# CHAPTER II

# THEORETICAL BACKGROUND AND LITERATURE REVIEW

## 2.1 Natural Gas

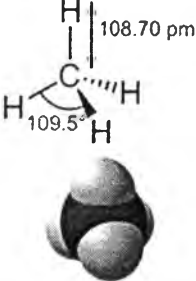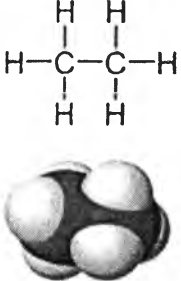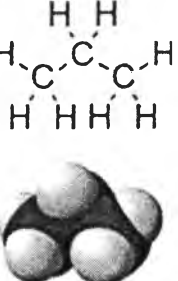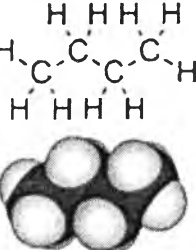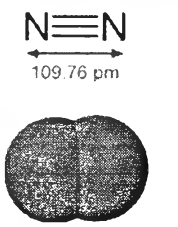Natural gas is composed mainly by 85-95% methane ($CH_4$), the remainder being carbon dioxide ($CO_2$), nitrogen ($N_2$), and small amounts of higher molecular weight hydrocarbons, such as ethane ($C_2H_6$), propane ($C_3H_8$), and butane ($C_4H_{10}$) (Esteves *et al.*, 2008). In its purified form, natural gas is colorless, odorless and cannot be liquefied at ambient temperature ($T_c$ = -82.6 °C). Natural gas is an attractive alternative fuel for a number of reasons. It is extremely clean-burning compared with other oil-based fuels like gasoline and diesel, which generate harmful emissions, causing pollution and contributing to the greenhouse effect. Moreover, natural gas is also readily available in much of the world (http://all-craft.missouri.edu/Presentations/Poster_Eastman_Howard.pdf, last visited on 10 Jun 2012). In the automotive sector, natural gas provides a secure, clean, and efficient combustion, practically free of sulfur and lead oxides, benzene, and solid particles. Also, carbon dioxide and carbon monoxide emission levels can be reduced by 23% and 85% relative to conventional vehicles (Esteves *et al.*, 2008). 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.

Table 2.1 Typical composition of natural gas (http://www.naturalgas.org, last visited on 10 Jun 2012)

| Constituent | Composition (vol%) |
| --- | --- |
| Methane, $CH_4$ | 70-90 |
| Higher molecular weight hydrocarbons | 0-20 |
| Carbon dioxide, $CO_2$ | 0-8 |
| Nitrogen, $N_2$ | 0-5 |
| Other gases ($O_2$, S, and etc.) | trace |

Table 2.2 shows the characteristics of natural gas components, which are $CH_4$, $C_2H_6$, $C_3H_8$, $C_4H_{10}$, $CO_2$, and $N_2$, respectively.

**Table 2.2** Characteristics of natural gas components (http://www.wikipedia.org, last visited on 5 Jun 2012)

| Chemical name | Methane, $CH_4$ | Ethane, $C_2H_5$ | Propane, $C_3H_8$ |
|---|---|---|---|
| Molecular structure | | | |
| Molecular shape | Tetrahedron | Tetrahedron | Tetrahedron |
| Molar mass | 16.04 g/mol | 30.07 g/mol | 44.1 g/mol |
| Density | 0.6556 mg/mL | 1.3562 mg/mL | 2.0098 mg/mL |
| Melting point | -182 °C | -183 °C | -188 °C |
| Boiling point | -164 °C | -89 °C | -42 °C |
| Critical temperature | -82.7 °C | 32.2 °C | 96.6 °C |
| Solubility in water | 22.7 mg/L | 56.8 mg/L | 40 mg/L (at 0 °C) |
| Kinetic diameter | 3.8 A° | 4.0 A° | 4.3 A° |
| Polarizability | $26.0 \times 10^{-25}$ cm$^3$ | $44.7 \times 10^{-25}$ cm$^3$ | $62.9 \times 10^{-25}$ cm$^3$ |
| Chemical name | Butane, $C_4H_{10}$ | Carbon dioxide, $CO_2$ | Nitrogen, $N_2$ |
| Molecular structure | | | |
| Molecular shape | Tetrahedron | Linear | Linear |
| Molar mass | 58.12 g/mol | 44.01 g/mol | 28.01 g/mol |
| Density | 2.48 mg/mL | 1.977 mg/mL | 1.251 mg/mL |
| Melting point | -140 °C | -78 °C | 210 °C |
| Boiling point | -1 °C | -57 °C | 195.8 °C |
| Critical temperature | 152 °C | 30.8 °C | -147.1 °C |
| Solubility in water | 61 mg/L (at 20 °C) | 1450 mg/L (at 25 °C) | 20 mg/L (at 20 °C) |
| Kinetic diameter | 4.3 A° | 3.3 A° | 3.6 A° |
| Polarizability | $82.0 \times 10^{-25}$ cm$^3$ | $25.1 \times 10^{-25}$ cm$^3$ | $17.1 \times 10^{-25}$ cm$^3$ |

