

CHAPTER II

THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Greenhouse Gas

Greenhouse gas is a gas in an atmosphere that absorbs thermal radiation from the earth surface and re-radiates within the thermal infrared range. Since part of the re-radiation is back toward the earth, this process can cause the elevation of the average surface temperature and it is the fundamental cause of the greenhouse effect. The primary greenhouse gases in the Earth's atmosphere are water vapor, carbon dioxide, methane, nitrous oxide and fluorinated gases. As shown in Figure 2.1, carbon dioxide accounted for about 84% of the greenhouse gas emission in the United States in 2010. The concentration of carbon dioxide in the atmosphere has increased from 280 ppm to 397 ppm from the burning of fossil fuels, since the beginning of the Industrial Revolution (en.wikipedia.org).

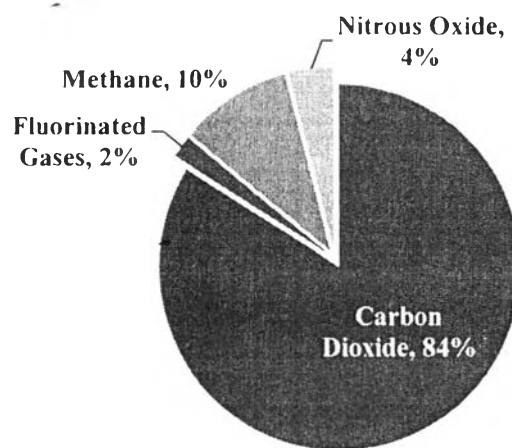


Figure 2.1 United States Greenhouse gas emissions in 2010 (www.epa.gov).

2.2 Carbon Dioxide

Carbon dioxide (CO_2) is a naturally occurring gas that can be found in the atmosphere. Each molecule of CO_2 consists of two oxygen atoms and one carbon at-

om ($O=C=O$). The bonding between carbon and oxygen atoms is covalently bonds (en.wikipedia.org). The properties of carbon dioxide are presented in Table 2.1.

Table 2.1 Properties of carbon dioxide (en.wikipedia.org)

Properties	Value
Molecular weight	44.01 g/mol
Density	1.977 kg/m ³ (gas at 1 atm and 0 °C)
Melting point	-78 °C
Boiling point	-57 °C at 5.185 bar
Viscosity	0.07 cP at -78.5 °C
Appearance	colorless gas
Acidity	6.35, 10.33 pK _a
Diameter	2.8-3.4 Å

CO₂ is considered as an important greenhouse gases. As shown in Figure 2.2, the emission of carbon dioxide is increasing every year from 1971 to 2010. Therefore, the environmental effects of carbon dioxide are of interest. Since the industrial revolution, carbon-based fuels have been burned to generate energy, and caused the concentration of carbon dioxide in the atmosphere to rapidly increase, and, consequently, caused global warming and the anthropogenic climate change. CO₂ is also a major source of ocean acidification when it dissolves in water to form carbonic acid.

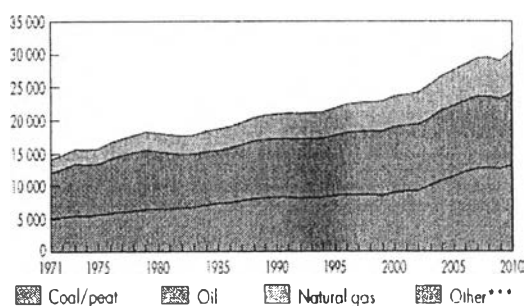


Figure 2.2 World CO₂ Emission by fuel from 1971 to 2010 (IEA, Key World Energy Statistics, 2012).

The effect of climate change is increasing rapidly and has become a global concern on the emission of greenhouse gases particularly the emitting of CO₂. Carbon capture and sequestration is a process of capture and long-term storage of atmospheric carbon dioxide and may refer specifically to the process of removing carbon dioxide from flue gases, such as from power plants or refineries, before being stored in underground reservoirs. In this study the focus is on CO₂ capture. Adsorption is one of the promising techniques that can be used for CO₂ capture.

Table 2.2 Annual energy-related CO₂ emitters in 2009 (en.wikipedia.org)

Country	% of global total annual emission	Tones of GHG per capita
People's Rep. of China	23.6	5.1
United States	17.9	16.9
India	5.5	1.4
Russian Federation	5.3	10.8
Japan	3.8	8.6
Germany	2.6	9.2
Islamic Rep. of Iran	1.8	7.3
Canada	1.8	15.4
Korea	1.8	10.6
United Kingdom	1.6	7.5

2.3 Carbon Capture and Storage

Carbon capture and storage (CCS) strategy has been invented in order to reduce CO₂ emission. CCS associate with a wide range of technologies that are implied to remove and store CO₂. The application of this strategy is an effective way to remove CO₂ from large emission source such as fossil plant, cement and iron plant. However, there are some penalties on the energy consumption and the operating cost,

therefore, the development of new technologies is required. CCS can be divided into three basic routes (Lee *et al.*, 2012).

2.3.1 Pre-combustion Capture

Figure 2.3 illustrate the schematic of pre-combustion process. The concept of this process is applying the decarbonizing fuel. Firstly, Syngas (CO and H_2) is produced from the fossil fuel. Then, syngas pass through the shift reactor to produce CO_2 and CO_2 is separated before feeding into a combustion furnace.

