CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Natural Gas

Natural gas is a hydrocarbon gas mixture consisting primarily of methane, but commonly includes varied amounts of other higher alkanes and even a lesser percentage of carbon dioxide, nitrogen, and hydrogen sulfide, depending on the gas fields. Natural gas is traditionally consumed in the residential and commercial sectors, mostly for heating, in the industrial sectors such as the manufacture of plastics and other commercially important organic chemicals, and in the power sector. Figure 2.1 shows the world natural gas consumption which industry sector is the largest user of natural gas with around 43% of global gas consumption. A more recent and rapidly developing sector is that of transport, which is expected to represent 9% of incremental demand over 2012 to 2018 (www.iea.org). From Table 2.1, it shows typical composition of natural gas, which has methane as a major component followed by higher molecular weight hydrocarbons, CO_2, N_2, and other trace gases.

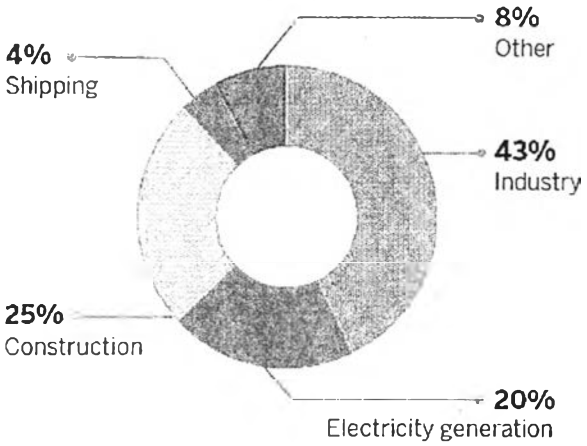

Figure 2.1 Global natural gas consumption in 2012 (www.usa.chinadaily.com).

Table 2.1 Typical composition of natural gas (www.naturalgas.org)

Constituent	Composition (mole %)
Methane, CH_4	70-90
Higher molecular weight hydrocarbons	0-20
Carbon dioxide, CO_2	0-8
Other gases (O_2, S, N_2, and etc.)	trace

Commercial natural gas is a heterogeneous mixture. The composition of natural gas varies by the location of extraction and by the season, where the gas is extracted. In addition, future variations in the concentration profiles can be caused by processing the gas before transmission and by the mixing of different gases during transmission (Brady *et al.*, 1996).

Kavalov *et al.* (2011) reviewed the oil and natural gas resources and analyzed the economical technology of natural gas application as an energy source for road transport in the European Union (EU). The results indicated three major advantages of natural gas-based fuels over conventional and other alternative fuels:

1. Security of energy supply: the natural gas reserve is bigger than oil reserve; therefore, natural gas is more abundant and accessible.

2. Diversity of energy supply: the reservoir of natural gas has many geological.

3. A multi-optional fuel technology

Over these advantages, natural gas-based fuels have also many strong points, which are of interest to the automotive fuel market. For example, the cost is less than conventional and other alternative fuels. Natural gas-based fuel is good environmentally because it results in the reduction of greenhouse gas emissions and has significant potential to improve local air quality. Compared to conventional fuels, most natural gas-derived fuels demonstrate acceptable performance when employed in current internal combustion engine due to it has fewer impurities and less chemically complex that results in less pollution. Table 2.2 shows comparison of carbon dioxide emission from fossil fuels, which natural gas is less emission of all fossil fuels.

Table 2.2 Comparison of carbon dioxide emission from fossil fuels (www.aga.org)

	Carbon dioxide emission (lb of emission/billion BTU of energy)
Natural gas	117,000
Oil	164,000
Coal	208,000

American Gas Association (AGA) reported that natural gas is helping the United State develop clean alternative energy sources in various ways such as used to make fertilizer for ethanol, used to make methane for hydrogen, used to generate clean power for electric utilities, and used as a raw material that go into lightweight cars, wind power blades, solar panels, and energy-efficient materials (www.aga.org).

At present, there is an important drawback of using natural gas in vehicles. Natural gas has lower energy density than conventional and other alternative fuels at ambient conditions, which causes the driving range of natural gas based-fuel less than conventional and other alternative fuels. Therefore, it requires larger volume of the natural gas-based fuel than the others to drive in the same distance. According to the volumetric basis and the limitation of the car space, a storage technology requires a higher energy density.

2.2 Natural Gas Storage

Natural gas storage is great to many industries, such as natural gas vehicles, because of its inherent clean burning characteristics. For using natural gas as a fuel, natural gas storage plays an important role to safely and efficiently store natural gas. Since natural gas composes mainly of methane, which is a small molecule, it is hard to store natural gas in a high density. Researchers have developed technologies to carry high amount of gas for transportation. The following are way to store it.

2.2.1 Liquefied Natural Gas (LNG)

LNG is another known gas storage method. Natural gas is liquefied under pressure of 10-20 bars at -161.5 °C; it is a clear liquid taking up 600 times less space than the corresponding gas and enabling practical transportation by specially designed ships. Two basic types of LNG carrier ships are shown in Figure 2.2.

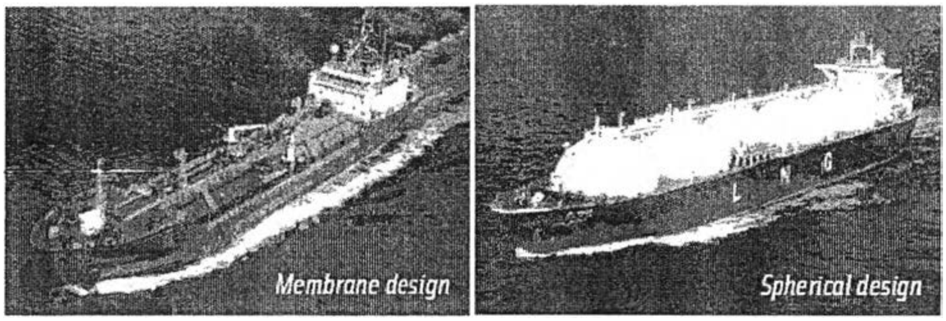

Figure 2.2 The two basic types of LNG carrier ships have distinctive shapes (Society of International Gas Tanker & Terminal Operators, 2004).

LNG requires the use of complex and expensive liquefaction equipment in the processes, thermos-like tank and significant energy consumption (25-35% of the original energy gas content) for the liquefaction and degasification. LNG storage tank can be in cylindrical or spherical shape. Even this technology is used in marine transportation; it is not yet mature enough for massive use in vehicles. On-board tank for small vehicle costs almost as much as for a heavy vehicle and has much lower net volumetric storage efficiency LNG vehicle refueling infrastructure costs even more than CNG (www.ge.com).

2.2.2 Compressed Natural Gas (CNG)

For CNG, essentially methane is stored at a high pressure, usually 20-25 MPa. Colorless, odorless, non-carcinogenic, and non-toxic, CNG has a limited flammability range and is lighter than air. CNG is increasingly becoming popular with automobile owners, commonly referred to as the green fuel because of its lead free characteristic; it reduces harmful emissions and is non-corrosive. CNG for vehicles require a greater amount of space for fuel storage the conventional gasoline powered vehicles. Since CNG demands very robust specially-designed cylindrical tanks, which use a lot of space and are heavy. A massive implementation of CNG vehicles in most markets is restrained by the need to invest in very expensive refueling infrastructure, and the inconvenience and additional costs of on-board CNG tanks. CNG vehicle refueling infrastructures deployment and operation is associated with the following problems:

1. The capital investment for the construction of a CNG filling station is several times bigger than for a petrol/diesel station and the operating cost of a CNG station requires high energy consumption and very expensive maintenance. So the price of CNG stations substantially increases natural gas cost for the vehicle user.

2. The classic market failure case: gas companies do not invest in costly stations network because there are not enough NGV users. Users do not buy NGVs due to a sparse stations network.

On-board tanks of CNG vehicles involve some functional problems beside the substantial additional cost. CNG tanks generally: occupy twice the volume of petrol/diesel tanks (about 100 liters of geometric volume) and allow for one-half the driving range of petrol fueled vehicle (about 300 km). Thus, the low energy density of CNG storage limits natural gas fueling application for many potential users. This limit is especially important for vehicles with high driving range. Since fuel comprises a larger part of the cost of their transportation, they could theoretically save more fuel costs using natural gas (Ginzburg, 2006).

