

## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Natural Gas

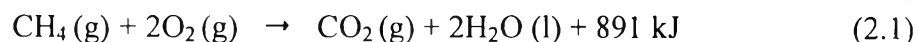
Natural gas is often referred to gas consisting mainly of methane and can be found associated with other fossil fuels. It can be used as a fuel for vehicles and offers many environmental benefits. NGV uses a conventional spark ignition engine with only minor modification. Natural gas burns more completely and produces less air pollutants than gasoline. It is well-known to be an important fuel source, a major feedstock for fertilizers, and notoriously a potent greenhouse gas. In retrospect, it had been dismissed as a useless by-product of crude oil production until the second half of the 20<sup>th</sup> century, natural gas become an important energy source and now provides 23 percent of all energy consumed in the world. Natural gas is an economical, environmental friendly, and efficient energy source. It produces lower levels of greenhouse gas emission than heavier hydrocarbon fuels, such as coal and oil do. 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<sub>2</sub>, N<sub>2</sub>, and other trace gases.

**Table 2.1** Typical composition of natural gas ([www.naturalgas.org](http://www.naturalgas.org))

<b>Constituent</b>	<b>Composition (mol%)</b>
Methane, CH <sub>4</sub>	70-90
Higher molecular weight hydrocarbons	0-20
Carbon dioxide, CO <sub>2</sub>	0-8
Other gases (O <sub>2</sub> , S, N <sub>2</sub> and etc.)	trace

Commercial natural gas is neither pure methane nor a homogeneous mixture. Natural gas composition varies by the location of extraction and by the season, in which the gas is extracted. In addition, further 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). In its purest form, it is almost pure methane. Methane molecule consists of one carbon atom and four hydrogen atoms. CH<sub>4</sub> is its formula. Natural gas is always filled up with mercaptan compound, which is an odorant compound before it is delivered to end-users because of safety reason. Mercaptan compound will give the odor-rotten egg smell when the natural gas leaks.

According to Equation (2.1), methane reacts with oxygen and produce carbon dioxide and water. The combustion of methane is an exothermic reaction.



In 2004, Kavalov reported techno-economic analysis of natural gas application as an energy source for road transport in the 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.

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. Therefore, the potential technological options are compression under high pressure (CNG), liquefaction under low temperature (LNG) or adsorbed natural gas (ANG).

## **2.2 Natural Gas Storage Method**

Natural gas storage is great to many industries, such as natural gas vehicle, 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 Compressed Natural Gas (CNG)

CNG is applied mainly for on-board gas storage of the natural gas vehicles (NGVs) industry. CNG is stored at a high pressure, usually 3,000-3,700 psi. CNG demands very robust specially-designed cylindrical tanks, which use a lot of space and are heavy. In addition, gas compression requires expensive multi-stage high-pressure compression technology. 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 ([www.energtek.com](http://www.energtek.com)). CNG vehicle refueling infrastructures deployment and operation is associated with the following problems:

- a. The capital investment for the construction of a CNG filling station is several times bigger than for a petrol/diesel station.
- b. The operation of a CNG station requires high energy consumption and very expensive maintenance.

c. The price of CNG stations substantially increases natural gas cost for the vehicle user. Without significant tax preference, CNG price is not attractive enough compared with petrol and diesel.

d. 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 ([www.greencar.com](http://www.greencar.com))

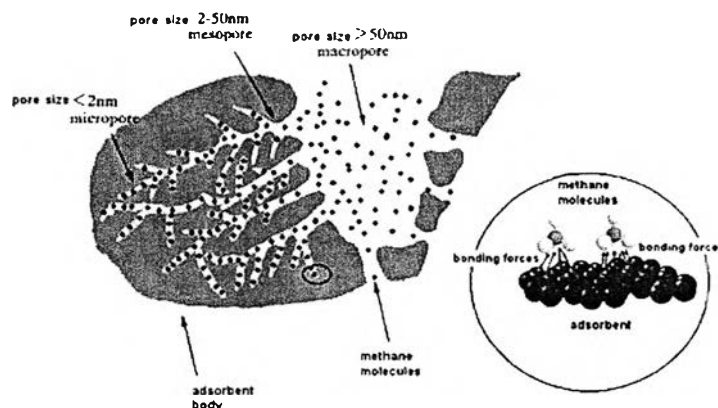
### 2.2.2 Liquefied Natural Gas (LNG)

LNG is another known gas storage method. Natural gas is liquefied under pressure of 10-20 bars at  $-161.5^{\circ}\text{C}$ . LNG requires the use of complex and expensive liquefaction equipment, 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.energtek.com](http://www.energtek.com)).

### 2.2.3 Adsorbed Natural Gas (ANG)

ANG or adsorbed natural gas technology allows the storage of natural gas at substantially higher volumetric capacity than pressurized storage for an equivalent pressure, making use of adsorption of gas on a adsorption agent (adsorbent) like low-cost activated carbon material, molecular sieve in cylinder. In other words, ANG is a technology providing a larger volume of natural gas that can

be stored in the same container, at the same pressure or can be stored in the same volume of natural gas in the container at a much lower pressure. For ANG, natural gas can be stored as an adsorbed phase in microporous materials, a process that enables gas molecules to adhere to a microporous solid material with the gas released when needed. This option can be an interesting alternative that overcomes the problems of CNG. The use of adsorbent materials in a storage vessel for storing natural gas, at relatively low pressure (500-600 psi) and room temperature, is a possibility for making natural gas vehicles competitive with the other types of vehicles. 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, it gives the ability to adsorb large quantities of natural gas ([www.energtek.com](http://www.energtek.com)). Figure 2.1 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.



**Figure 2.1** Adsorption of methane molecules on the activated carbon adsorbent in micropore, mesopore, and macropore structures ([www.greencar.com](http://www.greencar.com)).

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

a. 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.

b. 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%.

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

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

e. 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 principles of ANG have been around for decades; however, no one has succeeded to develop commercially viable technology until now. The commercialization of ANG method has been hindered due to several unsolved technological problems. The main challenges of ANG storage products development are ([www.energtek.com](http://www.energtek.com)):

a. Sufficient volumetric storage ability that will be competitive with existing natural gas storage methods.

b. Gas filling and release from ANG tank for automotive application require the control of efficient thermodynamic processes.

c. ANG fueling system cost should be competitive with the cost of existing fueling systems.

