

CHAPTER II

BACKGROUND AND LITERATURE REVIEW

2.1 Global Warming

Global warming and climate change are the phenomenon of increasing in Earth's average surface temperature. The climate change is caused by various factors, both natural and human activities, such as changes in greenhouse gas (GHG) concentrations, solar energy and volcanic eruptions. Between 1906 and 2005, the global mean surface temperature rose from 0.6 to 0.9 degrees Celsius and the rate of temperature increase is almost double that over the last 50 years (Figure 2.1).

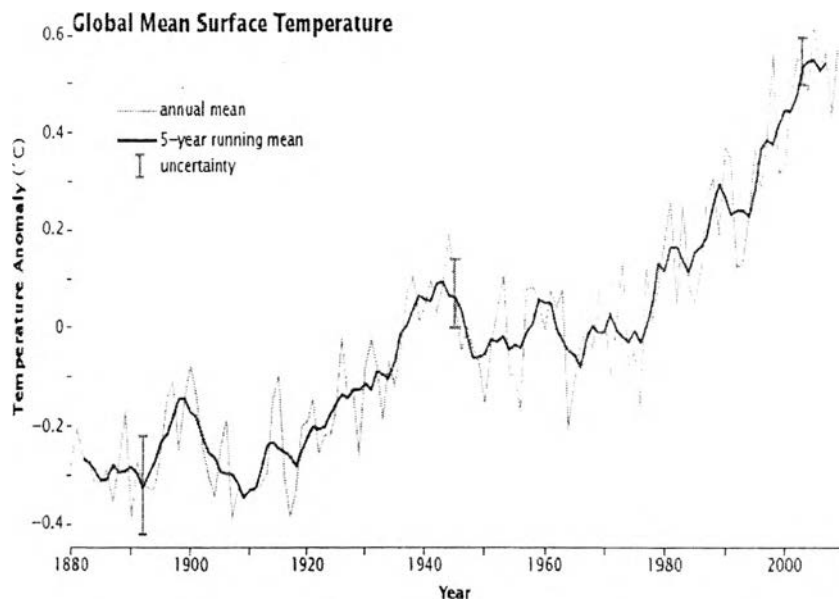


Figure 2.1 Global mean surface temperature (Riebeek, 2010).

The greenhouse gases such as water vapor (H_2O), methane (CH_4), carbon dioxide (CO_2), and nitrous oxide (NO_2) are produced directly by human activities in significant amounts. These greenhouse gases absorb infrared radiation that would otherwise escape from earth leading to an increase of Earth's surface temperature. The major human activities that can generate greenhouse gases come from the burning of fossil fuels for electricity, transportation, and industrial as shown in Figure 2.2

(a). In Figure 2.2 (b), CO₂ is the most attracted attention owing to its greatest contribution which accounts approximately 82 % of the greenhouse gas emissions in the United State in 2013.

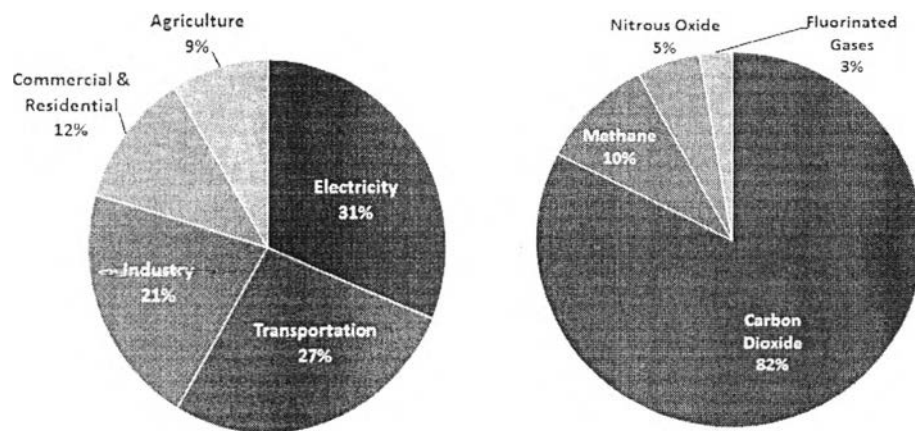


Figure 2.2 U.S. Greenhouse gas emissions (a) by Sector and (b) by Gas (2013) (United States Environmental Protection Agency, 2015).

2.2 Carbon Dioxide

Carbon dioxide is a chemical substance formed by one carbon and two oxygen atoms with chemical formula CO₂. The carbon and oxygen atoms are connected by covalent bonds. At standard temperature and pressure it is a gas with colorless and odorless. It is widely used for industrial applications such as food industry, foamed plastic, refrigerant, fire extinguishers, etc. CO₂ is considered to be an important greenhouse gas due to the capability to absorb infrared radiation.

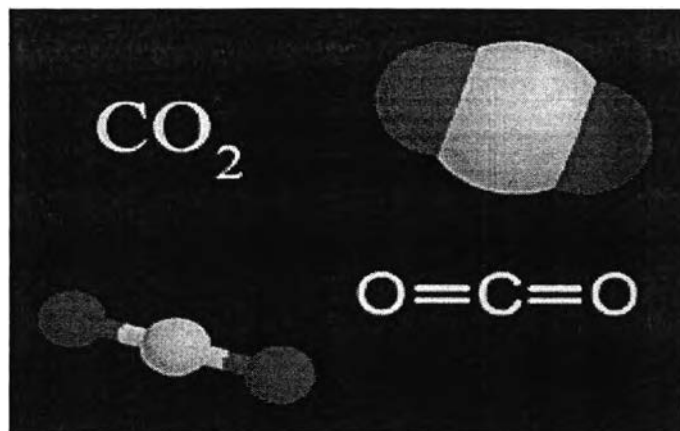


Figure 2.3 Carbon dioxide molecule (Bergman, 2011).

CO_2 is a linear molecule with centrosymmetry. As shown in Figure 2.3, each oxygen and carbon atoms share two electrons to form two $\text{C}=\text{O}$ bonds. The CO_2 molecule has no electrical dipole because of its centrosymmetry. CO_2 is a colorless, odorless, slightly acidic liquefied gas and soluble in water. It is moderately reactive and is non-flammable. It has a density around 1.98 kg/m^3 (standard temperature and pressure), which is heavier than air. The critical temperature of CO_2 is $31.1 \text{ }^\circ\text{C}$. The critical pressure of CO_2 is 7.38 MPa . The triple point of CO_2 occurs at 518 kPa and $-56.6 \text{ }^\circ\text{C}$. It becomes liquid at pressure above 5.1 atm and becomes solid at $-78.5 \text{ }^\circ\text{C}$ (1 atm) (Universal Industrial Gases, 2003).

CO_2 is the major cause of climate change and increasing of Earth's surface temperature. The burning of fuels such as oil, diesel, natural gas, organic-diesel results in the production of CO_2 . Since the industrial revolution, a large amount of fossil fuel has been burned resulting in an increase of CO_2 in the atmosphere (Bergman, J). As illustrated in Figure 2.4, the atmospheric CO_2 concentrations in Mauna Loa, Hawaii are measured. The CO_2 concentrations have been recorded from 1958 onward. The CO_2 level has risen from 315 ppmv to 380 ppmv (in 2006), with a recent growth rate of about 2 ppm per year. The current CO_2 atmospheric concentrations are around 30% higher than the pre-industrial levels.