2.2.3 Adsorbed Natural Gas (ANG)

ANG is a technology, in which natural gas is adsorbed by a porous adsorbent material at relatively low pressures, 500 to 600 psig. When a natural gas storage vessel is filled with a suitable adsorbent material, the gas capacity will be greater than that of the same vessel without the adsorbent, when filled to the same pressure. When compared to CNG, ANG can store half two-thirds the amount of gas, but at one-sixth the pressure. The capital and operating cost of compression and refueling equipment also have the potential to be lower than current CNG equipment, a significant benefit for infrastructure. Moreover, the global warming potential for ANG is also reduced because less energy is required to compress natural gas, resulting in fewer carbon dioxide emissions. From a safety and utilization perspective, lower ANG pressure may be more readily accepted compared to CNG. In this application, the maximum gas storage density becomes the ultimate requirement, in order to store and deliver the maximum gas volume per volume of storage vessel (v/v). Depending on the adsorbent characteristics, the volumetric adsorption capacity and delivery would be different as well as the volumetric energy density (Namvar-Asl *et al.*, 2008). ANG technology allows storing large amounts of natural gas in a relatively thin-walled tank filled with adsorbent and refueling the tank using simple and cheap equipment or sometimes refueling directly from natural gas pipelines. The addition of a microporous material into the tank, such as activated carbon, makes it possible to do one of two things: (i) store a larger volume of natural gas in the same container at the same pressure or (ii) store the same volume of natural gas in the container at a lower pressure. Since activated carbon has a very large surface area because of its porous nature, so it gives the ability to adsorb large quantities of natural gas (www.energtek.com).

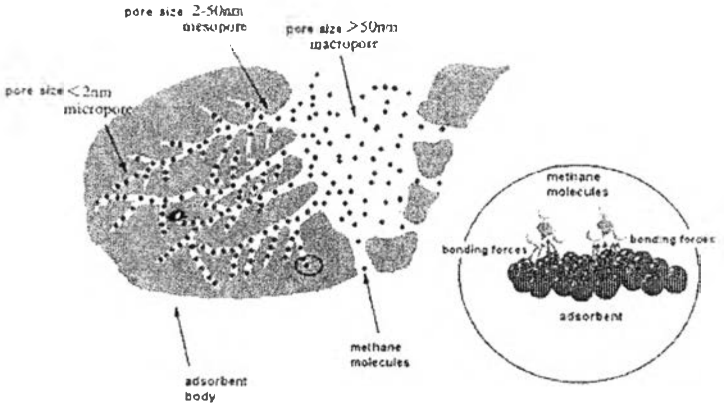

Figure 2.3 Adsorption of methane molecules on the activated carbon adsorbent in micropore, mesopore, and macropore structures (www.greencar.com).

Figure 2.3 shows the adsorption of methane molecules on the activated carbon adsorbent in micropore (<2 nm), mesopore (2-50 nm), and macropore (>50 nm) structures. Micropore structure is important for methane storage because it gives the highest capacity of adsorbed methane. It can be said that a natural gas storage tank with an adsorbent inside has higher capacity of adsorbed natural gas than that of a storage tank without an adsorbent at the same pressure and temperature.

ANG storage has many advantages compared to CNG storage such as (www.glnoble-denton.com): .

1. Space efficient, flexible storage: ANG storage can use more flexible shape and lighter storage systems than CNG cylinders. Hence, ANG storage has higher space efficiency than traditional CNG storage.

2. Increased equivalent capacity: ANG storage units can store much more natural gas than an equivalent storage cylinder with CNG at the same pressure that is typically more than 25%.

3. Safety benefits: lower fuelling pressure coupled with gas storage on a carbon rather than in free space confers real safety benefits in most instances.

4. Reduction of infrastructure costs: reduced pressure of ANG allows for reduction up to 50% in infrastructure and operating costs for filling stations.

5. Flexibility in filling options: a wide range of filling options for ANG can be employed; fixed filling stations, mobile filling stations, home based refueling, and cartridge refilling system.

The development of ANG automotive fuel system has been done by several organizations during past decades all over the world such as Atlanta Gas Light Research Group, Brazilian Gas Technology Center, HONDA Research Company, EU-FP5 funded project, Oak Ridge National Lab, Osaka Gas Company, University of Alicante, and University of Petroleum (www.glnoble-denton.com). The improvement of ANG storage can be described in the short conclusion as the followings:

1. Maximum volumetric density reached up to the present is 150 v/v with prohibitively high cost of adsorbent.

2. Adsorbents with more or less acceptable cost provide 120-130 v/v.

3. All existing tanks are based on multi-cell concept that requires an adsorbent block with high mechanical strength.

4. The volume of tank delivery is 15% less than tank uptake.

5. All tanks made up to the present do not include any active thermal management systems.

6. High-pressure ANG storage was researched much less than low-pressure ANG storage.

7. The combination of adsorption and low-temperature storage has almost never been researched.

From above conclusions, the development of ANG storage technology still has some limitations. which are reasons why ANG storage cannot be used in commercialization. Nowadays, some researchers try to research and develop natural gas storage system for automotive applications under the idea of improvement CNG by coupling with ANG method. They hope that the addition of adsorbent materials, like activated carbon, molecular sieve, and metal organic framework, inside the vehicle CNG cylinder tank will give higher storage capacity of natural gas at the same pressure operation to increase a driving range of natural gas vehicles or the same amount storage capacity of natural gas at lower pressure operation to reduce an operating cost (www.glnoble-denton.com).

2.3 Adsorption

Adsorption is present in many natural physical, biological, and chemical systems, and is widely used in industrial applications such as gas separation, transportation, and storage. Adsorption is the adhesion of atoms, ions, or molecules from a gas, liquid, or dissolved solid to a surface. This process creates a film of the adsorbate on the surface of the adsorbent. Adsorption is an exothermal phenomenon, while desorption, the reverse process of adsorption, is an endothermic phenomenon. Adsorption forces can be categorized into two main groups: (i) van der Waals forces (physisorption), directly correlated with adsorbate molecular polarizability and (ii) electrostatic forces such as polarization forces, surface field-molecular dipole interactions and surface field gradient-molecular quadrupole interactions. Adsorption is usually promoted by synergies among these different kinds of interactions. For example, carbon dioxide and nitrogen adsorption on polar surfaces (e.g. zeolites) is mainly promoted by surface field gradient-molecular quadrupole interactions. Conversely, adsorption of large non-polar molecules (e.g. hydrocarbons) is essentially due to their molecular polarizability. In general, adsorbents operating exclusively by van der Waals forces (e.g. most activated carbons) are referred as hydrophobic (Tagliabue *et al.*, 2009). Figure 2.4 shows the example of adsorption for cleaning raw water; powdered activated carbon has innumerable microporosity and offensive smell and taste in raw water of the water supply are adsorbed in the surface of microporosity, and then they are removed from the raw water.

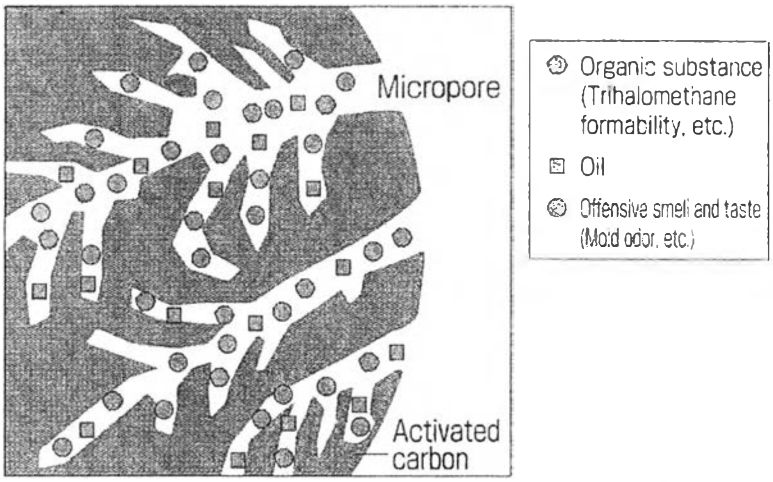

Figure 2.4 Offensive smell and taste in raw water of the water supply are adsorbed in the surface of activated carbon (www.kobelco-eco.co.jp).

The essential requirement of adsorption processes is an adsorbent that preferentially adsorbs a family of related components from a mixed feed. Adsorbent selectivity may depend on difference in adsorption at equilibrium (equilibrium selectivity or thermodynamic selectivity) or on a difference in adsorption rates (kinetic selectivity). Kinetic selectivity is possible when a great difference among adsorption/desorption rates of different components exists. The concept of adsorption equilibrium is deeply involved in the evaluation of adsorbent specific capacity, selectivity and regenerability (working capacity). For the same adsorbent, adsorbed and desorbed amounts can differ significantly from different conditions of pressures and temperatures (Tagliabue *et al.*, 2009).