The new innovative technology to solve described above problems should be based on several new concepts such as:

a. Novel method to process the adsorbent material and manufacture the gas adsorption structure having high volumetric storage ability and low cost.

b. An efficient thermo-managing control system for cooling or heating the adsorbent material as required for controllable gas filling/discharging.

c. Development of a new design concept of combined tanks, which store either gas only, or liquid and gas, in the same tank of prismatic or free shape form. This allows additional increasing of the total volumetric storage ability of the tank.

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.glnobledenton.com](http://www.glnobledenton.com)). The improvement of ANG storage can be described in the short conclusion as the followings:

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

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

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

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

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

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

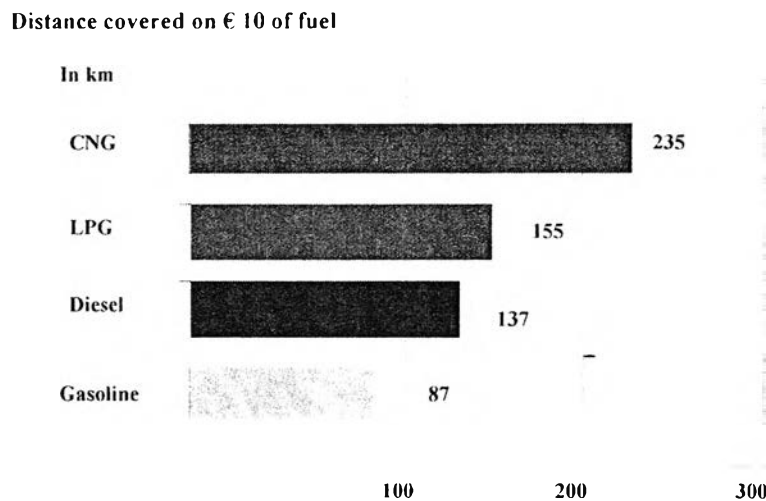
g. The combination of adsorption and low-temperature storage has almost never been researched.

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.glnobledenton.com](http://www.glnobledenton.com)).

### **2.3 Natural Gas Vehicles (NGVs)**

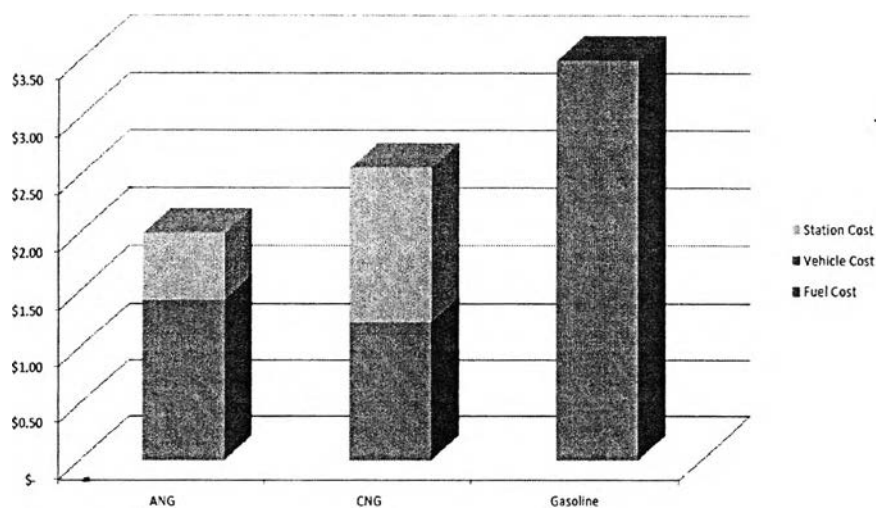
There are two basic types of natural gas vehicles: dedicated NGVs operate only on natural gas, while bi-fuel NGVs can operate on either natural gas and traditional gasoline or diesel fuel. In some cases, this is driver selectable with the flip of a switch, while others offer either manual switching or automatic switch over to conventional fuel operation when the on-board natural gas fuel supply is exhausted. In general, dedicated NGVs demonstrate better performance and have lower emissions than bi-fuel vehicles because their engines can be optimized to run on natural gas alone. In addition, dedicated vehicles do not carry two types of fuel, which means they do not sacrifice cargo capacity or carry around additional weight. The plus for bi-fuel vehicles, of course, is that they reduce the possibility of being stranded if natural gas fueling is not readily available since they can also run on conventional fuel ([www.greencar.com](http://www.greencar.com)). Figure 2.2 shows the comparative of CNG, LPG, diesel and gasoline costs for using natural gas fuel systems, and traditional gasoline fuel system.





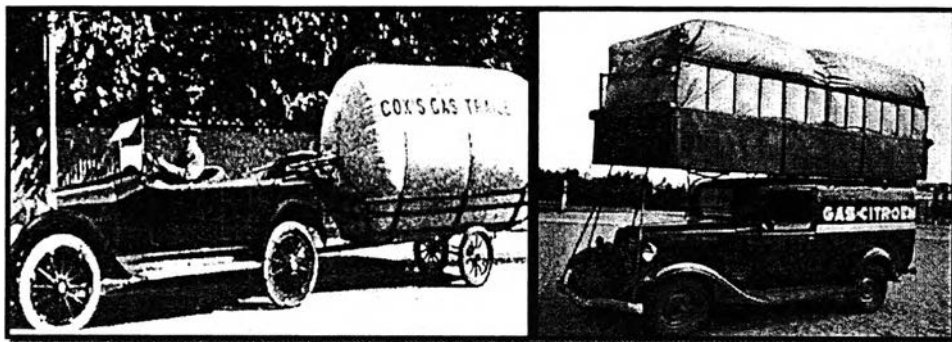
**Figure 2.2** Comparison between natural gas fuel systems and gasoline fuel system in terms of fuel costs (www.eon.com).

Drivers save around 50 percent compared to gasoline and around one third compared to diesel. With fuel costs below € 5 per 100 kilometers in connection with a greater variety of attractive car models, natural gas drives are becoming increasingly important for various user groups. Figure 2.3 shows the comparative of fuel, vehicle, and station costs for using natural gas fuel systems (both ANG storage and CNG storage), and traditional gasoline fuel system (www.eon.com).