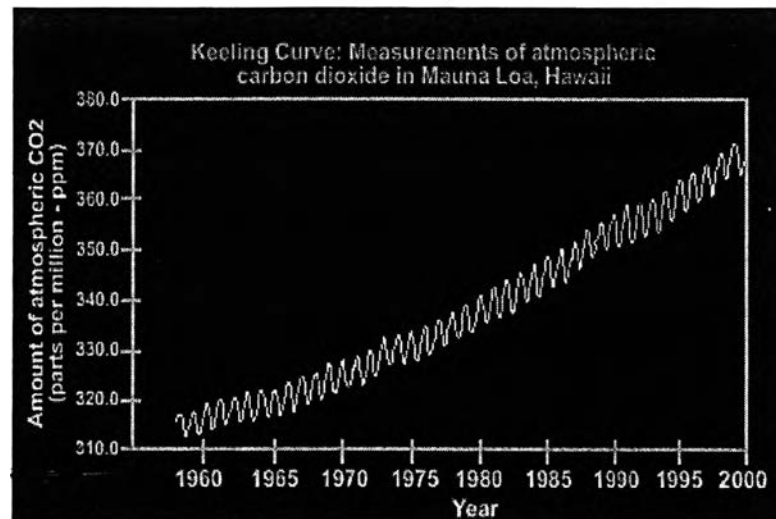


Figure 2.4 Atmospheric carbon dioxide concentration in Mauna Loa, Hawaii (Gardiner, 2007).

2.3 CO₂ Capture/Separation Technologies

2.3.1 Carbon Capture and Storage

Carbon capture and storage (CCS) is the process by which CO₂ is captured, transported and stored before it is emitted into the atmosphere. It has been considered as an effective method for reducing CO₂ emission from large industrial plants such as power plants. There are three main techniques developed for CO₂ separation and capture for power generation, including post-combustion capture, pre-combustion capture, and oxyfuel capture (Lee *et al.*, 2012).

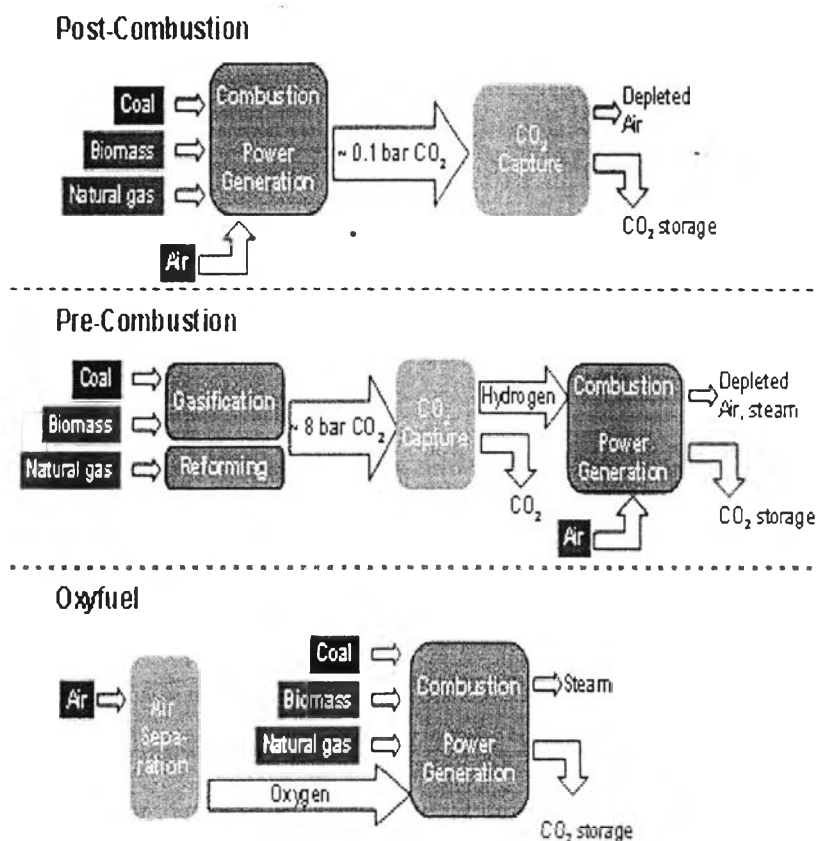


Figure 2.5 CO₂ capture systems (The American Ceramic Society, 2010).

2.3.1.1 Post-Combustion Capture

It is the process by which CO₂ is separated from the exhaust after the combustion process. For this process, the fuel material is combusted by air for generating the electricity. CO₂ is then separated from flue gas (CO₂ concentration <15 %) at atmospheric pressure. There are many methods can be used to capture CO₂ from flue gas of post-combustion process such as absorption, adsorption, membranes and cryogenics. Due to a more mature technology than other processes, absorption is the most commonly used process for post-combustion capture. The technology of post-combustion capture is much more mature than of the pre-combustion capture and oxyfuel capture. The disadvantages of post-combustion capture are the low concentration of CO₂ in flue gas and high energy required for solvent regeneration.

2.3.1.2 Pre-Combustion Capture

It is a process by which carbon in the fuel can be removed before the combustion process. The fuel materials are converted into synthetic gas mainly consisting of carbon monoxide (CO) and hydrogen (H₂) by gasification with limited amount of oxygen. CO is then reacted with water steam to form CO₂ and H₂ through water gas shift reaction. Then, the CO₂ from both gasification and water gas shift reaction are removed from flue gas, while H₂ can be sent to a turbine and burned for producing electricity or employed for electric cells. Due to the high pressures and high CO₂ concentrations of flue gas, post-combustion capture can reduce the capture costs. The drawback of this process is the huge capital expense.

2.3.1.3 Oxyfuel Capture

This process can separate almost 100% of CO₂ from flue gas. The combustion of oxyfuel capture is carried out by using pure oxygen instead of air. The fuel material is combusted by pure oxygen mixed with recycle flue gas, producing flue gas that contains mainly CO₂ and water, which is easily separated by cooling. The disadvantage of oxyfuel CO₂ capture is the high cost of producing pure oxygen, which is based on cryogenic separation of air. For the additional development, oxyfuel CO₂ capture process will become a very good alternative for CO₂ capture in the future.

2.3.2 Carbon Separation Techniques

As mentioned earlier, the technology of post-combustion capture is much more mature than the pre-combustion capture and oxyfuel capture. This makes post-combustion capture the most used approach for CO₂ capture. As shown in Figure 2.6, several CO₂ separation techniques can be used with post-combustion capture, including physical absorption, chemical absorption, adsorption, cryogenics, and membranes.