Heat of adsorption is a measure of the strength of interactions between adsorbate and adsorbent. The heat of adsorption is extracted from the isotherm data, which is functional for the reproduction of thermal properties during charging and discharging of the adsorptive gas storage system (Rahman *et al.*, 2010). Physisorption is based on attraction forces among the solid phase and the species constituting the gas phase, with relatively low heat of adsorption.

2.4 Adsorption Isotherms

When a gas contact with a solid surface, molecules of the gas will adsorb to the surface in quantities that are a function of their partial pressure in the solid. The measurement of the amount of gas adsorbed over a range of partial pressures at a single temperature results in a graph known as an adsorption isotherm. Adsorption isotherm in physical chemistry is generally expressed as concentration of adsorbed phase (or amount of gas adsorbed) per unit mass of adsorbent. It is a function of both pressure and temperature, besides the nature of the gas. The data may be represented as isotherms, V (P), at constant T, isobars, V (T) at constant P, or isosteres, P (T) at constant V. Among them, isotherms are the closest one to direct experiments. Measurements of pure component isotherms can easily be conducted and are generally available for adsorption design study. Meanwhile the investigation of multi-component isotherms often hit a difficulty since the experimental data over design ranges of pressure, temperature, and composition are impractically measurable. Therefore, many literature models are available to predict the mixture behaviors from pure component isotherm data (Jeong *et al.*, 2007).

2.4.1 IUPAC Classification of Adsorption Isotherms

It has many different types of isotherms and these isotherms can have different shapes depending on the type of adsorbent, the type of adsorbate, and intermolecular interactions between the gas and the surface of solid. The first systematic attempt to interpret adsorption isotherms for solid-gas equilibrium was introduced by Brunauer, Deming, Deming, and Teller (BDDT) in 1940. These authors classified isotherms into five types. The BDDT classification has become the core of the modem IUPAC classification of adsorption isotherms; these BDDT isotherms and an additional one introduced much later by Sing, which completes the IUPAC classification. In physical adsorption, adsorption isotherms can be classified as one of six types, as shown in Table 2.3 and Figure 2.5, respectively.

Type I isotherms are observed for the adsorption of gases on microporous solid, whose pore sizes are not much larger than the molecular diameter of the adsorbate and the adsorption is limited to the completion of a single monolayer of adsorbate at the adsorbent surface. Type II indicates the multi-layer formation after completion of the monolayer. Type III is obtained when the amount of gas adsorbed increase without limit as its relative saturation approaches unity. Types IV and V represent adsorption isotherms with hysteresis. Finally, Type VI has many steps (www.separationprocesses.com).

Table 2.3 Features of adsorption isotherms for all six types (Soo-Jin and Min-Kang, 2011)

Type	Interaction between sample surface and adsorbate	Porosity
I	Relatively strong	Micropores (< 2 nm)
II	Relatively strong	Macropores (> 50 nm)
III	Weak	Macropores (> 50 nm)
IV	Relatively strong	Mesopores (2-50 nm)
V	Weak	Mesopores, Micropores
VI	Relatively strong (sample surface has an even distribution of energy)	Nonporous

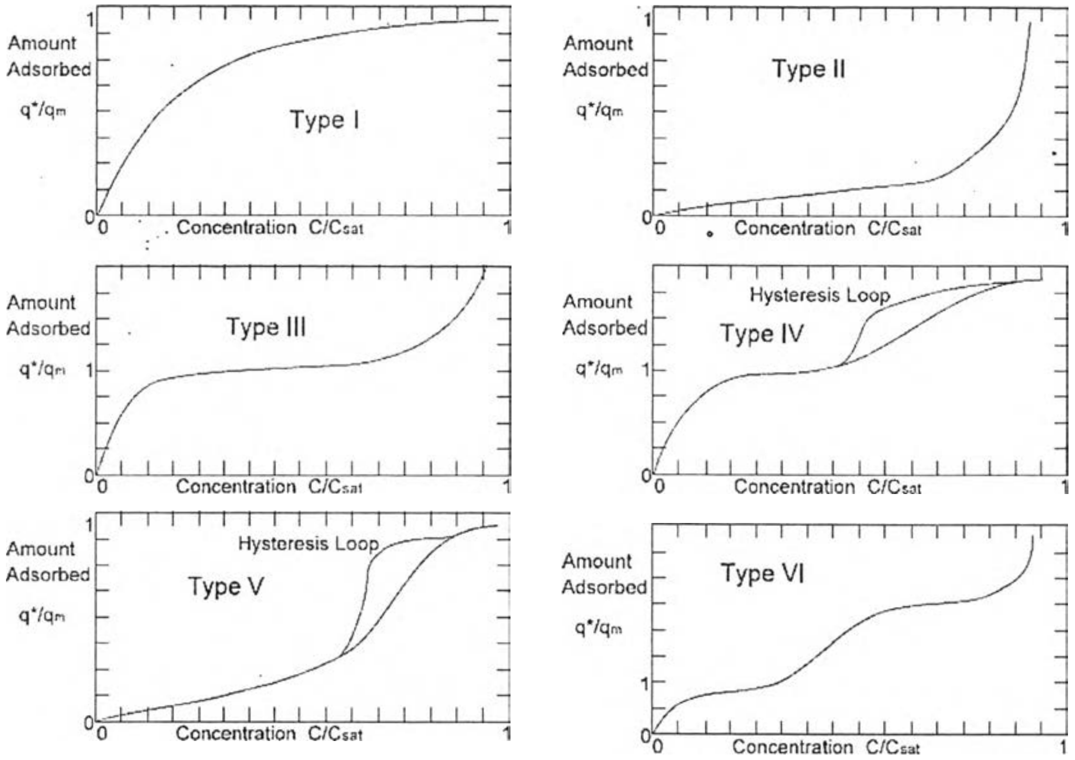

Figure 2.5 IUPAC classification adsorption isotherms (Knaebel, 2011).

The pore size distribution is a related property that indicates the fraction of the space within a particle occupied by macropores, mesopores, and micropores. Figure 2.6 shows the pore size distributions of some common adsorbents. The classification of pores, according to their size, which is recommended by IUPAC are described below:

1. Macropores have a diameter larger than 50 nm. Macropores are so wide that gases adsorb virtually to flat surfaces.

2. Mesopores are in the diameter range of 2-50 nm. Capillary condensation often dominates the filling of mesopores. Below the critical temperature, multilayers arise.

3. Micropores are smaller than 2 nm. In micropores, the structure of the adsorbed fluid is significantly different from its macroscopic bulk structure. Confined liquids are a highly active area of research because of their unique

properties. An important example of microporous materials are zeolites and activated carbon.

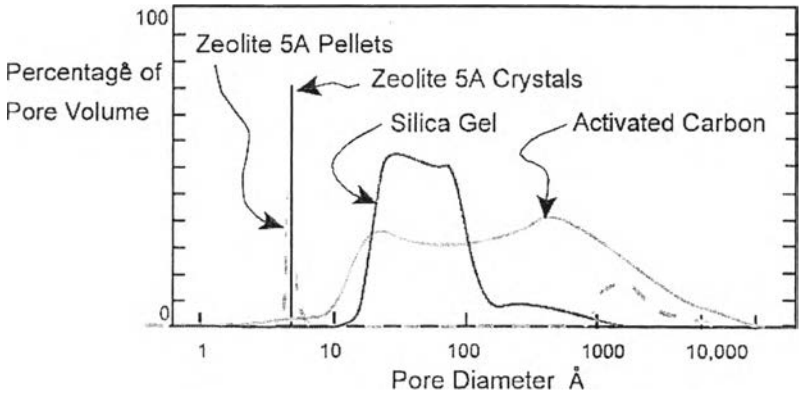

Figure 2.6 Pore size distributions of common classes of adsorbents (Knaebel, 2011).

2.4.2 Measurement of Adsorption Isotherms

The most important attributes of an adsorbent for any application are: capacity, selectivity, regenerability, kinetics, compatibility, and cost. Adsorption capacity is the most important characteristic of an adsorbent, per unit mass (or volume) of the adsorbent. It depends on the fluid phase concentration, the temperature, and other conditions (especially the initial condition of the adsorbent). Several experimental methods have been applied to measure adsorption isotherms. The main problem is to determine the amount adsorbed. Because the adsorbent needs to be regenerated for most commercial applications, adsorption processes are necessarily cyclic (Maglara *et al.*, 1994). A number of cyclic adsorption processes are available, depending on the way the adsorbent is regenerated. These processes have been discussed extensively elsewhere. For the measurement of gas adsorption isotherms, three different methods known as the volumetric method, gravimetric method, and inverse gas chromatography can be used.