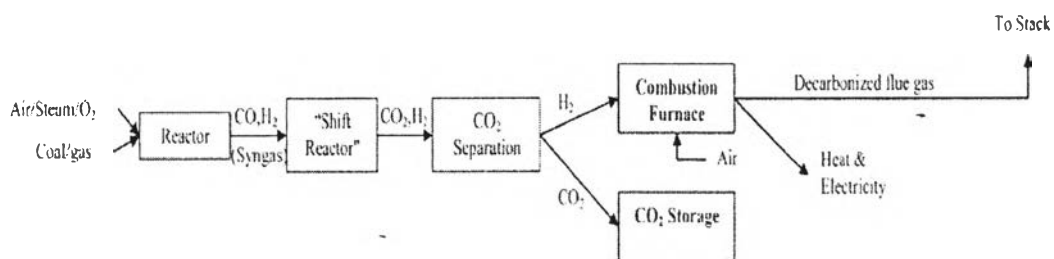
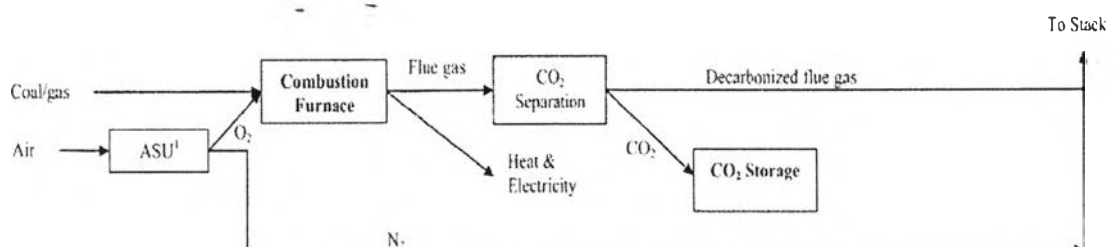


Figure 2.3 Pre-combustion CO₂ removal.

2.3.2 Oxy-fuel Combustion Capture

Oxy-fuel combustion process needs high purity oxygen to combust with fuel instead of ambient air. Fuel gas produced from the complete combustion contains mainly CO₂ and water, where CO₂ can be separated easily.



¹Air Separation Unit

Figure 2.4 Oxy-fuel combustion CO₂ removal.

2.3.3 Post-combustion Capture

CO₂ capture from fuel gas is occurred after combustion. This is the most feasible approach process because it can be retrofitted into the existing processes without much modification. The process of post-combustion mainly involves to absorption, adsorption, cryogenic separation and membrane.

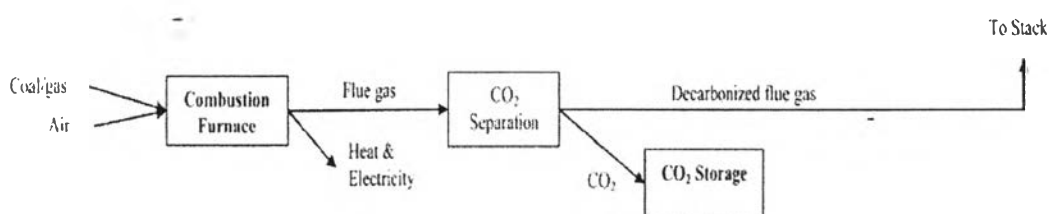


Figure 2.5 Post-combustion CO₂ removal.

2.4 CO₂ Capture Techniques

There are 4 mainly techniques used to capture CO₂ from fuel gas of post-combustion namely absorption, adsorption, cryogenic separation and membrane. Absorption seems to be a promising technique because of their rapid reactions (Chapel *et al.*, 1999); however, this process has many drawbacks including the loss of absorbent during the regeneration because of its high volatilities, and the degradation of amine by small amount of sulfur content in the flue gas (Lee *et al.*, 2010). Furthermore, the operating cost and capital cost are relatively high as same as cryogenic separation and membrane. Therefore, adsorption is more preferred technique.

Adsorption is a process to enrich one or more components in an interfacial layer, normally present in one phase. The term of adsorption may also be used to denote the process in which adsorptive molecules are transferred to, and accumulated in, the interfacial layer. In monolayer adsorption, all the adsorbed molecules are in contact with the surface layer of the adsorbent. In multilayer adsorption, the adsorption space accommodates more than one layer. For the capillary condensation, the residual pore space which remains after multilayer adsorption has occurred is filled with condensate. The binding to the surface is usually reversible. The driving force

for adsorption is the reduction in interfacial tension between the fluid and the solid adsorbent as a result of the adsorption of the adsorbate on the surface of the solid. Usually adsorption is described through isotherms which are the amount of adsorbate adsorbing onto the adsorbent as a function of its pressure for gas or concentration for liquid at constant temperature. There are six types of the majority of isotherm shown in Figure 2.6 (Sing *et al.*, 1985).

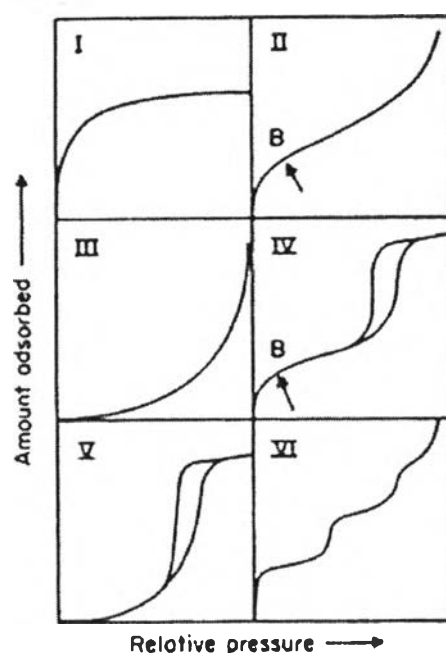


Figure 2.6 Types of isotherm (Sing *et al.*, 1985).

Type I isotherms are given by microporous solids having relatively small external surface such as activated carbon, molecular-sieve zeolite and certain porous oxide. The adsorption is limited by the filling of micropore volume rather than by the internal surface area.

Type II isotherms normally obtain by a non-porous or macroporous adsorbent. The type II isotherm represents unrestricted monolayer-multilayer adsorption. Point B is often indicated the stage where monolayer coverage is complete and multi-layer is beginning at this point.

Type III isotherms are not common, but system typically of nitrogen on polyethylene. This type is convex shape and therefore there is no point B.

Type IV isotherms have their hysteresis loop, which is associated with capillary condensation taking place in mesopores. The initial part is attributed to monolayer-multilayer adsorption since it follows the same path as the corresponding part of type II.

Type V isotherms are not common. This type is related to type III isotherm in case of the interactions between adsorbent and adsorbate are weak, but this type is obtained with certain porous adsorbents. -

Type VI isotherms, in which the step depends on the system and temperature; represent stepwise multilayer adsorption on a uniform non-porous surface. The example of this type is obtained with argon or krypton on graphitized carbon blacks at liquid nitrogen temperature.