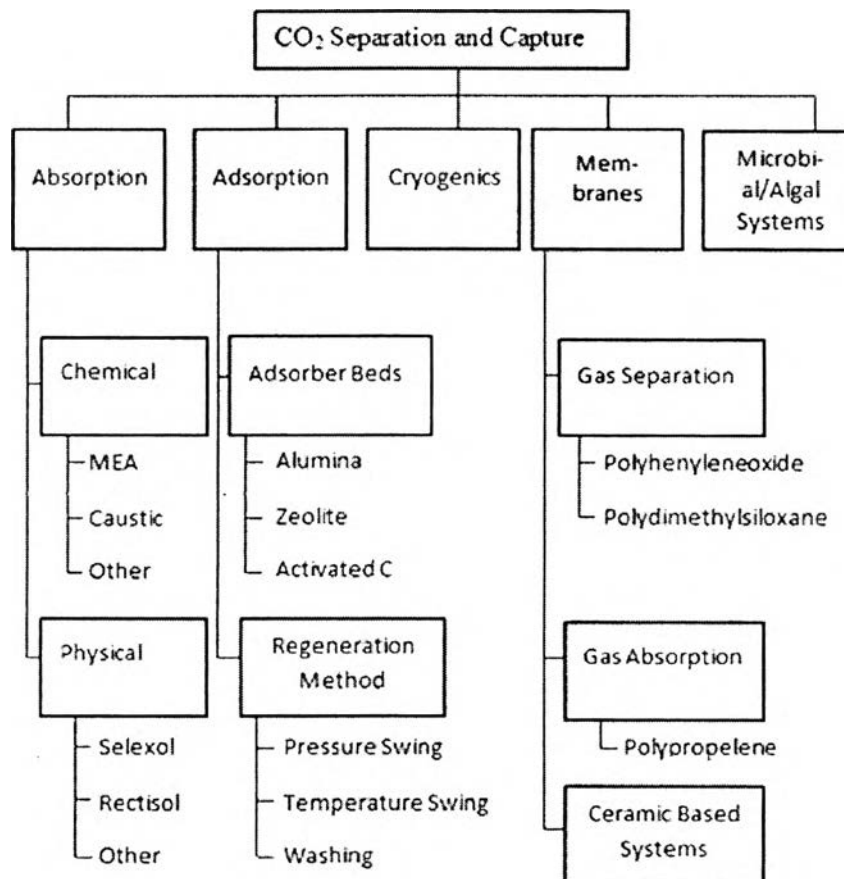


Figure 2.6 Process technologies for post combustion CO₂ capture (Rubin *et al.*, 2012).

2.3.2.1 Absorption Process

Absorption is a process that CO₂ molecules transfer from CO₂ rich stream into chemical solvent. Two main parts of absorption process are absorber and regenerator. The CO₂ uptake occurs in absorber unit. In the absorber, CO₂ is introduced at the bottom and flow up the column countercurrent with the down-flowing solvent. Absorption process is classified into two different types: physical absorption and chemical absorption. In physical absorption, CO₂ is absorbed into a solvent based on Henry's law (Yu, 2012). This type of absorption is not suitable for flu gas with low CO₂ partial pressures. The solvent can be regenerated by using heat, pressure reduction or both. In chemical absorption, CO₂ is absorbed into a solvent by chemical reaction between the CO₂ and chemical solvent. A number of chemical sol-

vents are available such as MEA, DEA, and MDEA, DIPA, etc. This type of absorption is best suitable for CO₂ capture of post-combustion process. However, there are several drawbacks of this type of absorption such as, energy penalty, corrosion, solvent degradation, etc (Mondal *et al.*, 2012).

2.3.2.2 Adsorption Process

To avoid the limit in using of absorption processes such as corrosion and high energy requirements, solid adsorption process is now being considered as an alternative for CO₂ recovery. Adsorption is the process by which CO₂ molecules attach to the surface of solid adsorbents. The adsorbents for CO₂ separation can be classified into physical and chemical adsorbents. In physical adsorption process, the adsorption of CO₂ onto solid surface is caused by Van der Waals force. There are many available types of physical adsorbents such as carbons, zeolites, silica and metal-organic frameworks (MOFs). However, there are some drawbacks of this type of adsorption such as, low CO₂ selectivity and low CO₂ capture capacity. Then, adsorbents need to be modified on their surface chemistry such as amine-based adsorbents which are developed by introducing nitrogen functionalities onto carbon surface. In the chemical adsorption process, the adsorption of CO₂ onto solid surface is driven by a chemical reaction, resulting in an increase of capacity and selectivity. The solid adsorbents can be regenerated by using temperature swing adsorption (TSA), pressure swing adsorption (PSA), or electrical swing adsorption (ESA) (Wanga *et al.*, 2011).

2.3.2.3 Membrane Technology

The membrane acts as the semi-permeable barriers that can be used to separate CO₂ from gas streams by permitting only CO₂ molecules to move through. The principle of this separation technology is a differential pressure over different membrane sides. Several materials are available for membranes such as polymer, zeolite, and carbon. The membranes technology can be classified into two groups, namely membrane absorption and membrane-based separation (Mondal *et al.*, 2012).

2.3.2.4 Cryogenic Process

Cryogenic process is used to separate CO₂ from gas streams by condensation. This process is not suitable for low CO₂ concentrations. There are several advantages of this process. This process does not need the chemical absorbents. It can be performed at ambient pressure. The liquid CO₂ can be formed via this process. However, a drawback is many costly stages are required to get rid of water from the gas streams (Mondal *et al.*, 2012). Very high purity CO₂, Economic for transportation

2.4 Adsorption Process

Adsorption is the process by which gases or liquids attached to the surface of solids. The solid where adsorption occurs is called adsorbent and the gas or liquid which is adsorbed on the solid surface is called adsorbate. Several parameters affect the adsorption, including the surface area of adsorbent, nature of adsorbate and adsorbent, temperature and pressure, and activation of adsorbent. There are two main categories of adsorption, including physical adsorption and chemical adsorption. The adsorption is called physical adsorption when the adsorption of adsorbate onto adsorbent is caused by Van der Waals force. In this type of adsorption, adsorbents can be easily regenerated, because there are no chemical bonds between adsorbate and adsorbent. When the adsorbent adsorb adsorbate by chemical bonds, this type of adsorption will be called chemical adsorption. Because the chemical bonds are formed in this type of adsorption, therefore adsorbents cannot be easily regenerated. In this type of adsorption, the products which are chemically different from the initial adsorbate can be evolved from the desorption processes. Table 2.1 indicates the differences between physisorption and chemisorption.

Table 2.1 Comparison between physisorption and chemisorption [adapted from (Rupasinghe, 2012)]

	Physisorption	Chemisorption
Heat of Adsorption (kJ mol ⁻¹)	Low heat of adsorption 20-40 kJ mol ⁻¹	High heat of adsorption 40-400 kJ mol ⁻¹
Force of Attraction	Van der Waals	Chemical bond
Reversibility	Reversible	Irreversible
Temperature	Low temperature	High temperature
Monolayer Coverage	Mono or multi-molecular layers	Monomolecular layers
Rate of Adsorption (at 273 K)	Fast	Slow

The process of adsorption is normally described by the adsorption isotherm, which is a graph showing the relationship between relative pressure and amount adsorbed at constant temperature. The adsorption isotherms can be divided into six major categories as shown in Figure 2.7.

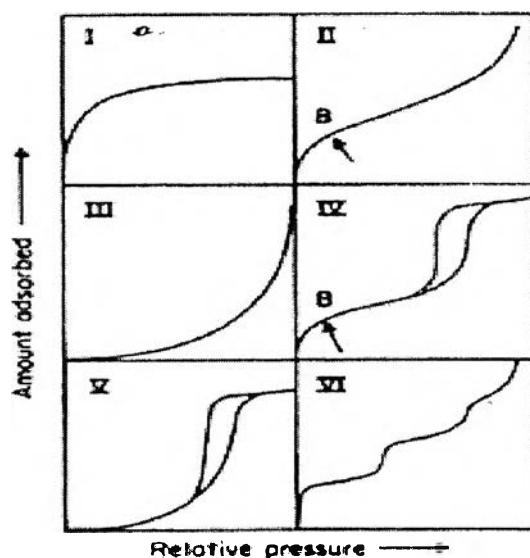


Figure 2.7 Classification of the isotherm types (Sing *et al.*, 1985).