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, $CH_4$ 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.

$$CH_4 (g) + 2O_2 (g) \rightarrow CO_2 (g) + 2H_2O (l) + 891 \text{ kJ} \qquad (2.1)$$

In 2004, Kavalov and coworkers studied 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 was bigger than oil reserve; therefore, natural gas was more abundant and accessible.

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

3. A multi-optional fuel technology

Over of 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 the 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

Three different categories are known for on-board natural gas storage: liquefied natural gas (LNG), compressed natural gas (CNG), and adsorbed natural gas (ANG). But only two methods are currently commercially applied: LNG and CNG (Ginzburg, 2006). Large-scale implementation of natural gas vehicle takes place in countries, where government applies massive subsidies and/or powerful administrative measures (at least for the initial development period).

### 2.2.1 Liquefied Natural Gas (LNG)

LNG is a known gas storage method. Natural gas is liquefied under pressure of 150-300 psi at -161.5 °C. LNG requires the use of complex and expensive liquefaction equipment, thermos-like tanks and significant energy consumption (25-35% of the original energy gas content) for the liquefaction and degasification. LNG storage tanks should have cylindrical or spherical shape. Due to a very distinctive advantage of scale, it is applied mainly in the marine transportation of very big quantities of gas. So, on-board LNG storage technology could be competitive only for heavy vehicles. This technology is not yet mature enough for massive use in vehicles. Several thousands LNG fueled heavy vehicles are operated around the world whereas LNG application for light vehicles is considered to be inefficient. On-board tank for a 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.

### 2.2.2 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. 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.

2. The operation of a CNG station requires high energy consumption and very expensive maintenance.

3. 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.

4. 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)

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 became 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 (http://www.energtek.com/t/1008-ang-technology, last visited on 10 Jun 2012). 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.
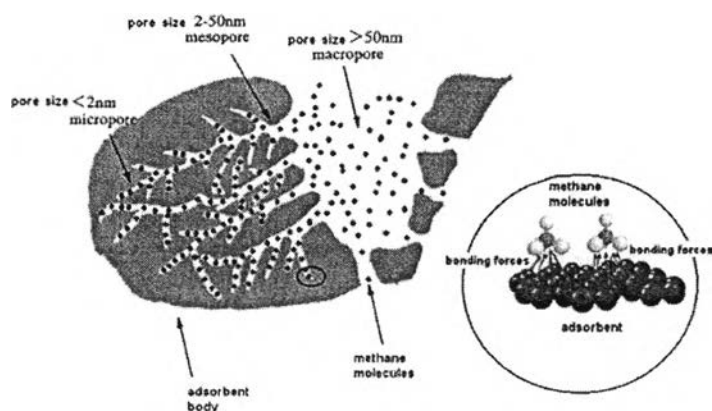
**Figure 2.1** Adsorption of methane molecules on the activated carbon adsorbent in micropore, mesopore, and macropore structures (http://www.greencar.com/articles/clean-burning-natural-gas-vehicles.php, last visited on 15 Jun 2012).

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. Figure 2.2 shows a prototype of ANG tank with monolithic activated carbons inside. ANG storage tank can be shaped into both cylindrical and non-cylindrical unlike CNG storage tank that must be in cylindrical shape only.
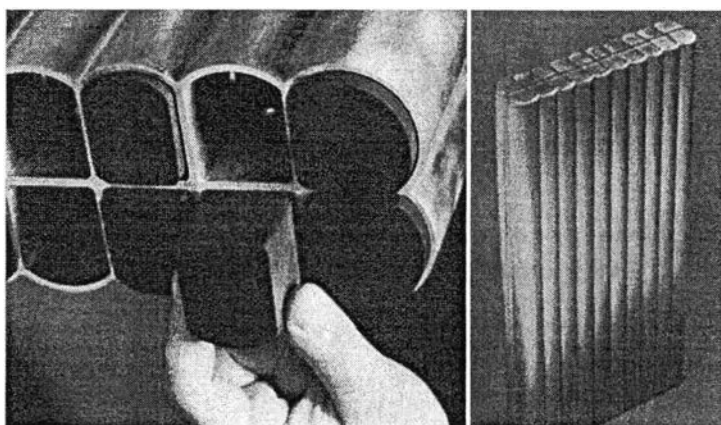


**Figure 2.2** A prototype of ANG tank with monolithic activated carbons inside (http://www.glnobledenton.com/assets/downloads/ANG_for_Vehicle_truck_DS.pdf, last visited on 10 Jun 2012).