2.5 Adsorbents and Activated Carbon

Adsorbents are usually in the form of spheres, pellets, powder, granules, or monoliths. They must have high abrasion resistance, high thermal stability, and small pore diameters, which results in high surface area and high surface capacity for adsorption. The adsorbents must also have a distinct pore structure, which enables fast transport of the gaseous vapors. Most industrial adsorbents fall into one of three classes: (i) oxygen-containing compounds are typically hydrophilic and polar, including materials such as silica gel and zeolites, (ii) carbon-based compounds are typically hydrophobic and non-polar, including materials such as activated carbon and graphite, and (iii) polymer-based compounds are polar or non-polar functional groups in a porous polymer matrix (www.en.wikipedia.org).

Among industrial adsorbents, activated carbon plays an important role in the technology of adsorbed natural gas because it adsorbs more non-polar and weakly polar organic molecules than other adsorbents do, and it exhibits low heat of adsorption, resulting in low energy intensive regeneration operations. Interactions between the methane molecules and the surface of carbon increase the density of the adsorbed methane (Rodríguez-Reinoso *et al.*, 2008).

Activated carbon is used for the adsorption of organic substances and non-polar adsorbates. It is the most widely used adsorbent because of its usefulness, which derives mainly from its large micropore and mesopore volumes and the resulting high surface area. Activated carbon is composed of amorphous carbon and graphite crystalline units (Qiao and Hu, 2000). It is made from natural products such as coconut shells, palm shells, corn cobs, peach stones, and coals. The carbon itself can be produced as powder, granules, pellets, or formed into monoliths or briquettes. Figure 2.7 shows activated carbons in powdered, granular, and pelletized forms, respectively.

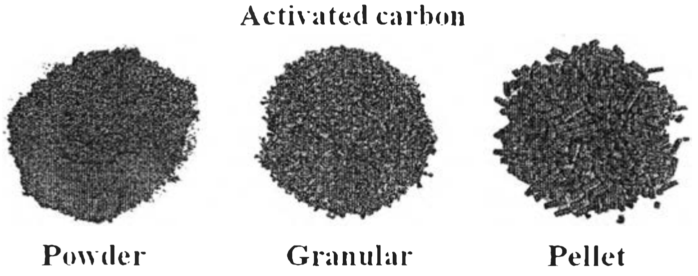

Figure 2.7 Commercial activated carbon from coconut shells-based precursor in powdered, granular, and pelletized forms (www.chemechel.com).

Starting with initial pores present in the raw material, more pores with desired size distributions are created by the activation process. There are two types of activation used in producing activated carbon, which are physical activation and chemical activation. The distribution of storage capacity is dependent on the activation process (www.web.anl.gov).

- Physical activation of activated carbon consists of two steps: the first step is the elimination of most of the hydrogen and oxygen contents by pyrolysis of carbonaceous material at a high temperature and an inert atmosphere. The second step is to activate the chars at a high temperature and in presence of steam or carbon dioxide as oxidizing gases. Carbon atoms are extracted by these agents from the structure of the porous carbon according to the endothermic reactions. This method of activation is done entirely within the gas phase.
- Chemical activation involves the treatments of precursor with a chemical agent followed by conventional heat treatment, which will affect the process of carbonization (at 600-900 °C) and generates the porosity. Among the numerous dehydrating agents, H_3PO_4, $ZnCl_2$, KOH and NaOH are widely used for the preparation of activated carbons by chemical activation.

On the other hand, combination of chemical and physical activation is another technique to prepare highly microporous activated carbon. This method of activation is a powerful technique for controlling and developing similar micropore, which enhances the overall adsorption capacity of the activated carbon (Arami-Niya *et al.*, 2011). For example, in 2008, Prauchner and Rodríguez-Reinoso synthesized granular activated carbon to adsorb natural gas. The grains were prepared from coconut shells using chemical activation with H_3PO_4 or $ZnCl_2$, physical activation with CO_2, or a combination of chemical followed by physical activation.

A good carbon adsorbent for natural gas storage has to exhibit a high adsorption capacity of methane storage on a volumetric basis. To reach this condition, the requirements for an ANG adsorbent (Namvar-Asl *et al.*, 2008) are: (i) high adsorption capacity, (ii) high adsorption/desorption rates, (iii) high microporous with pores around 0.8-1.0 nm, which optimizes the density of the adsorbed phase, (iv) high packing density which contributes to increase the bulk density and the volumetric storage capacity, (v) low adsorption heat and high heat capacity to minimize the changes in the vessel temperature during the adsorption and desorption processes, (vi) good mass transfer properties, (vii) extremely hydrophobic and (viii) inexpensive for the final user.

2.6 Silane Coupling Agent

A silane compound is a monomeric silicon-based molecule containing four constituents. The general structure of a function silane coupling agent is shown in Figure 2.8. The organic arm typically has a structure that terminates in a functional group or reactive component, which facilitates the covalent linkage to another organic molecule. The other part consists of the silane-reactive groups attached directly to the silicon atom and can be of several types.

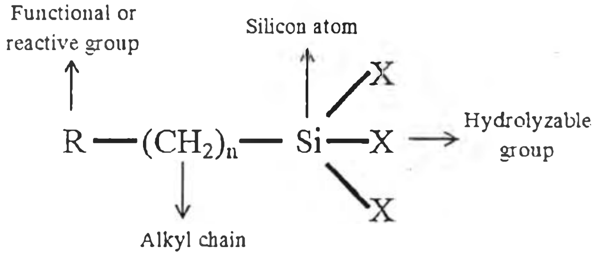

Figure 2.8 General structure of a silane coupling agent includes a functional group or reactive group at the end of an organic spacer (Hermanson, 2013).

The general reactions of silane coupling agents toward inorganic substrates are illustrated in Figure 2.9. The reaction mechanism and formation of a reactive intermediate can be different from that usually encountered with organic reactive groups. The most common silane coupling groups (alkoxy) often must first undergo hydrolysis to form a reactive intermediate, which actually is the highly reactive form necessary for coupling to inorganic surface hydroxyls (Hermanson, 2013).

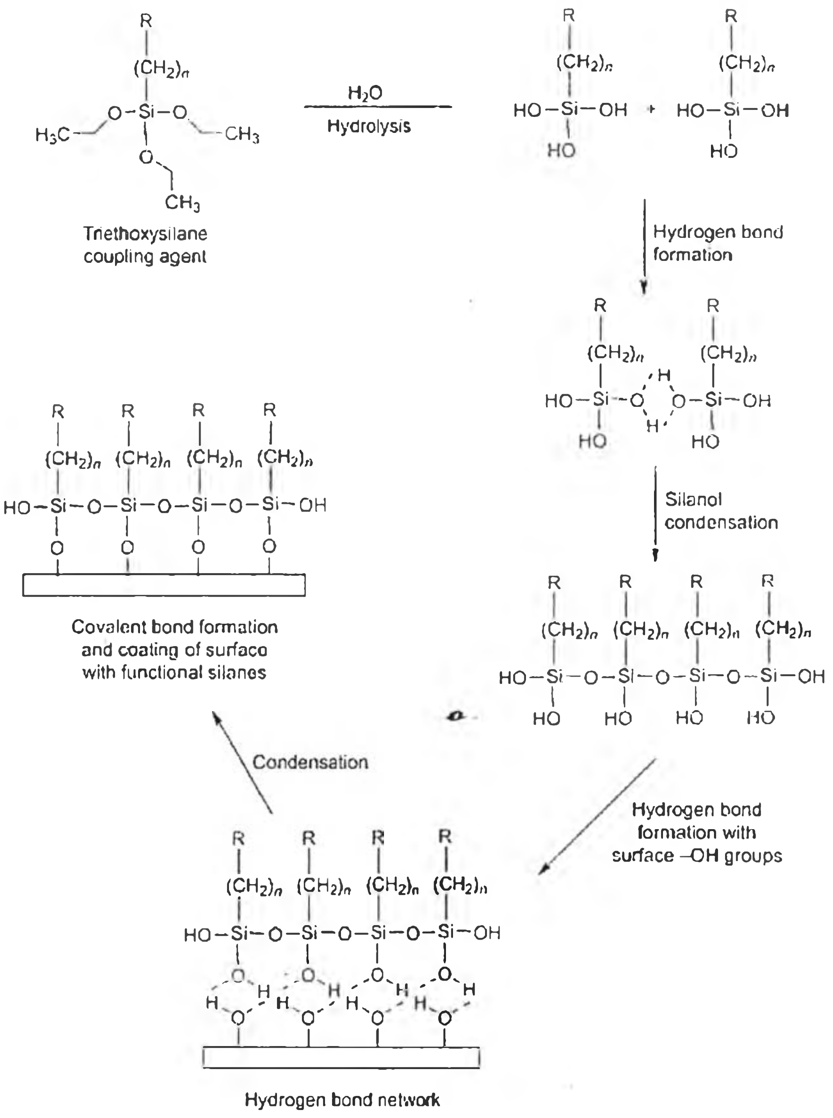

Figure 2.9 Reactions involved with the coupling of an organosilane compound to an inorganic surface containing available –OH groups (Hermanson, 2013).