Type I Isotherm refers to the sorption characteristic of adsorbents with a predominantly microporous structure. The filling of the greater portion of micropore will take place at low relative pressures. The horizontal plateau at higher relative pressures on the graph represents the completion of adsorption process.

Type II Isotherm represents the adsorption of adsorbates on nonporous or macroporous adsorbents. In this process, the shape is caused by monolayer coverage then followed by multi-layer adsorption at point B.

Type III Isotherm refers to the sorption characteristic of adsorbents with weak interactions between adsorbate and adsorbent. The adsorbents can be nonporous and microporous. The weak interactions cause the low uptakes at low relative pressures.

Type IV Isotherm is similar to types II. A hysteresis loop is caused by the presence of mesopores.

Type V Isotherm is similar to types III. The weak interactions between adsorbate and adsorbent cause an increase of uptakes at higher relative pressures. This type of Isotherm, the adsorbents can be microporous or mesoporous.

Type VI Isotherm refers to the sorption characteristic of nonporous adsorbents with homogeneous surface. The shape is caused by monolayer coverage then followed by a subsequent layer. The example of this type is the adsorption of krypton on carbon black at 90 K.

2.5 Adsorbents

Adsorbent is a material that usually has high porosity and has very large specific surface area. It has the capability to trap molecules into its surface using intermolecular attractive forces. Adsorbent materials are used typically in the form of spherical pellets, moldings, rods or monoliths. The efficient adsorbents should have high thermal stability, high abrasion resistance, and small pore diameters. There are three regimes of their pore sizes, including macropores ($d > 50$ nm), mesopores (50 nm $> d > 2$ nm), and micropores ($d < 2$ nm) (Figure 2.8).

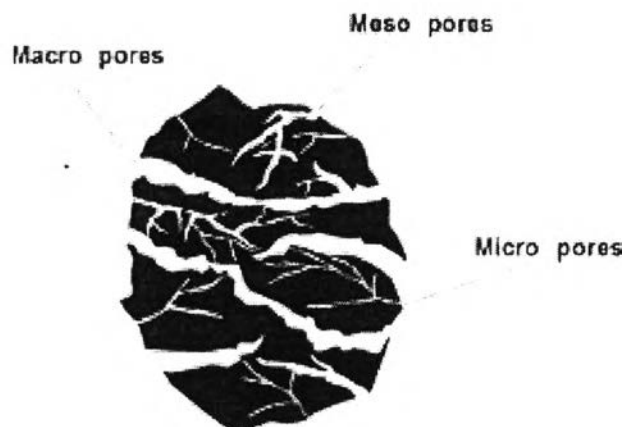


Figure 2.8 Classification of pore sizes (Sujata Carbons Pvt. Ltd., 2011).

The efficient adsorbents for CO₂ adsorption should satisfy: high CO₂ adsorption capacity, high selectivity, fast adsorption and desorption kinetics, low cost materials, infinite stability and regenerability, and mild conditions for regeneration. The adsorbents for carbon capture can be classified into two types, namely physical (i.e., carbon based materials, zeolites and metal organic frameworks) and amine functionalized adsorbents (Sayari *et al.*, 2011).

One of most interesting adsorbents used to capture CO₂ is the activated carbons (ACs). Activated carbon, also called activated charcoal, is the porous substance that has very large specific surface area. A typical activated carbon is constituted of Carbon 88 %, Hydrogen 0.5 %, Nitrogen 0.5 %, Sulfur 1.0 %, and Oxygen 6-7 %, with the balance inorganic ash contents (Boehm, 2002). Since activated carbon presents several advantages such as high surface area, low cost, wide availability, high hydrophobicity and thermal stability, this material is widely used as an adsorbent. This type of adsorbents is made from carbonaceous substances such as wood, coconut shells, coke pitch, and coal via a two-step process, including the carbonization process and activation process.

Carbonization is the process of converting of carbon-rich raw material to carbon or a carbon-containing residue by heating. This heating process is known as a pyrolysis, which carbon-rich raw material is heated in inert atmosphere (usually argon or nitrogen) at the temperatures below 800 °C. During the carbonization process, the non-carbon elements (hydrogen, oxygen, and nitrogen) of raw material are elimi-

nated into gaseous state. The remaining element carbon atoms are formed into elementary graphite crystallites. Because the arrangement of these crystallites is disorganized, the carbonized materials therefore exist of free interstices. The property and the yield of the carbonized materials are affected by several factors, including heating rate, temperature and duration. After the carbon-rich raw materials were carbonized, carbonized materials need to undergo the activation process (Manocha, 2003).

The carbonized materials have very low adsorption capacity, because their pores are closed or partially closed with the products of decomposition during carbonization. Activation is used to improve the internal pore structures that are formed from the carbonization step and used to generate more porosity. This results in a very large internal surface area, which leads to high adsorption capacity of materials. There are two ways used to activate carbonaceous materials: physical activation and chemical activation.

Physical activation is the process for improving quality of carbonized product by heat treatment at a high temperature, usually 900 to 1200 °C under environment of oxidizing gases such as CO₂, steam, or air. In this type of activation, the carbonization process must occur in inert atmosphere at the temperatures range of 600 to 900 °C. During this process, all of the volatile compounds are removed causing the enlarged pores. The internal surface area of the material is increased due to decreasing the number of carbon atoms.

These reactions take place during the activation process of carbonaceous materials by using oxidizing gases (Equations 2.1-2.5).

Activation by steam and CO₂ (Manocha, 2003):



Activation by oxygen (Manocha, 2003):





Chemical activation process has several advantages over physical activation, including the shorter production time, lower temperatures required and this process results in a very high surface area. It is the process by which the chemicals are impregnated onto the carbonized materials. The chemical substance is commonly an acid, a strong base or a salt (e.g., H_3PO_4 , $ZnCl_2$, H_2SO_4 , K_2S). After the impregnation process, the material is carbonized at lower temperature, usually 450 to 900 °C. It is believed that the carbonization and chemical activation occur simultaneously (Manocha, 2003).

2.6 Carbon Nano Spheres

In 1991, Iijima first discovered carbon nanotubes (CNT) from arc discharge technique (Iijima, 1991). After that, many researchers have prepared and investigated various forms of carbons such as carbon nanofibers, carbon trees, carbon spheres and carbon nanowalls. Carbon nano spheres (CNS), as a new form of carbon based materials, has increasingly received research attention due to their attractive characteristics, such as high thermal stability, high strength, and light weight. CNS has been applied in a wide range of applications such as energy storage, adsorbents, nano-additives, purification, and novel catalysts supports. There are different techniques used to synthesize the CNS such as chemical vapor deposition, ultrasonic treatment, templating method, arc discharge, and pyrolysis.