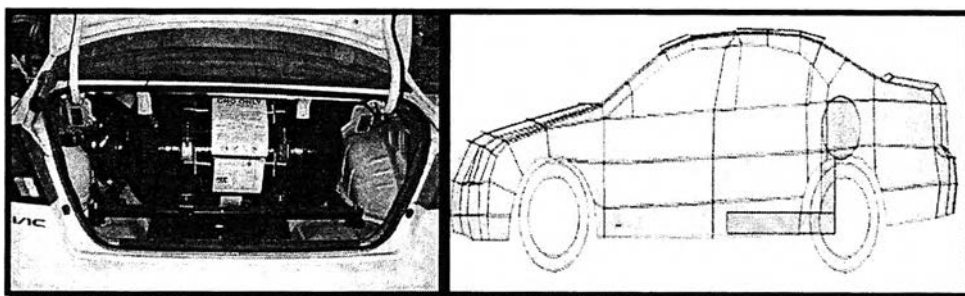


**Figure 2.3** Comparison between natural gas fuel systems and gasoline fuel system in terms of fuel, vehicle, and station costs (Pfeifer, 2011).

From Figure 2.3, we can see that, even though natural gas fuel systems have much lower fuel cost than that of gasoline fuel system, the addition of vehicle and station costs for natural gas fuel systems are added and then resulted to higher overall costs. Thus, the different costs of gasoline fuel system and natural gas fuel systems were reduced. In fact, natural gas vehicles had been used for long time ago but they were not popular as gasoline and diesel vehicle systems. Figures 2.4 and 2.5 show natural gas vehicles over the time.



**Figure 2.4** Natural gas vehicles in the past; the first natural gas vehicle 1910 (USA) with balloon tank on trailer (left) and natural gas vehicle ~1930 (France) with balloon tank on roof (right) (Pfeifer, 2011).



**Figure 2.5** Natural gas vehicles in the present and future; current natural gas vehicle with high-pressure in trunk (left) and future natural gas vehicle with low-pressure tank in unused space (right) (Pfeifer, 2011).

## 2.4 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 synergy 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 (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. 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).

## 2.5 Adsorption Isotherms

Adsorption is usually described through isotherms to determine the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass (or specific surface area) of the adsorbent to allow comparison of different materials. Many different types of isotherm can be observed by their unique characteristic, which depends on types of adsorbate, types of adsorbent and intermolecular interactions between the gas and the surface. When a gas comes into 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).

### 2.5.1 Measurement of Adsorption Isotherms

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. 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.

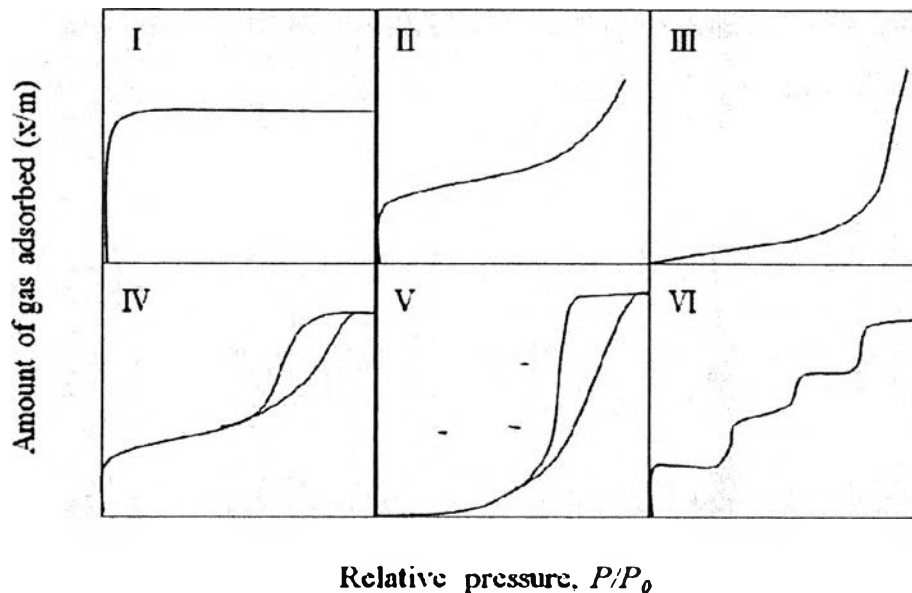
ANG storage capacity is usually expressed in terms of volumes of gas stored per unit storage volume ( $v/v$ ) (Esteves *et al.*, 2008). The volume of an adsorbed gas, at a constant pressure and temperature is determined. First, determine the 'dead space' or volume of the bulb by admitting some non-adsorbing (or weakly adsorbing) gas such as helium. Then, after evacuating the bulb, the gas of interest is admitted into the bulb. This is done at a constant pressure and temperature. The volume admitted into the bulb minus the dead space is the amount adsorbed. The advantages of this method are a relatively simple construction and a good heat contact between the adsorbent and the cooling (or heating) device.

#### 2.5.2 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. In 1940, the first systematic interpreting adsorption isotherm for gas-solid equilibria was introduced by Brunauer, Deming, Deming, and Teller (BDDT). They classified isotherms into five types. These BDDT isotherms and 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 2.2 and Figure 2.6, respectively. The BDDT and IUPAC classification have two deficiencies: they are incomplete and they give the incorrect impression that adsorption isotherms are always monotonic functions of pressure (Soo-Jin and Min-Kang, 2011).

**Table 2.2** 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 ( $\approx$ 50 nm)
IV	Relatively strong	Mesopores (2-50 nm)
V	Weak	Mesopores, Micropores
VI	Relatively strong	Nonporous



**Figure 2.6** IUPAC classification of adsorption isotherms (Soo-Jin and Min-Kang, 2011).

Type I isotherms characterize microporous adsorbents. Types II and III describe adsorption on macroporous adsorbents with strong and weak adsorbate-

adsorbent interactions, respectively. Types IV and V represent adsorption isotherms with hysteresis. Finally, Type VI has many steps (Soo-Jin and Min-Kang, 2011).

The classification of pores, according to their size, which is recommended by IUPAC, is described below:

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

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

c. 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.

## 2.6 Adsorbents

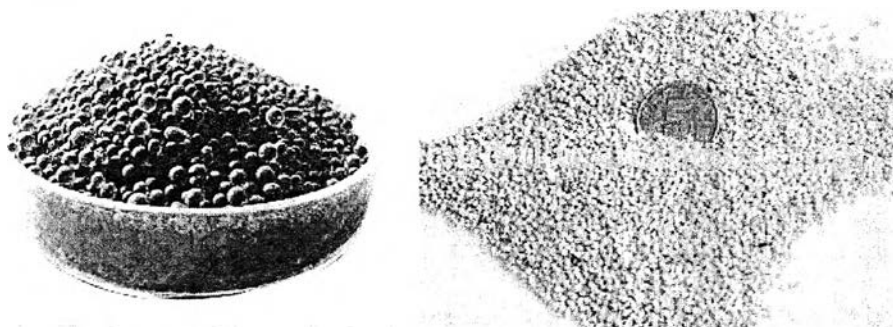
Adsorbents are usually in the form of spheres, pellets, powder, granules, or monoliths. They must have high abrasion resistance, high thermal stability, and small pore diameters, which results in high surface area and high surface capacity for adsorption. The adsorbents must also have a distinct pore 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 (en.wikipedia.org).