Some common inorganic substrates for use with silane coupling agents in approximate order of efficiency and stability for modification include silica, quartz, glass, and the oxides of aluminum, copper, tin, titanium, iron, chromium, zirconium, nickel, and zinc. All of these substrates can have functional inorganic –OH groups on their surface that react with the silanols on the silane coupling agents to form siloxane bonds (Hermanson, 2013). In addition, treatment with a mixture of 25% sulfuric acid and 15% hydrogen peroxide for about 30 minutes is carried out to create a high density of hydroxyl functionalities suitable for silane modification.

2.7 Literature Review

Adsorbed natural gas (ANG) has recently become competitive to compressed natural gas (CNG) for storage and transportation purposes with high energy density and at much lower pressure than CNG. Most researchers in the field of ANG storage focused on the development and evaluation of the economic performance of ANG for using in vehicle applications (Farzad *et al.*, 2007). The interesting points such as characteristics of carbon adsorbents (e.g. pore size, shape, selectivity and activation process), optimum pressure-temperature conditions, and adsorption/desorption cycles were investigated to give more information for improving the ANG storage.

The application of adsorbent materials for storing natural gas in vehicles is another application trying to make natural gas vehicles competitive with current vehicles using other fuels. Many researchers proved that methane can be stored by adsorption on porous carbon materials with high energy density at room temperatures and pressures up to 500-600 psi (Rashidi *et al.*, 2011). Due to adsorption of methane on activated carbon adsorbent is an exothermic phenomenon; the stored methane capacity is sensitive to the heat limitation. When the pressure continually increased from 500 to 1,500 psi, the stored methane capacity increased about 42% from 120 to 160 v/v. As temperature increased from 25 to 30 °C, the stored methane capacity was decreased about 72% from 120 to 70 v/v (Bagheri and Abedi, 2011).

Prauchner and Rodríguez-Reinoso (2008) used granular activated carbon, which was prepared from coconut shells using chemical activation with H_3PO_4 or

$ZnCl_2$, physical activation with CO_2, or a combination of chemical followed by physical activation for adsorbing natural gas. It is worth noting that activation with metallic hydroxides (KOH and NaOH) also leads to materials with high methane adsorption capacity. However, activation with hydroxides usually leads to powdered carbon, which is not very practical for storage applications. Activated carbon with its high porosity and surface area can be utilized as an ANG adsorbent. It is generally accepted that van der Waals forces (physisorption) play an important role in methane adsorption on activated carbon (Bagheri and Abedi, 2011). Regarding methane adsorption capacity, it is known that a reasonably linear relationship exists between micropore volume and methane uptake (Lozano-Castelló *et al.*, 2002). Micropore is the only range of porosity useful for methane storage (Alcañiz-Monge *et al.*, 1997). The advanced ANG adsorbent needs to have micropore volume near 50%, solid carbon near 40%, and mesopore and macropore volume near 10% (Vasiliev *et al.*, 2000). The amount of methane adsorbed increases with pressure as a function of the micropore volume (space available for adsorption) and the micropore size (it conditions the intensity of the adsorption potential) (Rodríguez-Reinoso *et al.*, 2008).

Rafael *et al.* (2009) also studied the adsorption of methane in activated carbons obtained from coconut shells prepared by chemical activation with H_3PO_4 as the activating reagent and followed by carbonization under N_2 flow. It was found that there was a close relationship between surface area, micropore volume, and methane adsorption capacity under pressures between 1 and 60 bar at 303 K. The highest methane storage capacity in the tested samples was 95 v/v at 303 K and 35 bar, which is comparable to results obtained for commercial samples. A moderate concentration of H_3PO_4, around 35%, seemed to favor high surface areas, micropore volumes and, hence, gas storage capacity. The inclusion of an acid wash step before carbonization and the use of inert gas flow during carbonization also enhanced the development of porosity. In the chemical activation process, the reagent acts as a dehydrating agent, in which H and O are removed. If carbonization takes place in the absence of an inert atmosphere, a very large amount of H and O is removed and reacts with carbon atoms forming hydrocarbons and/or carbon monoxide and/or carbon dioxide (Molina-Sabio and Rodríquez-Reinoso, 2004). Probably, this phenomenon decreased the gasification efficiency, leading to a less developed porous structure. Regarding the average pore size, it was reported that an adsorbent for methane storage should have an optimal pore size ranging from 8 to 15 Å (Sun *et al.*, 1997). Furthermore, the activated carbon prepared from coconut shells can use $ZnCl_2$ as an activating reagent too. Diana *et al.* (2006) prepared microporous activated carbon by chemical activation with $ZnCl_2$ and physical activation under N_2 atmosphere for methane adsorption at pressure between 0.1 Mpa and 7 Mpa and temperature from 283 to 333 K. The sample that presented the best characterization results was then evaluated for methane adsorption at 298 K and 40 bar. 122 mg of methane/g of carbon (80 v/v) capacity was observed, just short of target for ANG in remote sites transportation (100 v/v). By subtracting the product of gas density and suspended volume from the measured mass, the adsorption isotherms for excess adsorbed mass were obtained and are shown in Figure 2.10, for some temperature, data for adsorption, pressure going upwards and desorption, pressure going downwards were measured. Hysteresis was found to be negligible.

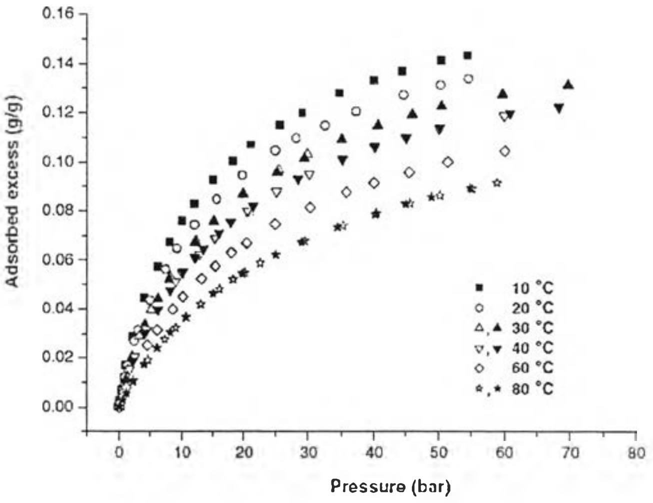

Figure 2.10 Excess adsorption isotherms of methane. Blank symbols: adsorption data; Filled symbols: desorption data (Diana *et al.*, 2006).

A typical physisorption behavior is observed yielding isotherms of type I. The adsorbed amount decreased with increasing temperature. These results suggested that activated carbons prepared from coconut shells, using chemical activation followed by physical activation, may be further developed as potential adsorbents for natural gas storage application.

The chemical activation is often the preferred method due to its shorter production time and lower temperature required to produce activated carbon. Dai *et al.* (2008) studied the treatment of activated carbon for methane storage by chemical activation with HNO_3, H_2SO_4, and H_2. Methane storage tests were carried out on untreated and treated activated carbons. It was found that the surface treatment significantly influenced the surface properties and pore structures of the activated carbon. The surface area and pore volume were enhanced by acid treatment owing to the removal of impurities in the carbon. The increase in the surface area and porosity was generally prevailing in micropores for H_2SO_4, while HNO_3 treatment just enhances the mesopores to some degree. For H_2 treatment, the surface area and porosity were significantly reduced because the large decrease in the surface area and porosity causing the decrease in the sorption capacity. Simultaneously, the acidity of carbons increased by the acid treatment, but basicity decreased relatively. With the acid treatment, the number and species of surface functional groups changed significantly, but they were unrelated to the type of acid. With the decrease in the number of functional groups through the surface treatment, a reduction in the active sites for adsorption resulted in the decrease in the adsorption capacity.