Qian *et al.* (2004) synthesized carbon spheres via a simple chemical vapor deposition (CVD) method using toluene in the absence of catalyst. The carbon spheres with diameters from 60 nm to 1 μm were obtained. The results showed that the carbon spheres consisted of carbon composition over 97.0 % and they did not contain a high degree of graphitization. Pure carbon spheres (99 % carbon) from styrene, toluene, benzene, hexane, cyclohexane and ethene were prepared by Jin *et al.* (2005) using a pyrolysis technique. Ultrasonic treatment was also applied to produce carbon spheres. The carbon spheres can be obtained from treating ultrasound on pyrolytic graphite material mixed with deionized water (Wang *et al.*, 2003). Plasma in

liquid method, as one of the technologies that can produce carbon materials, has attracted more attention and studied by many researchers in recent years because of its advantages such as simple to handle, potential for high yield, and economical method. There is a novel type of plasma in liquid technique called solution plasma process (SPP). To produce CNS, this technique presented several benefits such as the utilization of graphite electrodes and the addition of feed gas was not necessary as compared to the conventional technique. Kang *et al.* (2013) has successfully synthesized carbon nano spheres from benzene using SPP. They reported that the diameters of obtained CNS were in a range of 20 nm to 100 nm and were able to control by adjusting the pulse frequency of the bipolar power supply.

2.7 Carbon Surface Chemistry

Two main parameters affect the adsorption properties of activated carbon: textural properties and surface chemistry. Carbon surface chemistry is described by the existence of surface chemical heterogeneity formed by cooperating between carbon atoms and heteroatoms (i.e., oxygen, nitrogen, hydrogen, sulfur, or phosphorus). The origin of material, activation conditions and agents are affecting in species and amount of these elements. The surface functional groups of the heteroatoms and the electron delocalization from carbon atoms are influential to the acid-base nature of carbon surfaces.

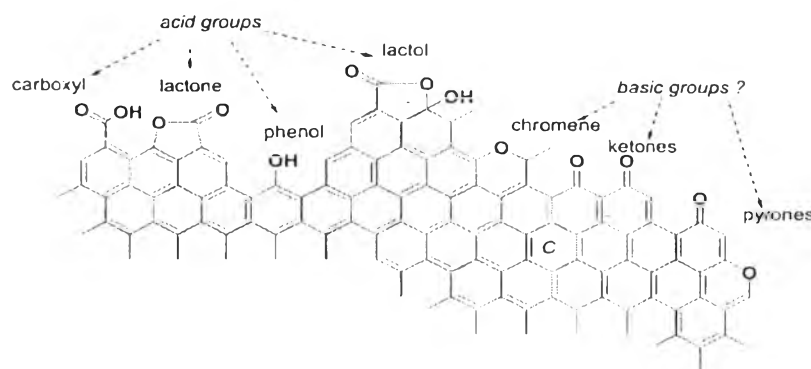


Figure 2.9 Oxygen containing functionalities (acidic and basic surface) of carbon precursor (Montes-Morán *et al.*, 2004).

2.7.1 Acidic Surfaces

The oxygen is the most significant heteroatom which is formed a covalent bond with carbon to create oxygen containing functional groups. These oxygen containing groups (mostly exist on the external surface and the edge of the basal plane) play an important role of the carbon properties (i.e., hydrophobicity, surface charge). Figure 2.9 illustrates various possible oxygen containing functionalities on carbon surface including carboxylic, lactone, phenol, pyrone, chromene, and quinone groups. The derivative formed of carboxylic groups such as anhydride can also present in the carbon surface. The oxygen containing functional groups of carbon surface may be categorized to acidic, basic and neutral. Surface acidity of carbon usually originated from carboxyl, lactone, or phenol. The oxygen functional groups can be introduced into the surface of carbon by oxidation process. There are two types of oxidizing agents used to activate carbon surface: oxidation with gases and liquids. In the gas phase, the oxygen containing functionalities are created mainly hydroxyl and carbonyl. The strong acidic groups such as carboxylic can be formed by oxidation with gases at low temperature while weak acid groups such as phenolic can be formed at high temperature. For the liquid phase oxidations, a higher quantity of oxygen functional groups (carboxylic and phenolic hydroxyl) can be formed at the lower level of temperatures compared with that of the oxidation by gases (Shafeeyan *et al.*, 2010).

2.7.2 Basic Surfaces

The basic functional groups of carbon surface (e.g., nitrogen containing functionalities) and π -electrons present on the basal planes contribute to basicity of activated carbon. The oxygen containing functionalities, including chromene, ketone, and pyrone have been proposed to contribute to basic properties of carbon surface. Nevertheless, the basicity of carbon surface generally occurs by the delocalization of π -electrons on the basal planes.

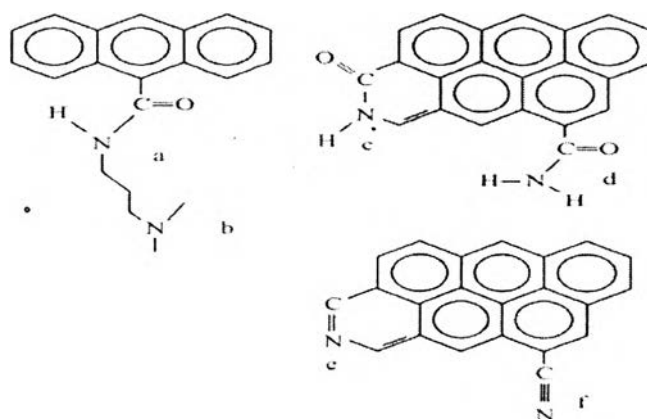


Figure 2.10 Nitrogen containing functionalities of carbon precursor. (a) and (d) amide groups, (b) tertiary amine, (c) lactam, (e) pyridine-pyrrole-like, (f) nitrile (Daud, 2010).

Increasing basicity of carbon surface is achieved either by removal of acidic functional groups or replacing acidic functional groups with basic functional groups (i.e., nitrogen containing groups). It has been reported that the ability to capture CO_2 gas can be improved by introducing the nitrogen functionalities to carbon structure. Because of the basic property of nitrogen functionalities, the CO_2 affinity of carbon surface is improved. To incorporate nitrogen functionalities into carbon sorbents, several techniques are employed such as NH_3 heat treatment, impregnation, chemical vapor deposition (CVD) treatment, or preparing activated carbons from N-containing polymers. There are several possible types of nitrogen functionalities on carbon surface, as shown in Figure 2.10, including amide group, lactame group, pyrrolic group, and pyridine-pyrrole-like and nitrile (Daud, 2010).

The summary of the previous works on the nitrogen modification of carbon by various techniques is provided in Table 2.2.