### 2.6.1 Silica Gel

Silica gel is granular, vitreous, porous form of silicon dioxide made synthetically from sodium silicate. Silica gel is tough and hard; it is more solid than common household gels like gelatin or agar. It is a naturally occurring mineral that is purified and

processed into either granular or beaded form. Silica gel is often described as "absorbing" moisture, which may be appropriate when the gel's microscopic structure is ignored, as in silica gel packs or other products. However, as material silica gel removes moisture by adsorption onto the surface of its numerous pores rather than by absorption into the bulk of the gel (en.wikipedia.org).

Silica gel is a chemically inert, nontoxic, polar and dimensionally stable (< 400 °C or 750 °F) amorphous form of  $\text{SiO}_2$ . It is prepared by the reaction between sodium silicate and acetic acid, which is followed by a series of after-treatment processes such as aging, pickling, etc. These, after treatment methods, results in various pore size distributions. Silica is used for drying of process air (e.g. oxygen, natural gas) and adsorption of heavy (polar) hydrocarbons from natural gas. Figure 2.7 shows silica gel typically hydrophilic.



**Figure 2.7** Silica gel is a commonly used desiccant as beads packed in a permeable bag (en.wikipedia.org).

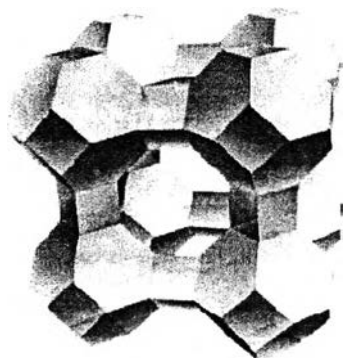
### 2.6.2 Zeolites

Zeolites are microporous, aluminosilicate minerals widely used as commercial adsorbents. The molecular sieves are crystalline, highly porous materials, which belong to the class of aluminosilicates. These crystals are characterized by a three-dimensional pore system with pores of precisely defined diameter. The corresponding crystallographic structure is formed by tetrahedras of  $(\text{AlO}_4)$  and  $(\text{SiO}_4)$ . These tetrahedras are the basic building blocks for various zeolite structures, such as zeolites A and X, the most common commercial adsorbents.

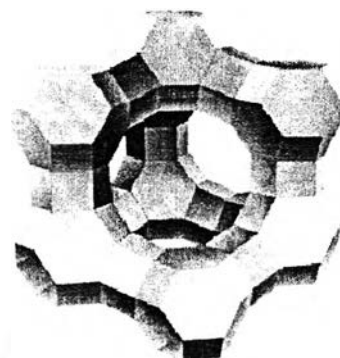


Figure 2.8 shows the microporous molecular structure of a zeolite ([www.grace.com](http://www.grace.com)). Zeolites are widely used in industry for water purification, as catalysts, for the preparation of advanced materials and in nuclear reprocessing. They are used to extract nitrogen from air to increase oxygen content for both industrial and medical purposes. Their biggest use is in the production of laundry detergents. They are also used in medicine and in agriculture.

Zeolites have a porous structure that can accommodate a wide variety of cations, such as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and others. These positive ions are rather loosely held and can readily be exchanged for others in a contact solution. Some of the more common mineral zeolites are analcime, chabazite, clinoptilolite, heulandites, natrolite, phillipsite, and stilbite. An example mineral formula is:  $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10} \cdot 2\text{H}_2\text{O}$ , the formula for natrolite.



Molecular Sieve Type A



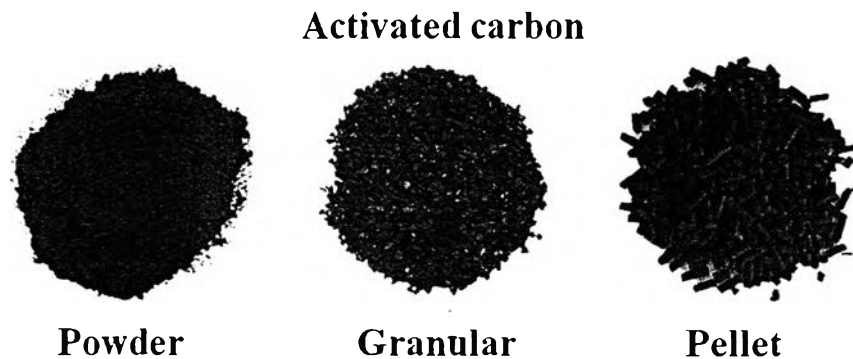
Molecular Sieve Type X

**Figure 2.8** Zeolites A and X, the most common commercial adsorbents ([www.molecularsieve.org](http://www.molecularsieve.org)).

### 2.6.3 Activated Carbon

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 2.9 shows activated carbons in powdered, granular, and pelletized forms, respectively.



**Figure 2.9** Commercial activated carbon from coconut shells-based precursor in powdered, granular, and pelletized forms ([www.chemechel.com](http://www.chemechel.com)).

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).

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.

#### *2.6.3.1 Physical Activation*

Physical activation of activated carbon consists of two steps: the first step is the elimination of most hydrogen and oxygen contents by pyrolysis of carbonaceous material at high temperature and inert atmosphere. The second step is to activate the chars at high temperature and in presence of steam or carbon dioxide

as oxidizing gasses. 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.

#### 2.6.3.2 Chemical Activation

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.

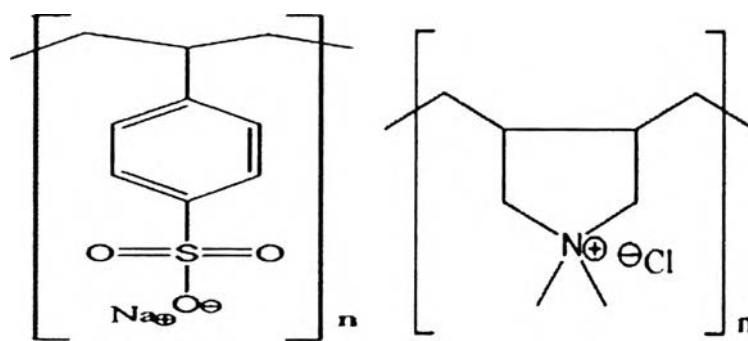
On the other hand, combination of chemical and physical activation is another technique to prepare highly microporous activated carbon. This method of activation is a powerful technique for controlling and developing similar micropore, which enhances the overall adsorption capacity of the activated carbon (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 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 (Namvar-Asl *et al.*, 2008).