2.4.1 Chemisorption

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

2.4.2 Physisorption

Physisorption, or physical adsorption, is one of the adsorption processes that are absence of the chemical bonding interaction. The interacting force of physisorption is caused by van der Waals force including attractions and repulsions between atoms, molecules, and surfaces. The interaction energy is relatively low (~ 10 - 100 meV) in physisorption as compared to the chemisorption (~ 1 - 10 eV). The differences between these two processes are summarized in Table 2.3.

Table 2.3 Comparison between chemisorption and physisorption (Ruthven, 1984)

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

The adsorption ability is dependent on the properties of the adsorbent. They must have high resistance, high thermal stability and small pore diameters, which results in higher exposed surface area and high surface capacity for adsorption. The adsorbents must also have a distinct pore structure that enables fast transport.

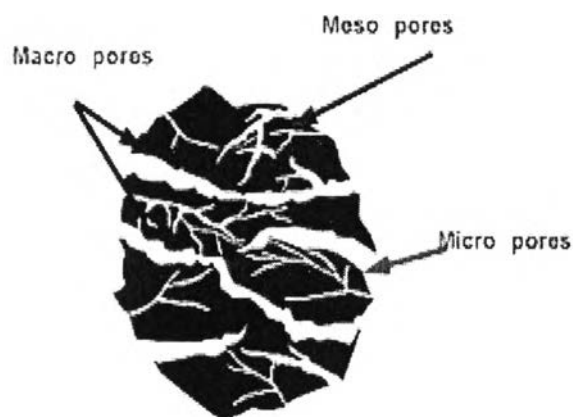
2.5 Adsorbent

Many of the adsorbents are porous materials which have high surface area. The adsorbent is often useful to distinguish between the external and internal surface. The external surface is usually considered as the envelope surrounding the discrete particles. The external surface comprises the cracks which are wider than they are deep; on the other hand, the internal surface comprises the wall of cracks, pores and cavities which are deeper than they are wide. The difference between external and internal surface is depending on the methods of the assessment and the nature of the pore size distribution because the accessibility of pores depend on the size and shape of the gas molecules (Sing *et al.*, 1985). The size and volume of pores are important, thus microporous materials are used for the sorption of light gases, whereas the larger pore size distributions are used for removal of toxins or other large molecules (Drage *et al.*, 2007). To classify the pore size, Ruthven (1984) had concluded in the Table 2.4.

Table 2.4 The classification of pore size (Ruthven, 1984)

	Micropore	Mesopore	Macropore
Diameter (Å)	<20	20-500	>500
Pore volume (cm ³ /g)	0.15-0.5	0.02-0.1	0.2-0.5
Surface area (m ² /g)	100-1000	10-100	0.5-2

Activated carbon (AC) is one of the most popular mass produced adsorption materials due to its high-degree of microporosity. Activated carbon is typically, powdered, granular or pelleted by extremely porous and very high surface area. The structure of activated carbon is shown in Figure 2.7. Activated carbon is produced via normally 2 steps which are carbonization and following by activation step. Carbonization is pyrolysis of raw materials such as nutshells, coconut hush, peat, wood and coal to form carbonaceous materials. The different raw materials lead to variations of pore size distribution, pore structure, surface area, etc. (Choi *et al.*, 2009). In the activation step, the carbonaceous materials are exposed to oxidizing atmosphere at temperature above 250 °C. Adsorption on activated carbon is considered as one of the potential techniques because of cost advantage, wide range of operation condition and low energy requirement.

**Figure 2.7** Activated carbon structure (www.afssociety.org).

2.6 Surface Properties of Carbon Materials

The chemical characteristics of the carbon material are largely determined by surface chemical heterogeneity, which is related to the presence of heteroatoms as referred to those non-carbon atoms present in the carbon structure such as oxygen, nitrogen and sulfur. The types and quantities of those elements are derived from the nature materials or introduced during the activation process. These heteroatoms are formed as the surface functional groups on the carbon structure. Figure 2.8 illustrates the acidic and basic functional groups on the carbon material.

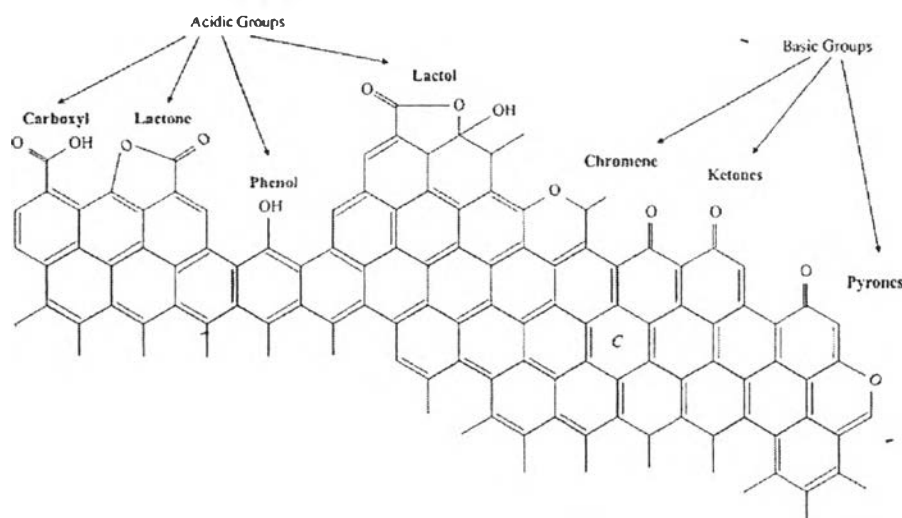


Figure 2.8 Acidic and basic surface functionalities on a carbon material (Shafeeyan *et al.*, 2010).