Table 2.2 Summary of the previous works on the nitrogen modification of carbon by various techniques

Adsorbent	Treatment Condition	CO ₂ Adsorption (mmol/g sorbent)	Surface Functionality	Reference
Template Carbon from Zeolite (EMC-2)	CH ₃ CN 750 °C/4 hours	4.38 (25 °C)	Pyrrole, Pyridinic-like functionalities	Xia <i>et al.</i> (2011)
Template Carbon from Zeolite (EMC-2)	CH ₃ CN 750 °C/3 hours	4.00 (25 °C)	Pyrrole, Pyridinic-like functionalities	Wang <i>et al.</i> (2012)
Activated Anthracite	PEI 33.5 wt.%	0.6 (75 °C)	Amine groups	Maroto-Valer <i>et al.</i> (2005)
Activated Fly Ash	MEA 39 wt.%	1.56 (30 °C)	Amine groups	Maroto-Valer <i>et al.</i> (2008)
Activated Fly Ash	MDEA 46 wt.%	0.39 (30 °C)	Amine groups	Maroto-Valer <i>et al.</i> (2008)
Activated Fly Ash	DEA 34 wt.%	0.48 (30 °C)	Amine groups	Maroto-Valer <i>et al.</i> (2008)
Commercial AC (Norit CGP)	DETA 39 wt.%	0.91 (25 °C)	Amine groups	Plaza <i>et al.</i> (2007)
Commercial AC (Norit CGP)	PEHA 40 wt.%	1.09 (25 °C)	Amine groups	Plaza <i>et al.</i> (2007)
Commercial AC (Norit CGP)	PEI 43 wt.%	1.11 (25 °C)	Amine groups	Plaza <i>et al.</i> (2007)
Melamine-formaldehyde-resin-derived Carbon	Carbonisation 600 °C/1 hour	2.25 (25 °C)	Pyrrole, Pyridinic-like functionalities	Pevida <i>et al.</i> (2008b)
Chitosan derived Carbon	Activation K ₂ CO ₃ /635 °C/1 hour	3.86 (25 °C)	Pyrrole, Pyridinic-like functionalities	Fan <i>et al.</i> (2013)
MWCNTs	TEPA 30 wt.%	2.97 (25 °C)	Amine groups	Ye <i>et al.</i> (2012)
MWCNT-COOH	APTS 12.50 wt.%	1.71 (60 °C)	Amine groups Amide group	Gui <i>et al.</i> (2013b)

Note: PEI = polyethylenimine.

MEA = monoethanolamine.

MDEA = methyldiethanolamine.

DEA = diethanolamine.

DETA = diethylenetriamine.

PEHA = pentaethylenhexamine.

APTS = 3-aminopropyl-triethoxysilane.

TEPA = tetraethylenepentamine.

2.8 Ammonia Heat Treatment

Ammonia treatment is the suitable method to improve the basicity of activated carbons for increasing CO₂ adsorption capacity. In this process, the surface of carbons is treated under ammonia flow at high temperature. During this process, free radicals such as NH₂, NH, and H are formed from the decomposition of ammonia gas. Then, the nitrogen containing functionalities will be created from the reaction between these free radicals and carbon surface. Moreover, the removal of oxygen containing functionalities during ammonia heat treatment is able to improve the basicity of activated carbons (Shafeeyan *et al.*, 2010).

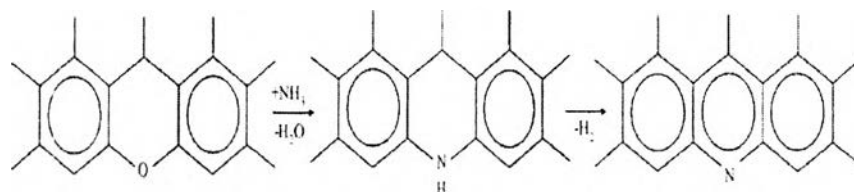
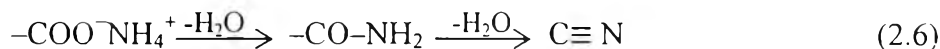


Figure 2.11 The imine and pyridine groups created from the reaction of ether-like oxygen on carbon surface with ammonia (Shafeeyan *et al.*, 2010).

During ammonia treatment, ammonia can react with carboxylic group on the carbon surface to create ammonium salts, then amides and nitriles are formed through dehydration reaction (Equation 2.6).



The formation of amines is able also to easily create from the replacing of OH groups (Equation 2.7).



As shown in Figure 2.11, the ether-like oxygen on carbon surface can be easily substituted with NH to form imine and pyridine functionalities via dehydrogenation reaction.

Many researchers have studied the treatment of activated carbons under ammonia atmosphere. Pevida *et al.* (2008a) improved the selectivity and capacity of activated carbons to adsorb CO₂. In this work, they used two commercial activated carbons (i.e., wood-based granular and peat-based extruded carbon). The activated carbons were modified by ammonia heat treatment at various temperatures from 200 to 800 °C. The results showed that all the treated carbons exhibited higher CO₂ adsorption capacities than corresponding original carbons. The basicity of activated carbons increases due to introducing of nitrogen functionalities onto the carbon surface. At high temperatures (>600 °C), nitrogen was generally incorporated into aromatic rings (e.g., pyrrole and pyridinic-like functionalities), while nitrogen was introduced into more labile surface functional groups (e.g., amide-like functional groups) at lower temperatures (<600 °C). The textural characteristics of the activated carbons was not significantly impacted by ammonia treatment. Plaza *et al.* (2009a) prepared adsorbents from olive stones using two different methods namely CO₂ activation and ammonia heat treatment. The ammonia treatment was performed at various temperatures ranging from 400 to 900 °C. The results indicated that these two methods are appropriate techniques used to develop the activated carbons with a large CO₂ capture capacity, comparable to that of commercial activated carbons. They found that the ammonia treatment at 800 °C exhibited highest CO₂ uptake and highest amount of nitrogen incorporation. The aminated samples exhibited CO₂ capture capacities up to 8.6 wt.% at 25 °C and 2.6 wt.% at 100 °C. Later, Plaza *et al.* (2009b) found that the amination (treated under pure ammonia) of activated carbon from almond shells introduced nitrogen into the carbon surface, up to a 5 wt.%, without out a pre-oxidation treatment. The aminated carbons exhibited remarkably higher capacities than the original carbon, and higher than the activated carbons.

Although ammonia treatment has shown to be an effective treatment at higher temperature (Pevida *et al.*, 2008a; Plaza *et al.*, 2009a; Plaza *et al.*, 2009b), a previous study by Przepiórski *et al.* (2004) reported the highest CO₂ adsorption capacity of a commercial activated carbon (CWZ-35) after ammonia treatment at 400 °C. They explained that the lower CO₂ uptake of samples treated above 400 °C was probably related to blocking of micropores by nitrogen containing functionalities or pore size alteration. The effects of ammonia treatment on adsorption capacities of

activated carbon toward phenol were also investigated (Przepiórski, 2006). They treated commercial activated carbons CWZ-series (CWZ-11, CWZ-30, and CWZ-35) with ammonia gas at various temperatures from 400 to 800 °C. They pointed out that all of the samples treated with ammonia resulted in higher phenol adsorption capacities than untreated carbons. The treated carbons exhibited highest phenol adsorption capacity at treatment temperature of 700 °C. The mainly enhancement of treated carbons was probably related to incorporating of nitrogen functionalities onto carbon surface. This work confirms that the ammonia treatment can improve the basicity of activated carbons and consequent enhancement affinity towards acidic substances such as CO₂ and C₆H₅OH.

The summary of the previous works on the modification of carbon by ammonia treatment technique is provided in Table 2.3.