#### 2.6.4 Polymer-Based Compounds

A polymer is a large molecule composed of repeating subunits bound together by covalent bonds. The adsorption of ions and molecules to polymer surfaces plays a role in many applications including: biomedical, structural, and

coatings. Different polymer surfaces have different side chains on their monomers that can become charged due to the adsorption or dissociation of adsorbates. For example, polystyrene sulfonate has monomers containing negatively charged side chains, which can adsorb positively charged adsorbates. Polystyrene sulfonate will adsorb more positively charged adsorbate than negatively charged. Conversely, for a polymer that contains positively charged side chains, such as (polydiallyldimethylammonium chloride), negatively charged adsorbates will be strongly attracted. Figure 2.10 shows the structure of different polymer surfaces (en.wikipedia.org).



**Figure 2.10** Shows the structure of different polymer surfaces; sodium polystyrene sulfonate (left) and Polydiallyldimethylammonium chloride (right) (en.wikipedia.org).

From Figure 2.10, the structure of sodium polystyrene sulfonate is shown (left). When this salt is dissolved in a solvent, the negatively charged side group can adsorb positively charged adsorbates and the structure of polydiallyldimethylammonium chloride (polyDADM<sup>+</sup>Cl<sup>-</sup>) (right). When the salt is dissolved in a solvent, the positively charged side group can adsorb negatively charged adsorbates.

Adsorption of molecules onto polymer surfaces is central to a number of applications, including development of non-stick coatings and in various biomedical devices. Polymers may also be adsorbed to surfaces through polyelectrolyte adsorption. One of the defining features of polymer surfaces and coatings is the chemical regularity of the surface. While many materials can be irregular mixtures of different components, polymer surfaces tend to be chemically uniform, with the same distribution of different

functional groups across all areas of the surface. Because of this, adsorption of molecules onto polymer surfaces can be easily modeled by the Langmuir or Frumkin Isotherms ([en.wikipedia.org](http://en.wikipedia.org)).

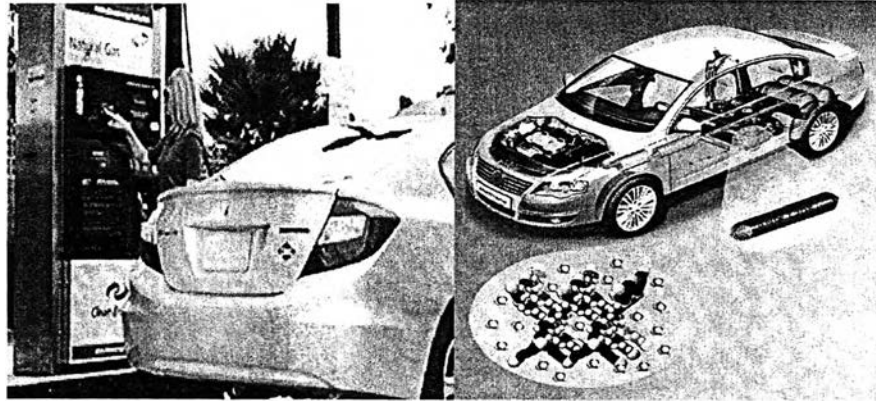
#### 2.6.5 Metal-Organic Frameworks (MOFs)

Metal-organic frameworks also known as coordination polymers, consist of metal or metal-ion vertices, connected by organic molecules, popularly known as organic linkers. There are numerous varieties of MOFs that have been synthesized using different molecular building blocks but only a fraction of them can be employed for hydrogen storage applications (Dipendu and Shuguang, 2010). The MOFs are crystalline compounds consisting of metal ions or clusters coordinated to often rigid organic molecules to form one-, two-, or three-dimensional structures that can be porous. In some cases, the pores are stable during elimination of the guest molecules (often solvents) and can be used for the storage of gases such as hydrogen and carbon dioxide. Other possible applications of MOFs are in gas purification, in gas separation, in catalysis and as sensors.

The general trend in MOFs used for hydrogen storage is that the greater the surface area, the more hydrogen the MOF can store. This is because high surface area materials tend to exhibit increased micropore volume and inherently low bulk density, allowing for more hydrogen adsorption to occur. In a microporous material where physisorption and weak van der Waals forces dominate adsorption, the storage density is greatly dependent on the size of the pores. Most recently, a new type of adsorbents, metal-organic frameworks (MOFs), were synthesized with numerous unique characteristics including extremely high surface area, uniform size distribution with median pore size less than 2 nm, large pore volume and promising adsorption properties for hydrogen storage and gas separation and purifications (Saha and Deng, 2010).

In this critical review, they provide the application of these two types of advanced porous materials in the storage of methane. Examples of materials exhibiting high methane storage capacities are analyzed and methods for increasing the applicability of these advanced porous materials in methane storage technologies described ([pub.rsc.org](http://pub.rsc.org)). MOFs provide a solution to this issue by enabling higher storage capacities at much lower pressures. This reduces the strength requirements on tanks, so they can be much lighter and be shaped to fit the free space available. The lower storage

pressure means that the heavy, expensive refueling infrastructure is no longer required and opens up the possibility of refuelling in the home, from domestic gas supplies ([www.moftechnologies.com](http://www.moftechnologies.com)). Figure 2.11 shows a tank filled with MOF material.



**Figure 2.11** A tank filled with MOF material can store much more gas than an empty tank ([growingtexas.tamu.edu](http://growingtexas.tamu.edu)).