The physical adsorption is an exothermic phenomenon. It is favored at lower temperatures, and the slope of its curvature decreases with increasing temperature. The average relative error in the estimated amount adsorbed is about 3-8 %. Figure 2.11 compares the single-component adsorption isotherms for the n-alkanes C_1-C_4 at 25 °C. The left graph is a magnification of the low-pressure region, whereas the right graph displays the isotherms over the full pressure region on a log-log scale. The isotherm slope in the low-pressure region increases strongly with hydrocarbon chain length; however, when the adsorption data are plotted on a log-log scale, the overall isotherms slope exhibit the inverse trend. Thus, the higher molecular weight hydrocarbons are not preferentially desorbed. This is the basis for the undesirable phenomenon of preferential adsorption of the heavier hydrocarbons on an unfiltered adsorption storage system and their progressive accumulation on extended cyclic operation.

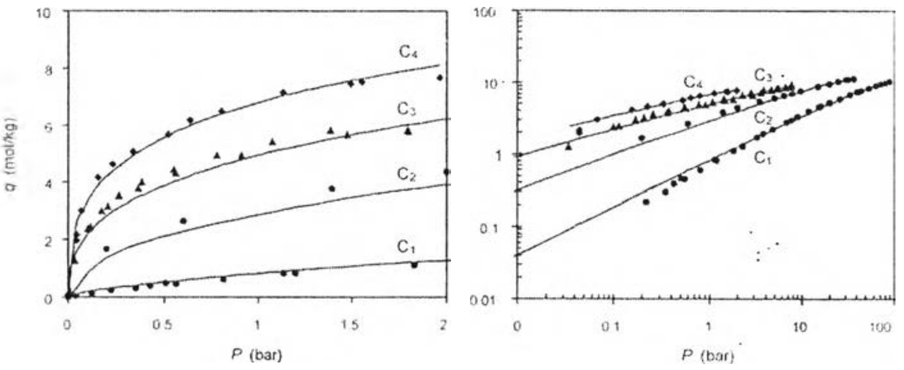

Figure 2.11 Comparative of adsorption isotherms for the n-alkanes C_1-C_4 at 25 °C (Esteves *et al.*, 2008).

Figure 2.12 compares the single-component adsorption isotherms for CO_2 and N_2 at 37 °C. There is no distinction between experimental adsorption and desorption data.

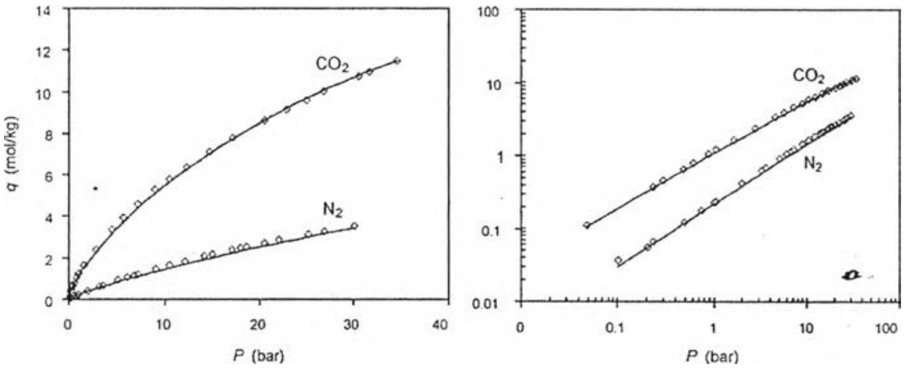

Figure 2.12 Comparative of adsorption isotherms for CO_2 and N_2 at 37 °C (Esteves *et al.*, 2008).

Daud and Ali (2004) compared properties of activated carbons produced from palm shell and coconut shell in terms of pore size distribution of micro, meso, and macropores. Both activated carbons were prepared using the same process. The activation rate of coconut shell char was almost five times higher than palm shell char. They concluded that the activation rate could be attributed to the high cellulose and hemicellulose content in the raw material. Bastos *et al.* (2007) textural characteristics were studied by nitrogen adsorption on a regular surface area analyzer. Elemental and surface analyses were carried out by X-ray photoelectronic spectroscopy (XPS) for the selected samples. For the carbons produced from the same source, it was clearly recognized that methane adsorption was higher from samples with a higher surface area, higher micropore volume, and narrower pore size distribution within the range of 8–15 Å. There was a common trend for the BET surface area and DR micropore volume to be directly proportional to methane adsorption capacity. Samples with slightly more hydrophobic surfaces had superior methane adsorption properties in comparison to the less hydrophobic samples with more favorable. Textural parameters were unable to unequivocally determine natural gas storage capacities. Surface chemistry and methane adsorption equilibria were subjects to be considered in the decision-making process when choosing the right adsorbent for gas storage.

Salehi *et al.* (2007) carried out the theoretical and experimental study to figure out the accurate amount of methane adsorption and desorption by using different types of granular activated carbons or GACs under different physical conditions. The experiments used the volumetric method to measure equilibrium of methane adsorption at 298 K and the maximum pressure of 500 psia. In doing so, the adsorption and desorption capacity of four different GACs in the adsorption of methane at different equilibrium pressures and a constant temperature were studied. The results indicated that the physical characteristics of activated carbon, which included BET surface area, micropore volume, packing density, and pore size distribution, were important factors in the adsorption and desorption amount of methane. The results of the isotherm testing suggested that the amount of adsorption would increase with the SSA of both temperatures. Therefore, SSA is an important factor in methane storage for activated carbon fibers. Furthermore, the increase in the temperature within the range of 258–280 K would rapidly decrease the adsorption capacity of methane and would also slowly decrease in the capacity in the temperature within range of 280–298 K. Therefore, it indicated that the temperature had the effect on the methane storage capacity for the activated carbon fibers, and the favorable temperature for methane adsorption is below 280 K (Shao *et al.*, 2007).

Chen and Wu (2004) used different physicochemical methods to modify the surface of activated carbon. In the experiment, HCl, HNO_3, and NaOH were used to modify activated carbon. In addition, the effects of surface modification on the activated carbon properties, such as SSA, total acidity capacity, and carbon pH were studied. The results of HCl, HNO_3, and NaOH treatment caused a significant change in the carbon chemical properties including the carbon pH and total acidity capacity; however, there was no change in the SSA of the carbons. According to the XPS and FTIR results, they showed that, with the HNO_3 treatment, the activated carbon produced a significantly large number of surface functional groups, which included carbonyl, carboxyl, and nitrate groups, whereas the NaOH treatment caused the increase in the hydroxyl group content. In addition, the HCl treatment caused the increase in the amount of single-bonded oxygen functional groups, which included ethers, lactones, and phenols.

Coconut shell based carbons were chemically treated by NH_4OH, NaOH, HNO_3, H_2SO_4, and H_3PO_4 to determine suitable modification for improving adsorption ability of hydrophobic volatile organic compounds (VOCs) on activated carbons. Li *et al.* (2011) removing surface oxygen groups, which constitute the source of surface acidity, and reducing hydrophilic carbon surface favors adsorption capacity of hydrophobic VOCs on carbons. The performances of modified activated carbons were also investigated in the purification of gases containing complex components (o-xylene and steam) in the stream. Surface functional groups such as phenolic group (–OH), carbonyl group (CO), and carboxylic group (–COOH) were determined by Boehm titration. The results of these surface functional groups for various activated carbon samples are shown in Figure 2.13.

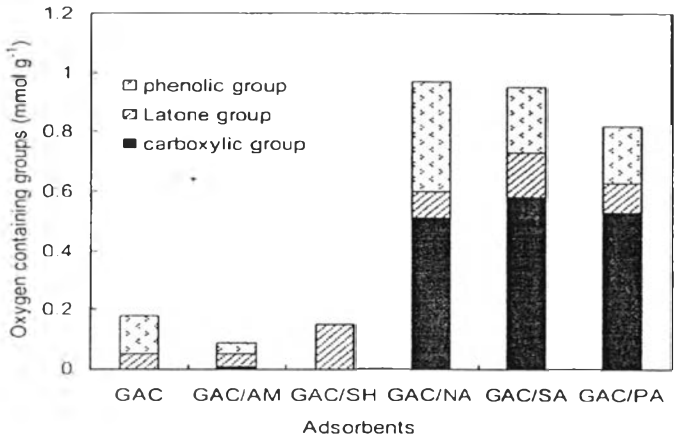

Figure 2.13 Surface functional groups of various GAC (Li *et al.*, 2011).