Table 2.3 Summary of the previous works on the modification of carbon by ammonia treatment technique

Adsorbent	Treatment Condition	CO ₂ Adsorption (mmol/g sorbent)	Surface Functionality	Reference
Commercial AC (Norit R)	NH ₃ 800 °C/2 hours	2.18 (25 °C)	Pyrrole, Pyridinic-like functionalities	Pevida <i>et al.</i> (2008a)
Olive-stone-based AC	NH ₃ 800 °C/2 hours	1.95 (25 °C)	Pyrrole, Pyridinic-like functionalities	Plaza <i>et al.</i> (2009a)
Almond-shells-based AC	NH ₃ 800 °C/3 hours	2.20 (25 °C)	Pyrrole, Pyridinic-like functionalities	Plaza <i>et al.</i> (2009b)
Commercial AC (CWZ-35)	NH ₃ 400 °C/2 hours	1.52 (36 °C)	-	Przepiórski <i>et al.</i> (2004)
Activated Anthracite	NH ₃ 650 °C/1.5 hours	0.6 (75 °C)	Pyrrole, Pyridinic-like functionalities	Maroto-Valer <i>et al.</i> (2005)
Almond-shells-based AC	NH ₃ +Air 300 °C/2 hours	1.61 (25 °C)	Amide, Imide, Lactam groups	Plaza <i>et al.</i> (2009b)
Commercial AC (Norit R)	NH ₃ +Air 300 °C/2 hours	2.14 (25 °C)	Nitrile, Amide-like functionalities	Plaza <i>et al.</i> (2010)

2.9 Oxidation Treatment

Oxidation treatment is the conventional process used to modify or pre-modify surface chemistry of carbon adsorbents by introducing the surface oxygen functionalities onto carbon surface. This reaction possibly takes place at the aliphatic side chains or at defect parts of the carbon surface since these parts are very sensitive to the oxidation treatment. The oxidation typically increases acidity on carbon surface and decreases basicity on carbon surface. However, oxidation can cause changes in the textural properties of the carbon materials. Oxidation treatment can be classified into dry oxidation and wet oxidation. Dry oxidation can be carried out by heating activated carbon at elevated temperature in the environment of oxidizing gases (e.g., steam, CO₂, O₂, and O₃) while wet oxidation is the process by which activated carbon reacts with the solution of oxidizing agents (e.g., H₂O₂, HNO₃, H₂SO₄, (NH₄)₂S₂O₈) under mild reaction conditions (Daud, 2010).

For wet oxidation, HNO₃ is one of the most used oxidizing agents since oxidizing properties can be handled by concentration of oxidizing agent and the temperature of reaction. The type of oxidizing agents, the conditions of oxidation, and the characteristic of starting carbon can affect the increasing/decreasing of pore volume and/or surface area of activated carbons. The types and quantities of oxygen containing functionalities formed on the carbon surface are determined by almost all of the parameters causing the changes of textural properties.

Many researchers have investigated the oxidation treatment of activated carbons. Jaramillo *et al.* (2010) studied the effects of two different oxidation techniques (i.e., dry and wet processes) on the surface chemistry and textural property of cherry-stones-base activated carbon. The activated carbons were oxidized by using O₂, O₃, HNO₃ and H₂O₂. They found that the surface chemistry and textural property of oxidized samples were altered by both oxidation techniques. All of the oxidized samples led to the increase in the quantity of oxygen groups on its surface. HNO₃ and O₃ were the most effective oxidizing agents in terms of creating the acidic oxygen groups on the surface. However, the decreasing microporosity and content of basic groups were observed, especially for HNO₃. The mesoporosity remarkably increases and macroporosity remains unchanged. Plaza *et al.* (2013) investigated the

effects of dry and wet oxidation on the CO₂ capture performance of phenolic resin carbon. The phenolic resin carbons were oxidized by using (NH₄)₂S₂O₈, HNO₃ and air. The results showed that the oxidation treatments increased the large amount of the oxygen of the phenolic resin carbon from 1.41 up to 15.90 wt.%. They also pointed out that liquid phase oxidation introduced a higher quantity of oxygen than the gas phase oxidation. The liquid phase oxidized sample contained mainly carboxylic groups, while the gas phase oxidized sample contained mainly ether and carbonyl functionalities. The pore volume was decreased by the liquid phase oxidation, while this is slightly increased by gas phase oxidation. It was reported that liquid phase oxidized sample exhibited highest CO₂ adsorption capacity owing to the most acidic carbon surface. In addition, the oxidized samples can be easily regenerated due to the physisorption process. Ania *et al.* (2002) found that the oxidation affected both of the surface chemistry and texture property of activated carbons. The activated carbons were oxidized by using HNO₃ at various concentrations (1 %, 20 % and 60 %, v/v). In this case, they found that oxidation with low concentration of HNO₃ developed microporosity and mesoporosity of the activated carbons. Shafeeyan *et al.* (2011) successfully enhanced the CO₂ adsorption capacity of the starting carbons by oxidizing with air before ammonia treatment. Two different approaches were compared, including ammonia heat treatment without pre-oxidation and ammonia heat treatment with pre-oxidation. For ammonia treatments, the reactions were performed at 400 °C and 800 °C. The results showed that both approaches, especially the ammonia treatment with pre-oxidation increased CO₂ adsorption capacity of the starting carbons. This was basically due to the increasing of microporosity and basic character of carbon surface. It was found that the oxidation followed by heat treatment with ammonia at 800 °C exhibited higher CO₂ adsorption capacity at higher temperatures. From the results, it can be indicated that the reactivity of free radicals for forming the formation of nitrogen containing functionalities can be increased by introducing oxygen containing functionalities. Recently, Surin (2013) studied the effect of oxidation on the CO₂ capture capacity of activated carbon. The carbon surface was modified by oxidizing with nitric acid (different concentration and duration) and impregnation with branched polyethylenimine (PEI). The different approaches were compared, including oxidation treatment, impregnation with PEI without preliminary ox-

idation, and impregnation with PEI with preliminary oxidation. In this case, it was found that the carbons impregnated with PEI without preliminary oxidation and with preliminary oxidation resulted in the lower CO₂ adsorption capacities than the starting carbon. This was due to the pore blocking. However, the oxidized carbons exhibited higher CO₂ adsorption capacity than untreated carbon. The enhancement of oxidized carbons was probably due to the introduction of hydroxyl, carbonyl and carboxyl functionalities on carbon surface.

The Summary of the previous works on the oxidation of carbon is provided in Table 2.4.

Table 2.4 Summary of the previous works on the oxidation of carbon

Adsorbent	Condition	Surface Functionality	Application/Remark	Reference
Cherry-stones - based AC	O ₂ (air)/300 °C /24 hours	Carbonyl, Phenols	Increase the content of acidic oxygen surface	Jaramillo <i>et al.</i> (2010)
Cherry-stones - based AC	O ₃ /100 °C/1 hour	Carboxyl, Lactone, Phenols	Increase in the quantity of acidic oxygen surface	Jaramillo <i>et al.</i> (2010)
Cherry-stones - based AC	HNO ₃ /90-95 °C/10 hours	Carboxyl, Lactone	Increase in the quantity of acidic oxygen surface	Jaramillo <i>et al.</i> (2010)
Phenolic-resin-derived Carbon	O ₂ (air)/420 °C /3 hours	Ether, Carbonyl	Enhancement of CO ₂ adsorption	Plaza <i>et al.</i> (2013)
Phenolic-resin-derived Carbon	HNO ₃ /16 M /90 °C/24 hours	Carboxyl, Lactone, Phenols	Enhancement of CO ₂ adsorption	Plaza <i>et al.</i> (2013)
Phenolic-resin-derived Carbon	(NH ₄) ₂ S ₂ O ₈ +1 M H ₂ SO ₄ /25 °C/24 hours	Carboxyl, Lactone, Phenols	Enhancement of CO ₂ adsorption	Plaza <i>et al.</i> (2013)
Commercial-palm-shell-based GAC	O ₂ (air)/400 °C /2.5 hours		Enhance the nitrogen incorporation during NH ₃ treatment	Shafeeyan <i>et al.</i> (2011)
Commercial AC (Merck)	HNO ₃ /11.20 M/80 °C/12 hours	Carboxyl, Ketone	A slight increase in surface area and micropore volume	Macias-García <i>et al.</i> (2006)
Coconut-shell-based AC	HCl/11.81 M /25 °C/48 hours	Carbonyl, Phenols	Enhance the dispersion of copper precursor on AC	Tseng, (2006)