## 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 economical 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 temperature and pressure up to 500-600 psi (Rashidi *et al.*, 2011). Due to adsorption of methane

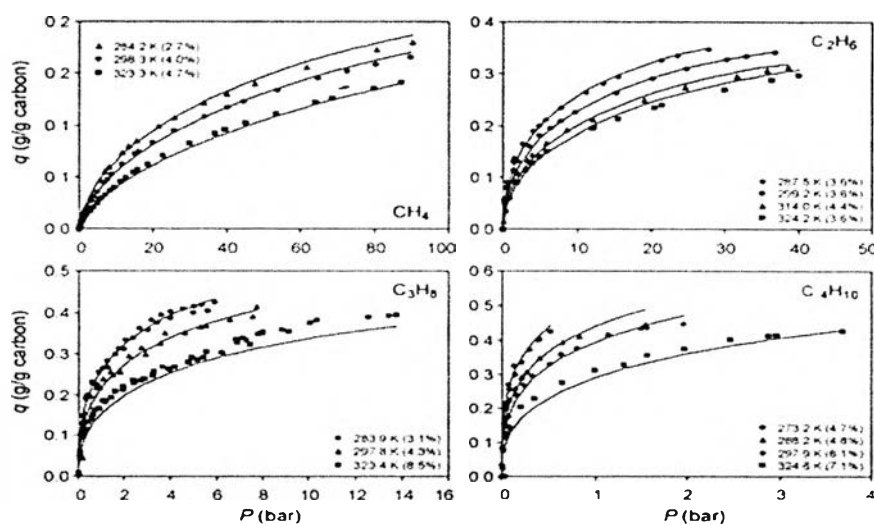
on activated carbon adsorbent is an exothermic phenomenon, the stored methane capacity is sensitive to the heat limitation. When the pressure continually increases from 500 to 1,500 psi, the stored methane capacity increased about 42% from 120 to 160 v/v. As temperature increases from 25 to 30 °C, reducing the stored methane capacity about 72% from 120 to 70 v/v (Bagheri and Abedi, 2011).

The granular activated carbon for adsorbing natural gas 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. 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 (Prauchner and Rodríguez-Reinoso, 2008). 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).

Since natural gas is composed of about 85-95% of methane mixed with other components, an important regression of the storage performance is observed after adsorption/desorption cycles of an ANG system (filling/delivery or charge/discharge). It is the result of adsorption of the other components present in natural gas that are mainly higher molecular weight hydrocarbons, carbon dioxide, and nitrogen (Pupier *et al.*, 2005). The higher molecular weight species are more strongly adsorbed than methane, especially in the low-pressure region. These higher molecular weight components will be preferentially adsorbed on activated carbon

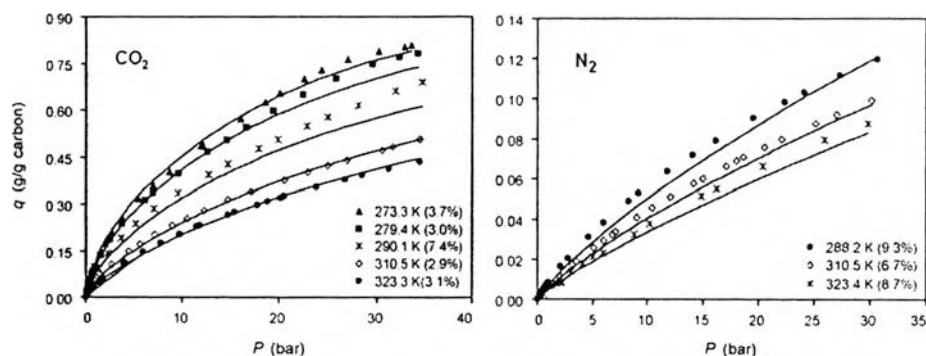
and therefore the amount of methane that can be delivered by the storage system will decrease (Najibi *et al.*, 2008).

The basic information required to design an ANG storage system is the adsorption equilibria of the various species involved. Equilibrium data for single-component adsorption of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_6$ ,  $\text{C}_3\text{H}_8$ ,  $\text{C}_4\text{H}_{10}$ ,  $\text{CO}_2$ , and  $\text{N}_2$  on an activated carbon was covered with a wide range of thermodynamic conditions (0-10,000 psi and 0-50 °C). The single-component adsorption isotherms for  $\text{C}_1$ - $\text{C}_4$  alkanes,  $\text{CO}_2$  and  $\text{N}_2$ , were measured using a standard static gravimetric procedure. Briefly, the method consisted of subjecting the adsorption chamber to pressurization/depressurization steps with the pure gaseous adsorbate, each followed by equilibration under isothermal conditions, to generate points along the adsorption isotherms. Pressure and weight change were continuously monitored until equilibrium was reached, which was assumed to be attained when the rate of the measured mass change approached zero. The procedure was repeated until there were enough points to generate the isotherms (Esteves *et al.*, 2008). Figures 2.12 and 2.13 show single-component adsorption isotherms for the n-alkanes  $\text{C}_1$ - $\text{C}_4$  and for  $\text{CO}_2$  and  $\text{N}_2$ , respectively. The shape of the adsorption isotherms is classified as type I (monotonically concave isotherms) in the IUPAC classification, which is typically characteristic of a microporous adsorbent.



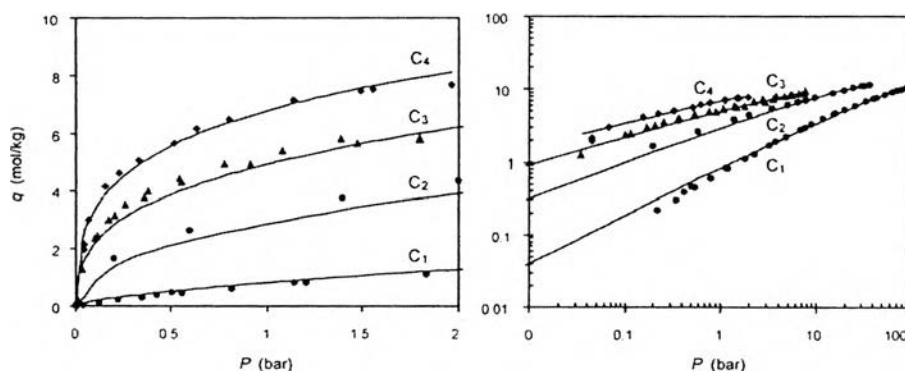
**Figure 2.12** Single-component adsorption isotherms for the n-alkanes  $\text{C}_1$ - $\text{C}_4$  (Esteves *et al.*, 2008).