The role of CO_2 as a weak Lewis acid is well established (Shafeeyan *et al.*, 2010). It is expected that the introduction of Lewis bases onto the activated carbon may favor the CO_2 capture process (Plaza *et al.*, 2009). One of the ways used to prepare activated carbon with increased basicity is to remove or neutralize the acidic functionalities, and another way is to replace acidic groups with proper basic groups for instance ammonia, nitric acid and amine. When the carbon materials are treated with ammonia, ammonia will react with the surface oxide, therefore, forming ammonia salts and amide groups through dehydration and dehydrogenation reactions. Possible structures of the nitrogen functionalities include the following: amine group,

imide group, lactame group, pyrrolic group and pyridinic group. At high temperature, ammonia also decomposes to free radicals such as NH_2 , NH , and atomic hydrogen and nitrogen. These free radicals may gasify the carbon causing HCN , CH_4 and H_2 to be released (Shafeeyan *et al.*, 2010). The appropriate activation process to introduce basicity on the surface is heat treatment, ammonia treatment and also chemical activation. These processes increase basicity by removing some of surface acidic functionalities and introducing basic nitrogen functionalities on the carbon surface.

2.7 Activation of Carbon Materials

Activated carbon is a highly porous, amorphous solid consisting of micro-crystallites with a graphite lattice, usually prepared in small pellets or a powder form. It is non-polar and cheap. One of its main drawbacks is that it reacts with oxygen at moderate temperatures (over $300\text{ }^\circ\text{C}$). Activated carbon can be made from carbonaceous material, including coal, peat, coke and wood (Yang, 2003). The advantages of activated carbon as adsorbent include high CO_2 adsorption capacity, easy to regenerate, and not requiring any moisture removal; therefore, activated carbon is being proposed a good candidate for CO_2 adsorption (Shafeeyan *et al.*, 2010). There are two methods to produce activated carbon: physical and chemical activations.

First, physical reactivation process consists of two phases, carbonization and activation. The carbonization process includes drying and then heating to separate by-products, including tars and other hydrocarbons from the raw material, as well as to drive off any gases generated. The process is completed by heating the material over $400\text{ }^\circ\text{C}$ in the absence of air that cannot support combustion. The carbonized particles are then activated by exposing them to an oxidizing agent, usually steam or carbon dioxide at high temperature. These agents burn off the pore blocking structures created during the carbonization phase and, hence, a porous, three-dimensional graphite lattice structure is developed. The size of the pores developed during activation is a function of the time that it spends in this stage. The longer the exposure time, the larger pore sizes of the activated carbon are obtained.

Another method is chemical activation which is preferred because this method operates at relatively low temperature. In carbonization step, a raw material,

which is impregnated with some chemical compounds such as phosphoric acid, potassium hydroxide and sodium hydroxide, is carbonized at 450-900 °C (Pich-aichanlert, 2011). The conditions of the pyrolysis and oxidation step are the main factor to determine the total pore volume and the pore size distribution. The most popular aqueous phase carbons are bituminous based because of their hardness, abrasion resistance, pore size distribution, and low cost. Activated carbon is used for adsorption of organic substances and non-polar adsorbates and it is also usually used for waste gas treatment. It is the most widely used adsorbent since most of its chemical (e.g. surface groups) and physical properties (e.g. pore size distribution and surface area) can be tuned according to what is needed. Its usefulness also derives from its large micropore (and sometimes mesopore) volume and the resulting high surface area.

Drage *et al.* (2007) used K_2CO_3 as a chemical activation agent incorporated into the resin on polymerization of urea-formaldehyde (UF) and melamine-formaldehyde (MF) resins. The activation temperature ranged from 400 to 700 °C for 1 hour under a constant flow of nitrogen gas. The results of both resins revealed that the resin with lower activation temperature gave a higher adsorption capacity in spite of its lower surface area. It is clearly evident that surface area is not the main determinant of CO_2 adsorption potential. Drage and co-worker concluded that the high activation temperature led to the elimination of nitrogen group, resulting in a decrease in affinity for CO_2 capture.

Hayashi *et al.* (1999) prepared activated carbons by chemical activation and examined the influence of preparation conditions. The surface area of activated carbon was prepared at different temperature using $ZnCl_2$, H_3PO_4 and some alkali metal as the activating reagent. Using of $ZnCl_2$ and H_3PO_4 as the reagent, it is observed that the surface area was more than 1000 m^2/g at 600 °C. This indicates that $ZnCl_2$ and H_3PO_4 work effectively at low temperature. On the other hand, the activation with alkali metal obtained a larger surface area than $ZnCl_2$ and H_3PO_4 particularly K_2CO_3 . The carbon prepared by K_2CO_3 activation has a surface of about 2000 m^2/g at 800 °C.

Plaza *et al.* (2009) developed adsorbents from low cost materials by physical activation with CO₂ and heat treatment with ammonia gas. The activation with CO₂ was conducted at 800 °C with different degrees of burn-off. The result of CO₂ activation for 3 hours obtained the highest surface area and pore volume (822 m²/g and 0.371 cm³/g, respectively). For heat treatment with ammonia, ammonia treatment can be carried out in pure ammonia flow referred to amination or in a mixture of ammonia and air referred to ammoxidation at ratio of 1:2. The amination increased the surface area and pore volume, whereas ammoxidation tends to reduce these parameters.

Zhang *et al.* (2003) studied the steam activation of high-unburned-carbon fly ash from different combustor types. The activation time was kept constant at 90 min, the pore volume and the surface area increased with the rise in the activation temperature. This was associated with the increase in burn-off of the wall, where the increase in pore volume was associated with the development of both micropores and mesopores. The highest surface area and pore volume occurring at 900 °C were 1270 m²/g and 0.815 mL/g, respectively. But at that high temperature the microporosity dropped to around 25%, while the burn-off was 88%. Therefore, to develop activated carbons with a high surface area and high microporosity a low activation temperature (850 °C) seems to be preferred.

Maroto-Valer *et al.* (2005) prepared high surface area activated anthracites by steam activation. Anthracite was activated by using fluidized bed reactor. The surface area and pore volume were 1071 m²/g and 0.588 mL/g, respectively, for anthracite activated at 890 °C for 2 hours. The highest CO₂ adsorption capacity (65.7 mg CO₂/g sorbent) was obtained when the anthracite was activated at 800 °C for 2 hours, resulting in a surface area of 540 m²/g.