ANG storage has many advantages compared to CNG storage (http://www.glnobledenton.com/assets/downloads/ANG_for_Vehicle_truck_DS.pdf, last visited on 10 Jun 2012) such as:

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 a 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 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 (http://www.energtek.com/t/ 1008-ang-technology, last visited on 10 Jun 2012) are:

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

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

3. 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:

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

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

3. 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 few last 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 (http://www.glnobledenton. com/assets/downloads/ANG_for_Vehicle_truck_DS.pdf, last visited on 10 Jun 2012). 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 the 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. For example, the experiment was carried out by using unmodified activated carbon and carbon nanotube adsorbents under high condition of 3,000-3,700 psi to prove the adsorbent abilities. Later, there are more studies and experiments to confirm the improvement of CNG by using ANG, so enhanced CNG can operate at lower pressure than normal CNG system by the new discovered adsorbent. However, there is none of the adsorbent system used for vehicle storage in Thailand.
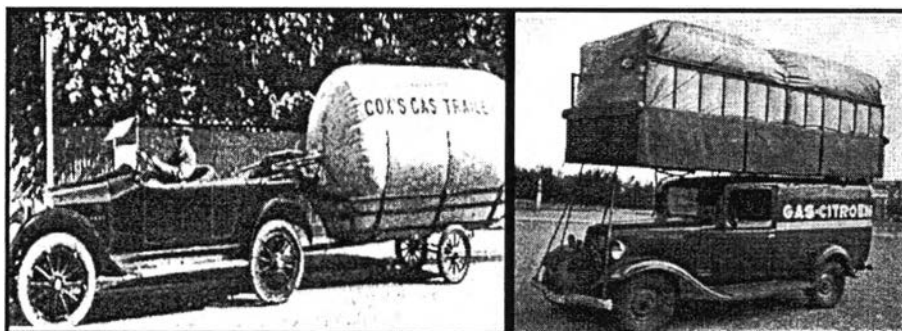
## 2.3 Natural Gas Vehicles (NGVs)

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. And for bi-fuel vehicles, the important point is they can also run on conventional fuel if natural gas fueling is not readily (http://www.greencar.com/articles/clean-burning-natural-gas-vehicles.php, last visited on 15 Jun 2012). 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.
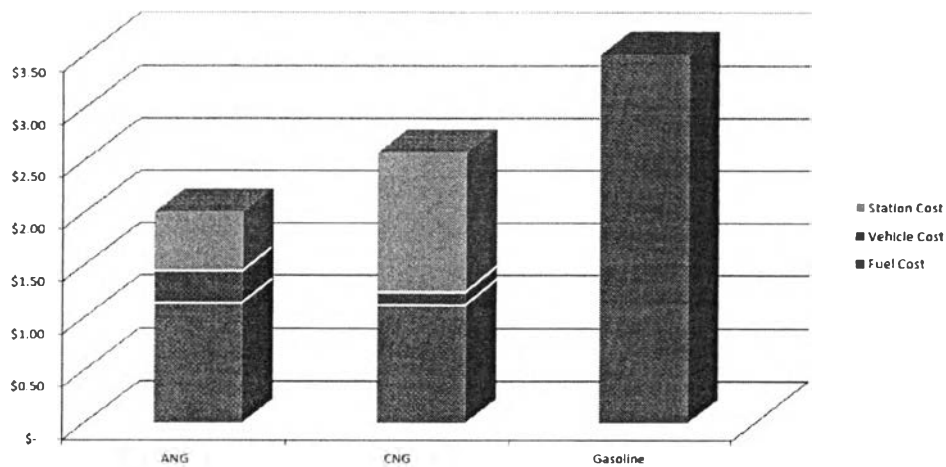
**Figure 2.3** Comparison between natural gas fuel systems and gasoline fuel system in terms of fuel, vehicle, and station costs (Pfeifer, 2011).