The major increase took place in the carboxylic group, which contributed to the strong oxidation property of treated acids. Alkali-treated GAC decreased total concentration of the oxygen containing functional groups from 0.18 mmol/g to 0.15 and 0.09 mmol/g for GAC/SH and GAC/AM, respectively. The decrease in oxygen containing functional groups occurred mostly on the phenolic group. Variation in surface area and porosity of the adsorbents plays a key role on adsorption of hydrophobic VOC. The adsorption capacity for o-xylene increased with the increase in surface area, total pore volume, and surface hydrophobicity. Modification by ammonia enlarged the surface area and decreased the concentration of surface oxygen groups, which benefits GAC uptake of hydrophobic VOC. Optimized carbon adsorbents for a specific organic compound can be produced by appropriate surface modification.

Himeno *et al.* (2005) studied the high pressure adsorption equilibrium of CH_4 and CO_2 on commercial activated carbons, which made from coal (BPL), chark (Maxsorb), petroleum pitch (A10 fiber), and coconut shell (Activated carbon A). The adsorption isotherms of CH_4 and CO_2 onto activated carbons were obtained for temperature from 273 to 333 K and pressure up to 6 MPa.

Figure 2.14 shows the adsorption isotherms of CH_4 and CO_2 on activated carbons by the gravimetric method. For all activated carbons, the amount of CO_2 adsorbed was about twice that of the CH_4 adsorbed. The highest adsorption capacity was Maxsorb. The adsorption capacity was ordered as follows: Maxsorb > Activated carbon A > A10 > BPL. All the carbons used in their study had micropores that contributed to the adsorption of CH_4 or CO_2 at room temperature. The order of the adsorption capacity of activated carbons was almost the same as order of the BET surface area and pore volume.

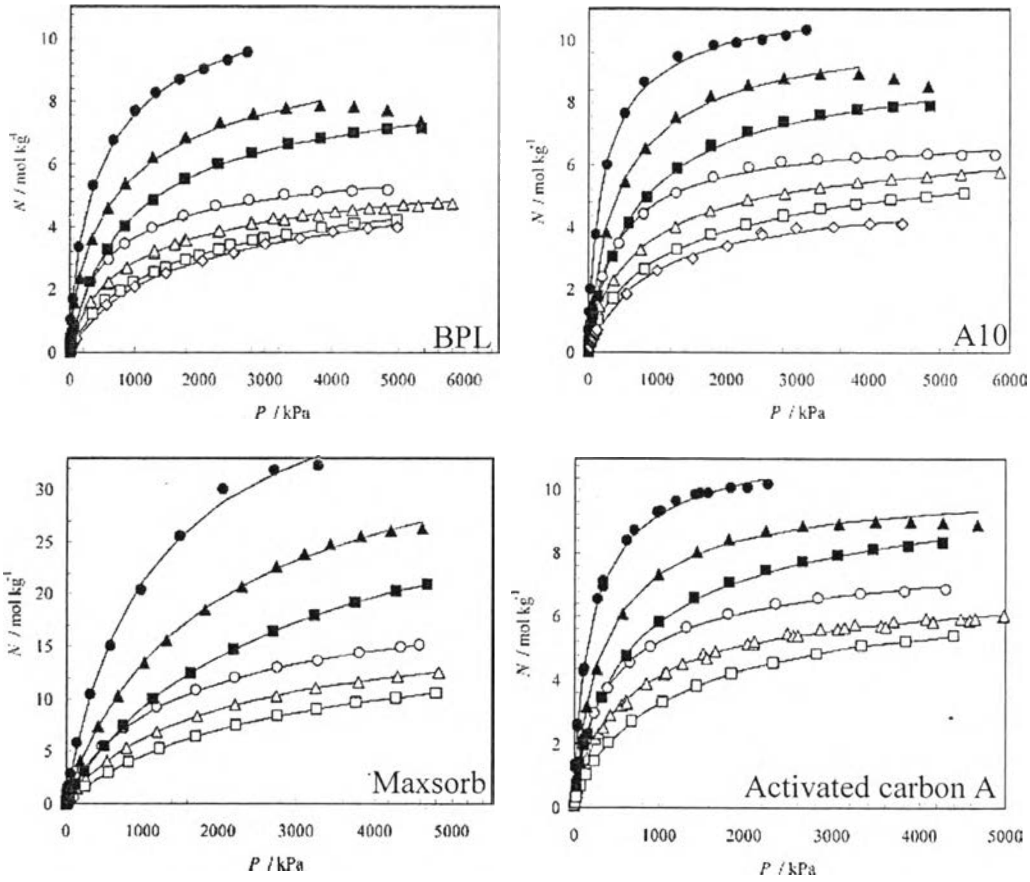

Figure 2.14 Adsorption isotherms of CH_4 and CO_2 on activated carbons: ○, CH_4 at 273 K; △, CH_4 at 298 K; □, CH_4 at 323 K; ●, CO_2 at 273 K; ▲, CO_2 at 298 K; ■, CO_2 at 323 K (Himeno *et al.*, 2005).

Ning *et al.* (2012) studied the adsorption equilibrium of CH_4 and CO_2 on microwave activated carbon (MAC) at temperature from 298 to 323 K. The adsorption isotherm of CH_4 and CO_2 adsorbed on MAC at different temperature are presented in Figure 2.15

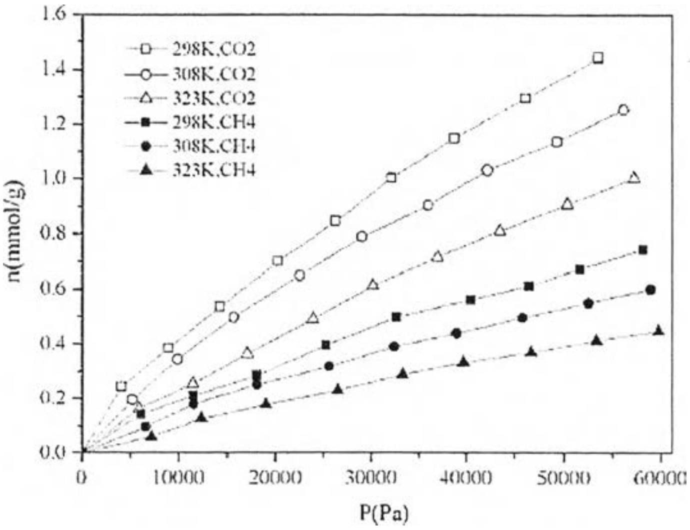

Figure 2.15 Adsorption isotherms of CH_4 and CO_2 on MAC at three temperatures (Ning *et al.*, 2012).

From Figure 2.15, all curves can be classified as type-I according to the IUPAC classification. It is also observed that the isotherms for CO_2 are much more favorable than CH_4 under the conditions investigated. This result is mainly concerned with the physical and chemical properties of adsorbates. Firstly, both of CH_4 and CO_2 have similar molecular diameter, when the critical temperature follows the order CO_2 (304.3 K) > CH_4 (190 K). Under the experiment condition, the gas critical temperature was lower, which indicated that the degree of the deviation of critical condition was greater and the gas was harder to be adsorbed. Secondly, the diffusion velocity of CO_2 faster than CH_4. So the adsorption capacity of CO_2 is higher than CH_4.

Yundong *et al.* (2013) studied the adsorption of CO_2 and CH_4 gas mixture on the commercial zeolite at atmospheric pressure to screen excellent adsorbents in related fields. They found that zeolites type-x and type-A had much better adsorption performance to CO_2 than ZSM-5 and Y, as shown in Figure 2.16.

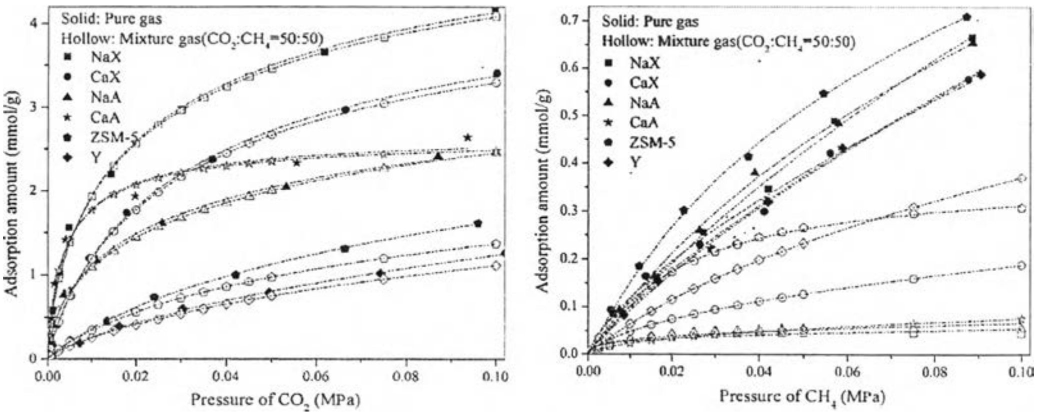

Figure 2.16 Pure gas and mixture gas isotherm of CO_2 (left) and CH_4 (right) on zeolites at 30 °C (Yundong *et al.*, 2013).