Table 2.4 Summary of the previous works on the oxidation of carbon (cont'd)

Adsorbent	Condition	Surface Functionality	Application/Remark	Reference
Coconut-shell-based AC	HNO ₃ /8.17 M /25 °C/48 hours	Carboxyl, Anhydride, Lactone	Enhance the dispersion of copper precursor on AC	Tseng, (2006)
Commercial GAC (Calgon BPL)	HCl/2 M /25 °C/24 hours	Carbonyl, Phenols	Dispersion and activity of copper on AC for N ₂ O and NO reduction	Zhu <i>et al.</i> (1999)
Commercial GAC (Calgon BPL)	HF/2 M /25 °C/24 hours	-	Dispersion and activity of copper on AC for N ₂ O and NO reduction	Zhu <i>et al.</i> (1999)
Commercial GAC (Calgon BPL)	HNO ₃ /2 M /25 °C/24 hours	Carboxyl, Lactone, Phenols	Dispersion and activity of copper on AC for N ₂ O and NO reduction	Zhu <i>et al.</i> (1999)
Nut-shell-based AC	HNO ₃ +H ₂ SO ₄ /25 °C/24 hours	Nitro groups	Removal of formaldehyde	Tanada <i>et al.</i> (1999)
Olive-stones-based AC	(NH ₄) ₂ S ₂ O ₈ in 1 M H ₂ SO ₄ /25 °C/48 hours	Carboxyl, Lactone, Phenols	Introduce oxygen surface complexes	Moreno-Castilla <i>et al.</i> (2000)
Olive-stones-based AC	H ₂ O ₂ /9.8 M /25 °C/48 hours	Carboxyl, Lactone, Phenols	Introduce oxygen surface complexes	Moreno-Castilla <i>et al.</i> (2000)
Olive-stones-based AC	HNO ₃ /13.9 M /80 °C/boiled until dryness	Carboxyl, Lactone, Phenols	Introduce oxygen surface complexes	Moreno-Castilla <i>et al.</i> (2000)
MWCNTs	HNO ₃ +H ₂ SO ₄ 5 M/100 °C/3 hours	Carboxyl, Hydroxyl	Introduce oxygen surface complexes	Gui <i>et al.</i> (2013a)
MWCNTs	HNO ₃ +H ₂ SO ₄ 90 °C/1 hours	Carboxyl, Hydroxyl	Introduce oxygen surface complexes	Khalili <i>et al.</i> (2013)
MWCNTs	HNO ₃ /14.5 M/20, 50, 70, 90, 110, 120 °C/8 hours	Carboxyl, Hydroxyl	Introduce oxygen surface complexes	Gerber <i>et al.</i> (2011)
MWCNTs	HNO ₃ /15.2 M/120 °C/50 hours	Carboxyl, Hydroxyl	Introduce oxygen surface complexes	Stobinski <i>et al.</i> (2010)
MWCNTs	HNO ₃ /14.5 M/48 hours	Carboxyl, Hydroxyl	Introduce oxygen surface complexes	Datsyuk <i>et al.</i> (2008)
MWCNTs	H ₂ SO ₄ +H ₂ O ₂ /5 hours	Carboxyl, Hydroxyl	Introduce oxygen surface complexes	Datsyuk <i>et al.</i> (2008)
MWCNTs	H ₂ O ₂ +NH ₄ OH 80 °C/5 hours	Carboxyl, Hydroxyl	Introduce oxygen surface complexes	Datsyuk <i>et al.</i> (2008)

2.10 Research Motivation

A number of researchers have studied enhancement in adsorption of CO₂ on modified AC. The ability to adsorb CO₂ of AC was strongly affected by the surface chemical properties. Previously, many authors reported that ammonia heat treatment introduced basic nitrogen groups (Lewis base) onto the carbon surface and thus improved the interaction between the adsorbent and CO₂ gas (Lewis acid). Therefore, it is of interest to modify the carbon surface to have high affinity toward nitrogen. Since nitrogen compounds are Lewis base, Lewis acid components such as oxygen containing functionalities on carbon surface can help increase the amount of nitrogen functionalities on its surface. It is expected that oxidation of carbon surface prior to ammonia treatment would increase the basic nitrogen functionalities on the carbon surface and enhance CO₂ adsorption.

In this work, two types of carbon are employed: commercial activated carbon and the CNS. According to the literature review, CNS, a new carbon material, has been applied in a wide range of applications such as energy storage, adsorbents, nano-additives, purification, and novel catalysts supports. However, the CO₂ adsorption by CNS has not been investigated in the previous studies. Since nitrogen-doped CNS can be synthesized by selecting appropriate carbon precursors, therefore, it is of interest to apply the CNS as a CO₂ adsorbent and compare with the commercial activated carbon.

2.11 Objectives

1. To study the potential of using CNS as CO₂ adsorbents.
2. To modify the surface chemistry of activated carbon via different approaches of oxidation and ammonia treatment.
3. To study the effect of surface treatments on the treated adsorbents in terms of chemical and textural characteristics and their effect toward CO₂ capture performance.

2.12 Scope of Research

The scope of this research covered as follows.

Scope of objective 1:

CNSs received from the Green Mobility Collaborative Research Center, Nagoya University were synthesized from benzene and pyridine, designated as benzene-derived carbon nano spheres (CB), and pyridine-derived carbon nano spheres (CP). These CNS were carbonized and activated with CO₂ to obtain activated carbon nano spheres. It is noted that the synthesis of CNS is outside the scope of this work.

Scope of objective 2:

In this work, commercial coconut-based activated carbon (AC), activated benzene-derived carbon nano spheres (ACB), and activated pyridine-derived carbon nano spheres (ACP) were applied as the CO₂ adsorbents.

The different conditions and methods for modifying surface chemistry of activated carbon were employed: oxidative treatment, ammonia heat treatment and oxidation followed by ammonia heat treatment. A first series of adsorbents was prepared by oxidation of activated carbon with HNO₃ for various durations. A second series of adsorbents were prepared by heat treatment of activated carbon with ammonia gas at different temperatures. A third series of adsorbents were obtained by heat treating the oxidized carbons with ammonia gas.

Scope of objective 3:

The effect of different treatment approaches were investigated and compared. The surface properties of treated sorbents were characterized through texture and chemical characteristics. The texture properties were characterized by surface area analyzer in order to measure the surface area, pore volume and pore size. The chemical characteristics of adsorbents were characterized in terms of chemical composition and surface chemistry. Ultimate analysis was used to determine the chemical composition and the surface chemistry were investigated by x-ray photoelectron spectroscopy. A gravimetric technique was employed to evaluate the CO₂ adsorption capacity of the adsorbents using a thermogravimetric analyzer.