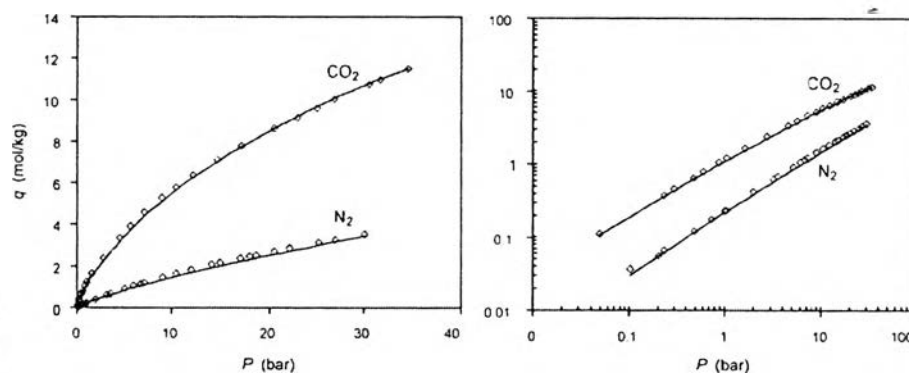
**Figure 2.13** Single-component adsorption isotherms for  $\text{CO}_2$  and  $\text{N}_2$  (Esteves *et al.*, 2008).

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 2.14 compares the single-component adsorption isotherms for the n-alkanes  $\text{C}_1$ - $\text{C}_4$  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 2.14** Comparative of adsorption isotherms for the n-alkanes C<sub>1</sub>-C<sub>4</sub> at 25 °C (Esteves *et al.*, 2008).

Figure 2.15 compares the single-component adsorption isotherms for CO<sub>2</sub> and N<sub>2</sub> at 37 °C. There is no distinction between experimental adsorption and desorption data.



**Figure 2.15** Comparative of adsorption isotherms for CO<sub>2</sub> and N<sub>2</sub> at 37 °C (Esteves *et al.*, 2008).

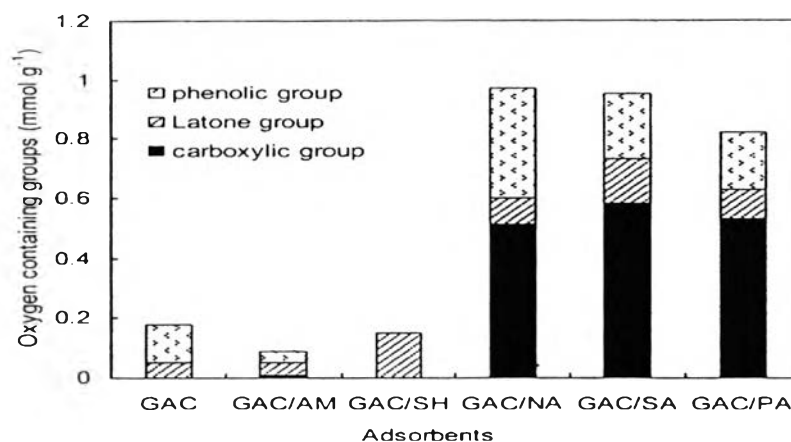
Daud *et al.* (2004) compared properties of activated carbons produced from palm shell and coconut shell in terms of pore size distribution of micro, meso, and macropores. Both types of activated carbons were prepared using the same process. The activation rate of coconut shell char is almost five times 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-Neto *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 favourable. 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 absorption would increase with the SSA of both temperatures. Therefore, SAA 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 favourable 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<sub>3</sub> and NaOH were used to modify activated carbon. In addition, the effects of surface modification on the activated carbon properties, such as specific surface area (SSA), total acidity capacity, and carbon pH were studied. The results of HCl, HNO<sub>3</sub>, 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<sub>3</sub> 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 ammonia, sodium hydroxide, nitric acid, sulphuric acid, and phosphoric acid to determine suitable modification for improving adsorption ability of hydrophobic volatile organic compounds (VOCs) on granular activated carbons (GAC). Li *et al.* (2011) found that 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 GACs 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 2.16 (Li *et al.*, 2011).



**Figure 2.16** Surface functional groups of various GAC (mmol/g) (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.

In 2000, the U.S. Department of Energy (DOE) set the target for material-based adsorbed methane storage at 180 cm<sup>3</sup> at 298 K and 35 bar. In terms of energy density, this volumetric storage capacity target is comparable to methane compressed at 250 bar (298 K). Two major classes of porous materials have been traditionally considered for methane storage: zeolites and porous carbon materials. Some porous carbon materials have been recently reported to modestly meet the DOE target, yet the potential to further improve their storage capacities is limited because of the difficulty in increasing their already high surface areas, which are known to strongly correlate with the methane uptake in these materials. In recent years, a new family of physisorptive materials, porous metal-organic

frameworks (MOFs) or coordination polymers in a broader sense, have emerged as promising adsorbents for methane storage (Zhou, 2011).

Metal-organic frameworks (MOFs), a new family of nanoporous materials, have emerged as the promising materials for gas storage, separation, and catalysis (Xue *et al.*, 2009). MOFs have very high capacity for hydrogen at 77 K. The higher heat of adsorption for methane allows the storage of significant amounts even at room temperature. While the number of methane adsorption studies on MOFs by physisorption is high, there is still only little insight in the mechanisms and location of methane molecules inside MOFs. In-situ diffraction studies were used as a valuable tool to determine the location of adsorbed molecules in the framework at low temperatures (Juergen *et al.*, 2010).

This technique has been successfully applied to study the adsorption of gases in zeolites and more recently has been extended to study the adsorption of hydrogen in MOFs. Thus, for MOF-5,  $\text{Cu}_3(\text{btc})_2$  (btc = 1,3,5-benzene tricarboxylate),  $\text{Cu}_3[\text{Co}(\text{CN})_6]_2$  and  $\text{Mn}_3[(\text{Mn}_4\text{Cl})_3(\text{btt})\text{CH}_3\text{OH}]_{10}2$  (btt = 1,3,5-benzene tristetrazolate)12 hydrogen (or deuterium,  $\text{D}_2$ ) was located by neutron diffraction. According to their studies,  $\text{Cu}_3(\text{btc})_2$  is highly efficient for methane storage due to a trimodal pore size distribution. At lower pressure, the smaller pores and, the open metal centers result in strong interaction, whereas at higher pressure there is still room for increasing capacity due to the filling of the larger pore. Compared to other MOF materials,  $\text{Cu}_3(\text{btc})_2$  also has a high volumetric adsorption capacity. The latter indicates efficient packing of methane inside the pores (Juergen *et al.*, 2010).