This experimental result was attributed to the low Si/Al ratio. Because zeolites with the lower Si/Al ratio had the higher electric field gradient, which can strongly adsorb quadrupole of CO_2 molecules. The CH_4 molecule without quadrupole and dipole was adsorbed depending on non-specific Van der Waals force related to specific surface area and pore volume of porous materials.

The competition of two gases on different zeolites is shown in Figure 2.17, where the selectivity of CO_2 to CH_4 was plotted with the mole fraction of CH_4 in gas mixtures at 0.1 MPa. The selectivity of CO_2 to CH_4 decreased in the order NaX > CaA > NaA > CaX > ZSM-5 ~ Y. The concentration of CH_4 is 50-55% for landfill gas, 65% for farm biogas, and higher than 90% for natural gas. This means that NaX was the most selective adsorbent for separating the land fill gas and farm biogas, and CaA was suitable for natural gas.

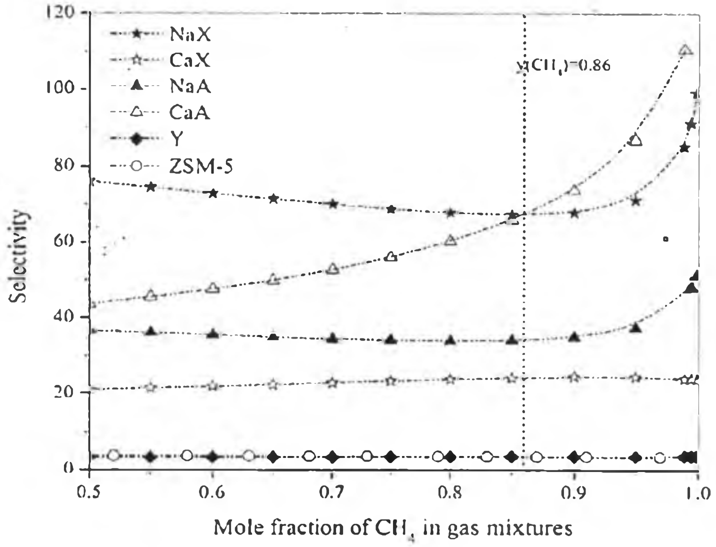

Figure 2.17 Selectivity of CO_2 to CH_4 adsorbed on zeolites in gas mixture with different concentration at 0.1 MPa (Yundong *et al.*, 2013).

Rios *et al.* (2012) studied the adsorption behavior of CO_2-CH_4 mixtures using activated carbon and comparison between experimental data and predicted values. were from two classical adsorption models. Binary adsorption equilibrium of CO_2 and CH_4 on the activated carbon at 293 K at total pressures of 0.1, 0.25, 0.5, and 1.0 MPa for different gas phase compositions was obtained using the volumetric-chromatographic method. The extended Langmuir (EL) model and the Ideak Adsorbed Solution Theory (IAST) were used to predict the amounts adsorbed of each gas in the CO_2–CH_4 binary mixtures. The IAST was applied in conjunction with the Langmuir equation (IAST-L) and with the Toth equation (IAST-T) are shown respectively in Eq. (2.1) and (2.2).

$$q_i = \frac{q_{max} \cdot b_i \cdot P_i}{1+b_i \cdot P_i} \tag{2.1}$$

$$q_i = \frac{q_{max} \cdot b_i \cdot P_i}{\left(1+(b_i \cdot P_i)^{t_i}\right)^{1/t_i}} \tag{2.2}$$

Experimental and predicted adsorption data of CO_2-CH_4 mixtures are shown in Figure 2.18.

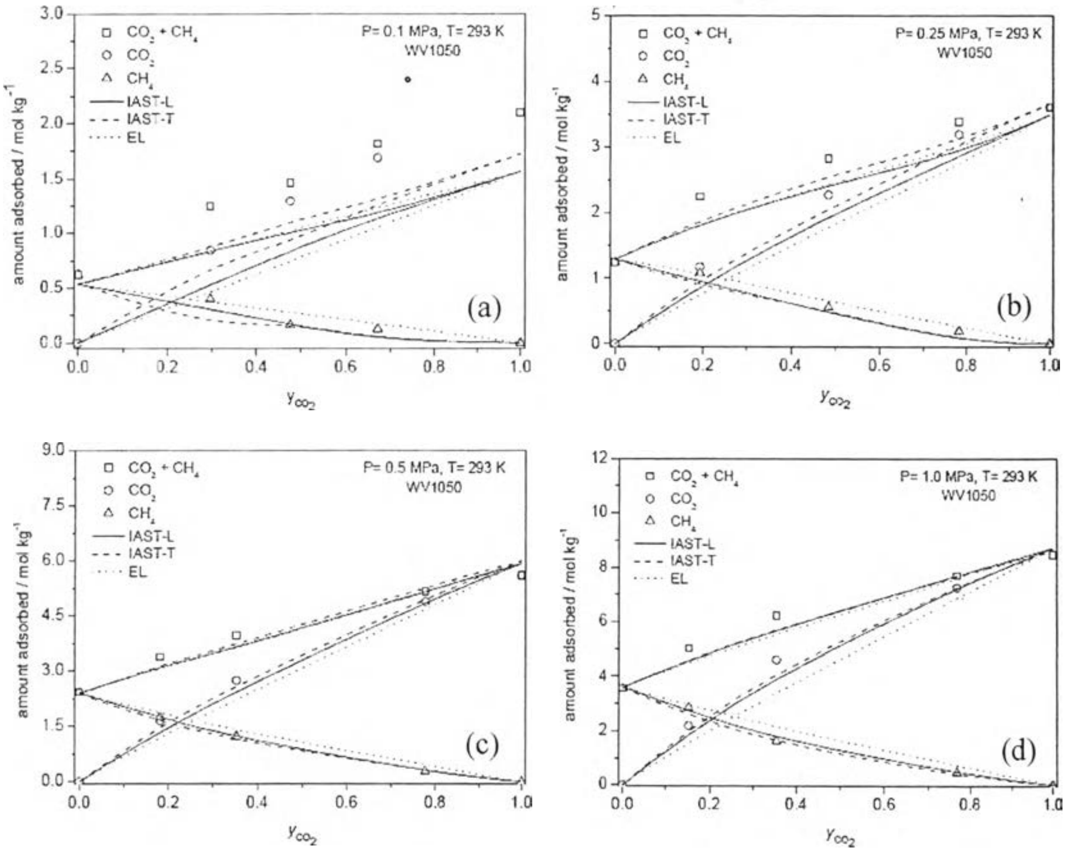

Figure 2.18 Binary adsorption isotherms for CO_2-CH_4 mixtures at 293 K on activated carbon: (a) 0.1 MPa; (b) 0.25 MPa; (c) 0.5 MPa; (d) 1.0 MPa (Rios *et al.*, 2012).

Figure 2.18 shows that the total adsorbed amount increased along with CO_2 composition, while the amount of methane adsorbed decreased, indicating competition for adsorption sites and preferential adsorption of carbon dioxide over methane. The main reason for this behavior is the significantly higher critical temperature of CO_2 in comparison with CH_4, as shown in Table 2.4. Carbon dioxide is more likely to behave as a condensable steam than as a supercritical gas, becoming less volatile and increasing its adsorption.

Table 2.4 Physical-chemical properties of CO_2 and CH_4 (Rios *et al.*, 2012)

Molecule	Kinetic diameter (Å)	Polarizability (Å^3)	Quadrupole moment (D. Å)	Critical temperature (K)
CO_2	3.30	2.51	4.30	304
CH_4	3.80	2.45	0.02	190

Moreover, CO_2 presents a higher polarizability which may enhance attractive forces with the surface and a permanent quadrupole, leading to stronger interactions with the solid surface.