Maroto-Valer *et al.* (2008) developed activated fly ash derived sorbent for CO₂ capture. The samples were activated by using steam at 850 °C for 30, 60, 90 and 120 min, resulting in a significant increase of the surface area and pore volume up to 1075 m²/g and 0.774 ml/g, respectively. The longer activation time resulted in an increase of the burn-off levels. The activation time was 30 min, the burn-off was 11% compared to after 120 min of activation time, and the burn-off of the sample was 67%.

Table 2.5 Summary of the previous work for various activation techniques

Type	Reagent or gas	Temperature (°C)	Duration (h)	Surface area (m ² /g), Pore volume (ml/g)	Reference
Chemical	ZnCl ₂	600	1	1400, 0.60	Hayashi <i>et al.</i> , 2000
	H ₃ PO ₄	600	1	1100, 0.40	Hayashi <i>et al.</i> , 2000
	K ₂ CO ₃	800	1	2000, 1.00	Hayashi <i>et al.</i> , 2000
	KOH	800	1	1500, 0.70	Hayashi <i>et al.</i> , 2000
	NaOH	800	1	1300, 0.75	Hayashi <i>et al.</i> , 2000
	K ₂ CO ₃	500	1	365, 0.21	Drage <i>et al.</i> , 2007
Physical	CO ₂	800	3	822, 0.37	Plaza <i>et al.</i> , 2009
	NH ₃	800	3	653, 0.28	Plaza <i>et al.</i> , 2009
	NH ₃ /Air	300	2	1, 0.001	Plaza <i>et al.</i> , 2009
	Steam	850	1.5	1270, 0.82	Zhang <i>et al.</i> , 2003
	Steam	800	2	540, 0.19	Maroto-Valer <i>et al.</i> , 2005
	Steam	850	2	1075, 0.77	Maroto-Valer <i>et al.</i> , 2008

2.8 Surface Treatment

2.8.1 Nitrogen Functional Groups

Several literatures were studied to modify the surface properties of the activated carbon in an attempt to increase their CO₂ capture capacity. There are a number of techniques used to modify the surface by introduce nitrogen functional groups such as impregnation with nitrogen compounds and ammonia treatment. As mentioned earlier, CO₂ is a weak Lewis acid. It is attractive to Lewis bases, thereby; CO₂ adsorption capacity can be increased by introducing nitrogen functional group on the adsorbent (Maroto-Valer *et al.*, 2005).

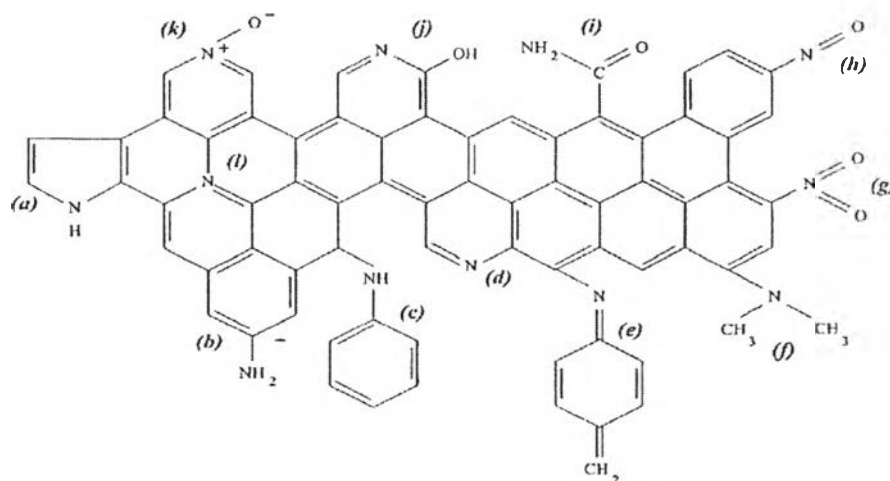


Figure 2.9 Types of nitrogen functional groups: (a) pyrrole, (b) primary amine, (c) secondary amine, (d) pyridine, (e) imine, (f) tertiary amine, (g) nitro, (h) nitroso, (i) amide, (j) pyridine, (k) pyridine-N-oxide, (l) quaternary nitrogen (Shafeeyan *et al.*, 2010).

Maroto-Valer *et al.* (2005) modified the surface properties of the activated anthracites in an attempt to increase their CO₂ capture capacity at high temperature including NH₃ heat treatment and polyethylenimine (PEI) impregnation. The NH₃ heat treatment increased the surface area and pore volume, especially at low treatment temperature. In contrast, the impregnation of PEI was dramatically decreased the surface area, and pore volume, probably due to the pore blockage and surface coverage by PEI. Both surface treatment methods can increase the CO₂ capture capacity of the activated anthracites at higher adsorption temperature, due to the introduction of alkaline nitrogen group on the surface.

Maroto-Valer *et al.* (2008) impregnated different amine compounds, for instance monoethanolamine, diethanolamine and methyldiethanolamine, into the activated fly ash derived sorbents and tested for CO₂ capture at different temperatures. The impregnation process resulted in a decrease of micropore and mesopore volume, because of the effect of pore filling. Each amine compound has its own pore filling effect, assumed that it was due to the difference in the molecular size and shape. The results showed that at 30 and 70 °C the activated samples impregnated

with MEA had the most adsorption capacities (68.6 and 49.4 mg CO₂/g sorbent respectively).

Sarmah *et al.* (2013) prepared and evaluated two classes of amine fly ash based composites for CO₂ capture. FAA₁₃ was prepared from primary and tertiary amines (monoethanolamine/N,N-dimethylaniline) while FAA₂₃ was prepared from secondary and tertiary amines (diethanolamine/N,N-dimethylaniline). The sample FAA₁₃ had a high CO₂ adsorption capacity compared to FAA₂₃. Due to a higher boiling point and more density of MEA with a greater of hydrogen bonding, as shown in the proposed reactions in Figure 2.10. In spite of a higher CO₂ capacity, FAA₁₃ has a lower diffusion coefficient, which led to higher activation energy.