A variety of MOFs have been screened for methane storage, but only a few can reach the DOE target. For example, Düren *et al.* (2004) proposed a theoretical MOF (IRMOF-993) with a methane adsorption capacity of 181 v(STP)/v. Ma *et al.* (2008) synthesized a MOF named PCN-14 that gave the highest methane adsorption capacity of 230 v(STP)/v so far. It seems that MOFs are a class of promising materials with practical applications in methane storage. The catenation structure strengthens the gas affinity for the material by an entrapment mechanism that improves the gas adsorption capacity and separation. Thus, catenation appears to be a useful strategy for designing new MOFs as efficient methane storage materials. Based on this consideration, a systematic molecular simulation study is performed in this work to investigate the effect of catenation on methane storage capacity to provide useful information for further MOFs development

with improved methane storage capacity. As a result, a rational combination of catenation with chemical composition may lead to new MOFs with large methane storage capacity (Xue *et al.*, 2009).

In the majority of MOF compounds (such as MOF-5), the methane binding on the pore surface is of weak van der Waals type, as is the case for most other methane sorbents. Consequently, the pore coverage is relatively “homogenous” upon methane adsorption, and indeed the total uptake strongly correlates with the pore surface area, as also found by Snurr’s group via molecular simulations for several MOFs (Düren *et al.*, 2004). Table 2.3 shows structural characteristics and methane adsorption properties of several benchmark MOF compounds.

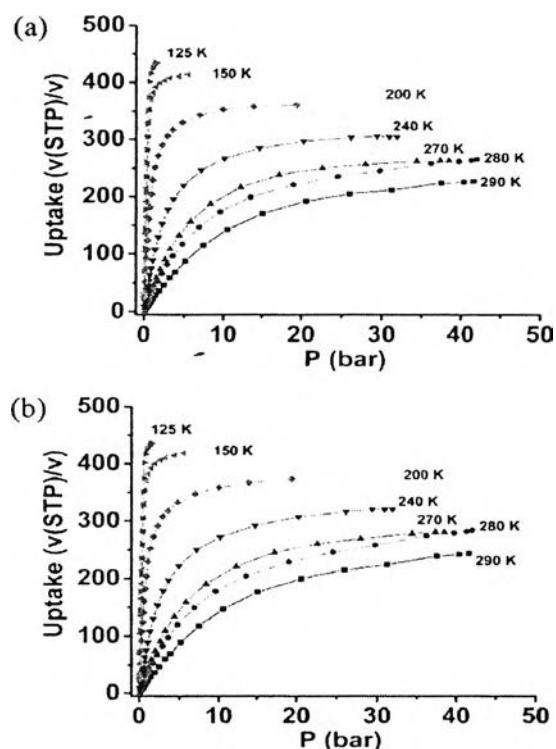
**Table 2.3** Structural characteristics and methane adsorption properties of several benchmark MOF compounds. PCN-14 is the current record holder in terms of storage capacity (Zhou, 2011)

	crystal density (g/cm <sup>3</sup> )	N <sub>2</sub> BET surface area (m <sup>2</sup> /cm <sup>3</sup> )	excess, volumetric/gravimetric CH <sub>4</sub> adsorption capacity [cm <sup>3</sup> (STP) /cm <sup>3</sup> /cm <sup>3</sup> (STP)/g]	Initial $Q_{st}$ (kJ/mol)
MOF-5 <sup>10</sup>	0.59	1870	110/185 (300 K, 36 bar)	12.2
HKUST-1 <sup>11</sup>	0.88	1511	160/181 (298 K, 35 bar)	18.2
MIL-53-Cr <sup>12</sup>	1.04	1144	165/159 (304 K, 35 bar)	17.0
PCN-11 <sup>14</sup>	0.75	1446	171/228 (298 K, 35 bar)	14.6
Ni-MOF-74 <sup>15</sup>	1.21	1240	190/158 (298 K, 35 bar)	20.2
PCN-14 <sup>13</sup>	0.83	1453	220/252 (290 K, 35 bar)	30.0

Methods to investigate the CH<sub>4</sub> adsorption in several of the above-mentioned benchmark MOF materials: MOF-74, HKUST-1, PCN-11, and PCN-14 (Wu *et al.*, 2009). These MOFs contain two types of unique surface sites that can strongly attract and store methane molecules. One is the coordinatively unsaturated

metal ions, and the other is what we call “enhanced van der Waals potential pockets (with a pocket dimension comparable to the kinetic diameter of methane,  $\approx 3.8 \text{ \AA}$ ). Considering the relatively short history of MOFs, the progress on applying these materials for methane storage has been impressive. The reported volumetric methane storage capacities of PCN-14 and Ni-MOF-74 have, in principle, already surpassed the DOE target, and clearly demonstrated the great potential of MOFs for methane storage in general (Zhou, 2011).

A microporous metal-organic framework, PCN-14, based on an anthracene derivative, 5,5'-(9,10-anthracenediyl)di-isophthalate (H4adip), was synthesized under solvothermal reaction conditions. Methane adsorption studies at 290 K and 35 bar show that PCN-14 exhibits an absolute methane-adsorption capacity of 230 v/v, 28% higher than the DOE target (180 v/v) for methane storage. Figure 2.17 shows high-pressure methane sorption isotherms at various temperatures.



**Figure 2.17** High-pressure methane sorption isotherms at various temperatures (a) excess adsorption; (b) absolute adsorption (Shengqian *et al.*, 2007).



From Figure 2.17, the methane saturation uptake of both excess adsorption and absolute adsorption decrease with increasing temperatures. The saturation of excess methane adsorption in PCN-14 at 125 K can reach 434 v(STP)/v, which corresponds to an adsorbed methane density of 310 mg/mL. The density is 73.4% of that of liquid methane (422.6 mg/mL) at 113 K. At 290 K and 35 bar, the excess adsorption capacity of methane in PCN-14 is 220 v(STP)/v, corresponding to an absolute adsorption capacity of 230 v(STP)/v. The excess methane adsorption value is 22% higher than the DOE target of 180 v(STP)/v for methane (Shengqian *et al.*, 2007). PCN-14 exhibits the highest methane uptake capacity among reported porous materials for methane adsorption (Düren *et al.*, 2004).

Qing *et al.* (2011) used in a cigarette filter activated carbon can selectively remove a number of the vapor phase compounds to varying degrees of efficiency. To improve the wet-feeling of cigarette smoke with AC in the filter, a new method is developed to chemically functionalize a coal-based activated carbon (AC) based on silanization reaction. They aim to restrict the water adsorption capacity of ACs by creating more hydrophobic surface group.