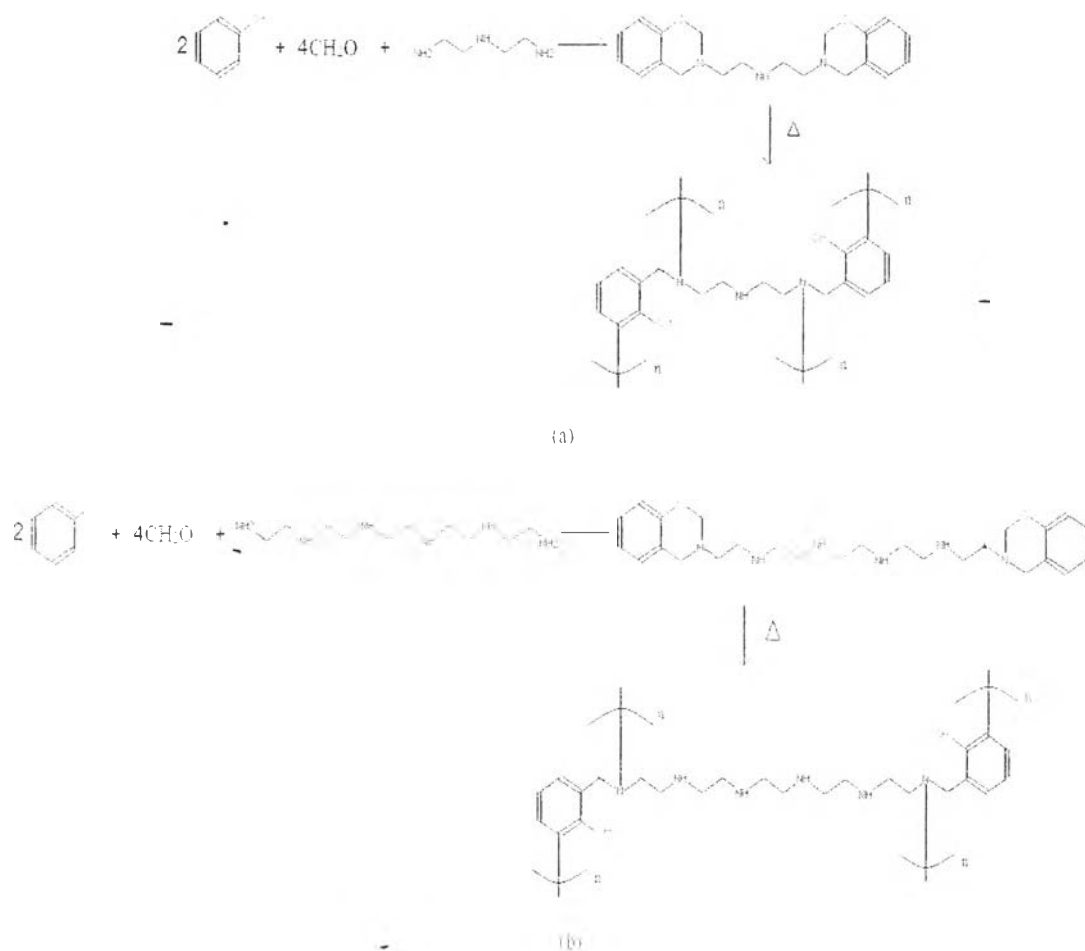


Figure 2.16 Polybenzoxazine structures with different types of amine a) Diethylene-triamine (DETA) and b) Pentaethylenehexamine (PEHA).

Objective 2: To characterize adsorbents developed from polybenzoxazine and to determine CO₂ adsorption capacity.

Two approaches were employed to develop the polybenzoxazine-based adsorbents: (1) polybenzoxazine impregnation on activated carbon and (2) activated carbon from polybenzoxazine. For polybenzoxazine as impregnating material, the effect of loading methods, loading amount and preparation methods, were studied. For the latter approach, carbonization conditions, i.e. temperature and hold time, were varied to determine a proper condition to obtain porous adsorbents while maintaining nitrogen functionalities of the polybenzoxazine. BET surface area analyzer was employed to identify the surface area and pore size distribution. STA was used

to analyze the decomposition of the adsorbent. XPS, CHN analyzer and FTIR were employed to confirm the adsorbent characteristics whether the impregnation, carbonization, and activation are successful.

CO₂ adsorption capacity was determined by employing gravimetric method. The effect of temperature was studied to determine a suitable adsorption condition. The effect of amine structure on the characteristics and properties of the adsorbents was analyzed and led to an understanding of these characteristics to CO₂ adsorption capacity.

The CO₂ adsorption capacity of the impregnating adsorbents (DETA and PEHA) and the activated polybenzoxazine adsorbents were compared and studied.