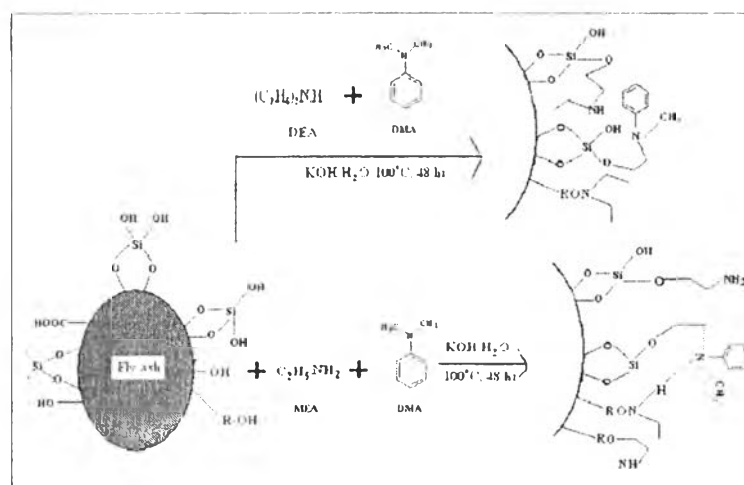


Figure 2.10 Possible reaction mechanism (Sarmah *et al.*, 2013).

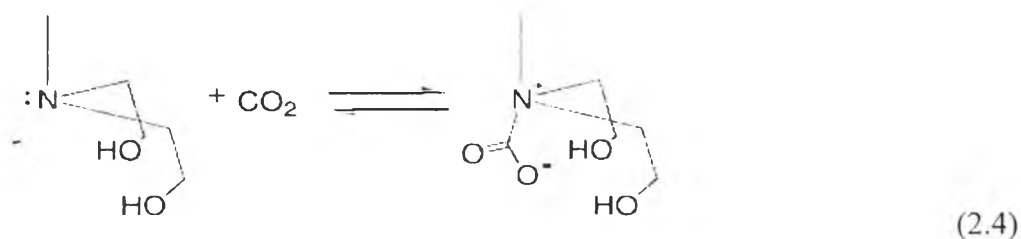
Wang *et al.* (2011) developed an inexpensive molecular basket sorbent (MBS) with high CO₂ sorption capacity by loading PEI with wet impregnation method on the carbon-based porous materials. The adsorption capacity was evaluated in a thermogravimetric analyzer at 75 °C. The adsorption of PEI impregnated onto the carbon black material comparable to that of PEI onto the SBA-15 (135 mg/g sorbent vs. 138 mg/g sorbent). In addition, the estimated cost for sorbent preparation was significantly reduced from 760 \$/kg for SBA-15 to 44 \$/kg for carbon-based.

The results indicated that carbon-based MBS was a promising for cost-efficient CO₂ capture.

Furthermore, it has been reported that the presence of hydroxyl groups enhances the chemical adsorption of CO₂ (Arenillas *et al.*, 2005). When only the amine groups are present, one mole of CO₂ requires two moles of amine. With the presence of hydroxyl groups, the CO₂ moles adsorbed per mole of amine group was 1:1. Without the hydroxyl group, the formation of carbamate is favored in the manner shown in Eqs. (2.1) to (2.3).



In the presence of hydroxyl groups, the formation of carbamate type zwitterions is stabilized in a manner depicted in Eq. (2.4).



Although PEG cannot adsorb CO₂, the presence of OH groups in PEG may influence the chemical adsorption mechanism. In the presence of hydroxyl group, the formation of carbamate type zwitterions maybe promoted and, therefore, amine groups will adsorb more CO₂ molecules (Xu *et al.*, 2003).

Xu *et al.* (2003) prepared the novel CO₂ molecular basket adsorbents by synthesizing and modifying the mesoporous molecular sieve of MCM-41 type with polyethylenimine (PEI) and studied the effect of preparation conditions. At 50 wt% of PEI loading in MCM-41 by a one-step wet impregnation, the sample obtained the highest CO₂ adsorption capacity of 246 mg/g sorbent. In the MCM-41 synthesis step, the lower Si/Al ratio of MCM-41 support and relative higher methanol/MCM-41 weight ratio can lead to a higher CO₂ adsorption capacity. The authors also ob-

served that addition of polyethylene glycol (PEG) into the MCM-41-PEI adsorbent increased not only the CO₂ adsorption capacity but also the rates of CO₂ adsorption and desorption.

Arenillas *et al.* (2005) developed the low cost adsorbent derived from fly ash that can operate at relatively high temperature (75 °C) for CO₂ capture. PEI was incorporated into the samples through the development of the impregnation method. The adsorption capacities were measured in a thermogravimetric analyzer. The 60 wt% of PEI loading had the most CO₂ uptake capacities and the addition of PEG can improve not only the adsorption capacities but also the shape of the adsorption profile, as shown in the Figure 2.11.

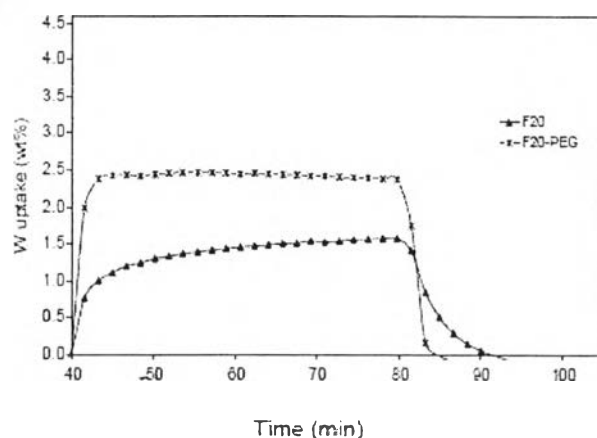


Figure 2.11 Adsorption/desorption profile which has an effect of the PEG loading (Arenillas *et al.*, 2005).

Table 2.6 Summary of the previous work used amine based solution

Adsorbent	Impregnate	Temperature, (°C)	Capacity, (mg/g sorbent) (mmol /g sorbent)	Reference
Activated fly ash	PEI	75	40.04 (0.91)	Arenillas <i>et al.</i> , 2005
Activated fly ash	PEI 60 wt% +PEG 20 wt%	75	44.88 (1.02)	Arenillas <i>et al.</i> , 2005

Table 2.6 Summary of the previous work used amine based solution (cont'd)

Adsorbent	Impregnate	Temperature, (°C)	Capacity, (mg/g sorbent) (mmol /g sorbent)	Reference
MF	-	75	19.8 (0.45)	Drage <i>et al.</i> , 2007
UF	-	75	35.64 (0.81)	Drage <i>et al.</i> , 2007
Activated fly ash	MEA	70	49.72 (1.13)	Maroto-Valer <i>et al.</i> , 2008
Activated fly ash	MDEA	100	40.6 (0.92)	Maroto-Valer <i>et al.</i> , 2008
Activated anthracite	PEI	75	26.4 (0.6)	Maroto-Valer <i>et al.</i> , 2005
Activated anthracite	NH ₃	75	26.44 (0.6)	Maroto-Valer <i>et al.</i> , 2005
Fly ash	MEA+DMA	-	293.92 (6.68)	Sarmah <i>et al.</i> , 2013
Fly ash	DEA+DMA	-	263.56 (5.99)	Sarmah <i>et al.</i> , 2013
SBA-15	PEI	75	136.4 (3.1)	Wang <i>et al.</i> , 2011
Carbon material	PEI	75	132 (3)	Wang <i>et al.</i> , 2011
MCM-41	PEI 75 wt%	75	132.88 (3.02)	Xu <i>et al.</i> , 2003
MCM-41	PEI 30 wt%	75	68.2 (1.55)	Xu <i>et al.</i> , 2003
MCM-41	PEI 30 wt% +PEG 20 wt%	75	85.8 (1.95)	Xu <i>et al.</i> , 2003

2.8.2 Oxygen Functional Groups

Nitrogen functionalities are not the only species capable of acting as Lewis bases. Oxygen functional groups such as carbonyl, alcohol and ether contain an electron-donating oxygen atom that can also participate in electrostatic interactions with CO₂. Carboxylic acids have also shown the strong interaction between Lewis acid and Lewis base with CO₂ molecule. Not only a carbonyl group presented in carboxylic acid that can act as Lewis base towards the carbon atom, as Lewis acid, but an acidic proton that can act as Lewis acid towards the oxygen atoms, as Lewis base, of the CO₂ molecule (Bell *et al.*, 2003). Hence, the present of oxygen functional groups on the carbon surface will enhance to capture CO₂ (Plaza *et al.*, 2013). Oxida-

tive treatment is one of the ways that can produce oxygen functional groups. A number of literatures have been worked on oxidative treatment.

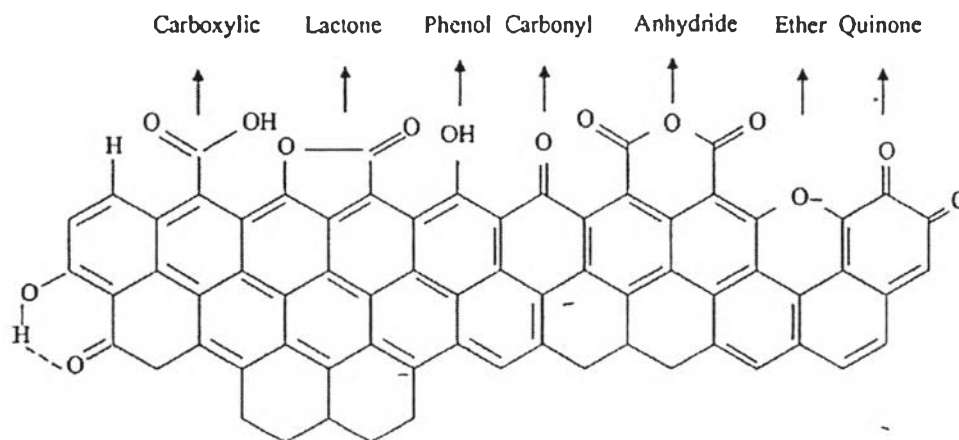


Figure 2.12 Surface oxygen containing groups on carbon material (Shafeeyan *et al.*, 2010).

Plaza *et al.* (2013) studied the effect of oxidation upon the CO₂ capture performance by using phenolic resin carbon as the base material. Liquid phase oxidation, using ammonium persulfate and nitric acid as oxidizing agents, presents a greater amount of oxygen incorporated onto the surface of carbon materials. These oxygen functional groups are carboxylic acids, carboxylic anhydrides, lactones, phenols, carbonyls and quinones. On the other hand, the gas treated samples introduce a combination of the thermally more stable lactones, phenols, carbonyls and ethers. The porous texture of the sample is also affected by oxidation. Pore volume was decreased by liquid phase oxidation, whereas air oxidation is slightly developed. The authors concluded that carboxylic acids, which are introduced through liquid phase oxidation, present strong Lewis acid-Lewis base interaction with CO₂ molecule. Thus, this might be a possible pathway for increasing the affinity towards CO₂ adsorption.

Figueiredo *et al.* (1999) modified surface chemistry of activated carbon including oxidation in gas and liquid phases. They concluded that liquid phase treatments have no significant impact on the texture of carbon materials, while gas

phase oxidation increases the micropore volume, mesopore surface area and the average micropore width. Moreover, it has been shown that oxidation in liquid phase increases especially carboxylic acids, whereas gas phase oxidation increases mainly hydroxyl and carbonyl groups.

2.9 Adsorption Measurement Techniques

2.9.1 Gravimetric Technique

Recently, there are many techniques employed to study the adsorption process. The first is called gravimetric technique that is typically carried out with about 1-10 mg of sample. This technique determines the adsorption capacity by measuring weight change when the sample uptakes CO₂ in thermo-gravimetric analyzer. Because this technique requires very small sample size, consequently, gravimetric technique is appropriate for the adsorbents that have high storage capacities (Blackman *et al.*, 2006).

2.9.2 Volumetric Differential Pressure Technique

This method determines the capacity of a material by measuring the pressure drop resulting from adsorption after exposing the sample to a gas at constant volume. A differential pressure is used to improve the accuracy and reliability of the method. This method eradicates many problems associated with the expansion of non-ideal gas, which can introduce large errors, by using simultaneous expansion in the reference cell into the sample cell.

Blackman *et al.* (2006) developed the apparatus that is a volumetric differential pressure set-up, shown in Figure 7 below. The set-up has two volumetrically balanced limbs each comprising a reservoir and sample cell. Carbon nanofiber and a series of activated carbon were used as the adsorbent. The experiment was done by measuring the differential pressure between the sample cell and the reference cell, and then the hydrogen adsorption capacity can be evaluated. From this work, the amount of hydrogen adsorbed was less than 1 wt% for all the adsorbent.

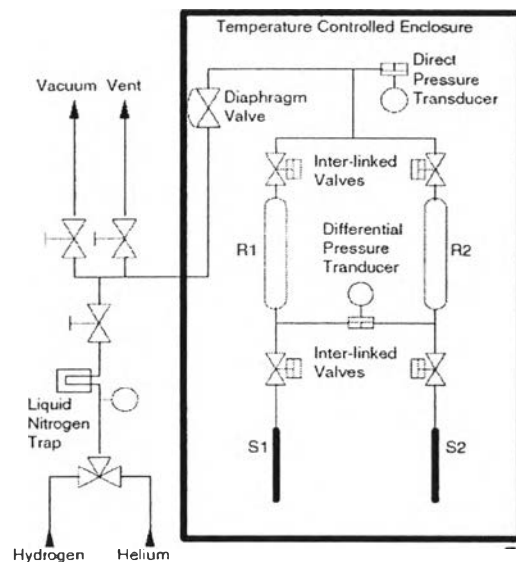


Figure 2.13 Schematic of the volumetric differential pressure hydrogen adsorption apparatus (Blackman *et al.*, 2006).

2.9.3 Pressure Decay Technique

Another technique employed to study gas sorption is “Pressure-Decay” which is the original and most popular method for high pressure sorption measurements. An experiment is conducted by isolating a sample and a high-pressure gas in a closed vessel. As the sample adsorbs the gas, the pressure drop in the vessel is monitored as a function of time. An equation of state for gas is used to convert the pressure into the mass uptake. Because pressure decay technique is reliable and suitable for laboratory section, this technique will apply in this work.

Davis *et al.* (2004) developed two new volumetric sorption techniques to measure thermodynamic and mass transport properties in polymer-solvent systems. They compared two types of pressure-decay. In the first type, the initial density was measured by extrapolation of the mass uptake curve. In the second type, the initial density was measured gravimetrically. Solubility and diffusion data were collected with techniques for carbon dioxide, ethylene and nitrogen in low density polyethylene at 150 °C. Both types of pressure decay gave identical results. This indicates that the simpler extrapolation technique was a valid technique. In some situation

where leaks were difficult to eliminate, the extrapolation technique was required because there were a few fitting.

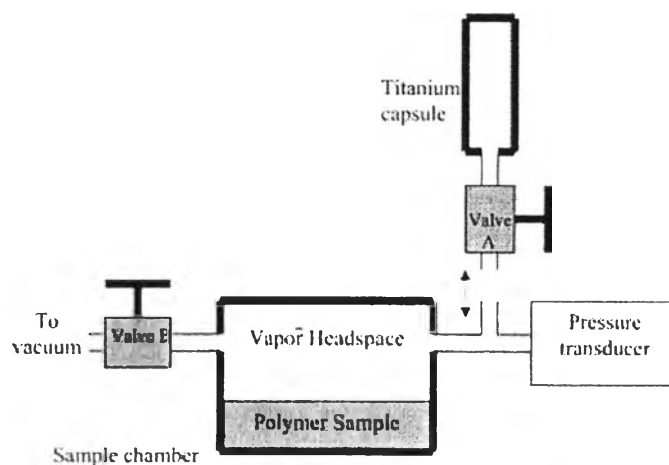


Figure 2.14 Schematic of the dual-chamber variation of the pressure decay experiment (Davis *et al.*, 2004).

Activated carbon, a cheap carbon material, is widely used in a large number of industrial applications. The properties of activated carbon can be improved and could be a potential cheap source of carbon for CO₂ adsorption application. Because CO₂ is a weak Lewis acid, it is hypothesized that the introduction of Lewis bases onto the activated carbon will help improve the CO₂ affinity. Furthermore, the introduction of Lewis bases, i.e. amine groups, on the acid surface obtained by oxidation, which very limited studied, may increase the interaction between amine compound and surface of activated carbon and, consequently, increase the CO₂ adsorption performance.

The objectives of this thesis were: (1) to prepare the adsorbent derived from cheap carbon materials and improve the surface properties. (2) to characterize the surface properties and study to understand differences in surface properties of adsorbents. And (3) to determine and compare the CO₂ adsorption and desorption performance of the adsorbent obtained from different surface treatment.

The scope of this thesis covered the following:

Scope of objective 1: The surface properties of the activated carbon will be improved by various methods such as oxidative treatment in nitric acid and impregnation with polyethylenimine (PEI) in order to enhance CO₂ adsorption capacity at relatively high temperature. Three approaches of surface treatment were performed including (1) acid treatment only, (2) PEI impregnation only and (3) acid treatment following by PEI impregnation. Various conditions for nitric acid treatment and PEI impregnation were studied such as acid concentration, acid treatment duration and loading amount of PEI.

Scope of objective 2: The surface properties will be studied by different techniques. Sorptomatic surface area analyzer will be used to measure the surface area, pore volume and pore diameter of adsorbents. XPS will be employed to confirm that the impregnation process is successful and characterize surface chemistry of the adsorbents. Ultimate analysis will be used to measure the elemental composition of each different surface treatment. TG/DTA will be used to study the thermal stability of adsorbents. And the surface morphology will be studied by SEM.

Scope of objective 3: The CO₂ adsorption and desorption performance of the modified activated carbon will be determined by using gravimetric technique and compared the mole adsorb and desorb of each adsorbents.