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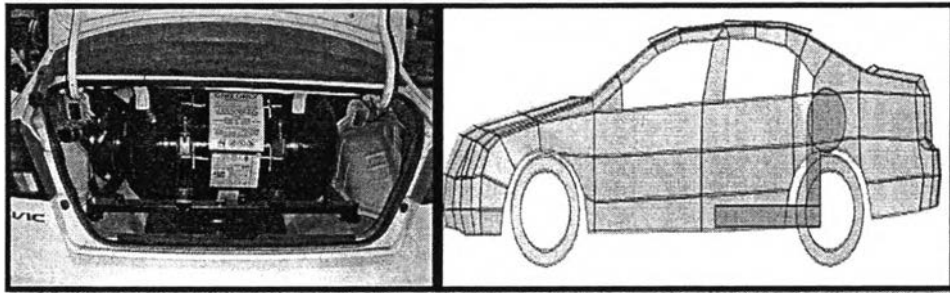
**Figure 2.5** Natural gas vehicles in the present and future; current natural gas vehicle with high-pressure in trunk (left) and future natural gas vehicle with low-pressure tank in unused space (right) (Pfeifer, 2011).

## 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 phemomenon. 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).

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.

## 2.5 Adsorption Isotherms

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 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 modern 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 2.6, respectively.

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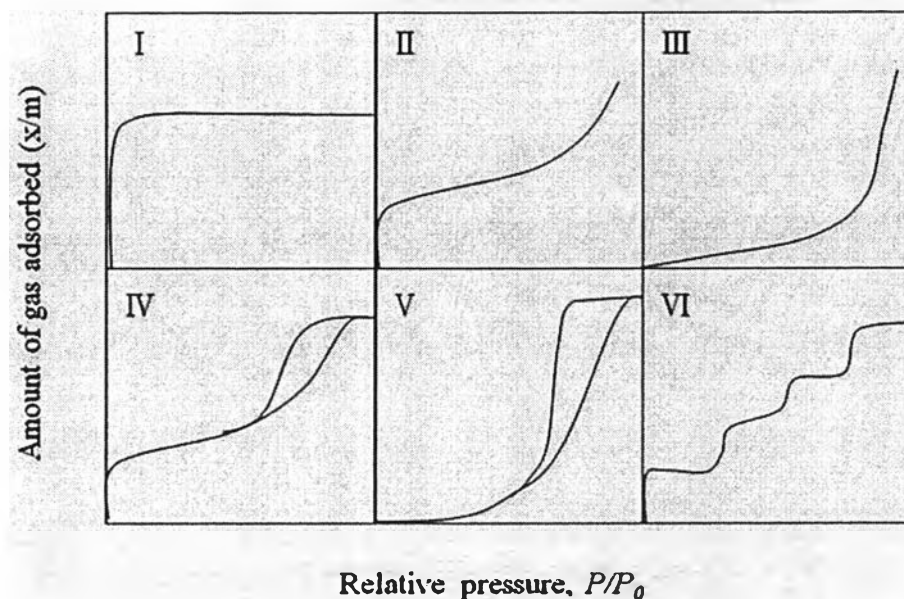
**Figure 2.6** IUPAC classification of adsorption isotherms (Soo-Jin and Min-Kang, 2011).

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.

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.

### 2.5.2 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 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.

## 2.6 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 (http://en.wikipedia.org/wiki/Adsorption, last visited on 5 Jun 2012).

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.

**Activated carbon**



**Powder**     **Granular**     **Pellet**
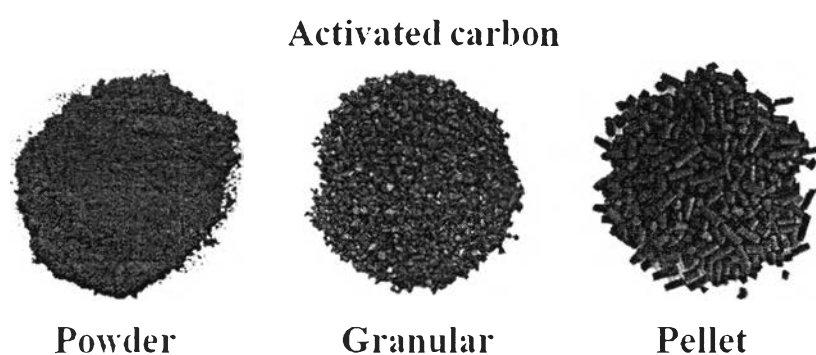
**Figure 2.7** Commercial activated carbon from coconut shells-based precursor in powdered, granular, and pelletized forms (http://www.chemechel.com/products.htm, last visited on 15 Jun 2012).

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 (http://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/43_3_ BOSTON_08-98_0575.pdf, last visited on 10 Jun 2012).

-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 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 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.

## 2.7 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 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 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 most successful adsorbent for methane storage is the well-known activated carbon designed as Maxsorb. The packing density of the activated carbon bed is 300 kg/m$^3$ in powder form and 700 kg/m$^3$ in monolith form. The total stored methane capacity is 101 and 172 v/v, respectively. And for an optimal pore size, the available methane capacity measured over an operating cycle and under specific conditions (15 psi, 5 °C) was close to 195 and 137 v/v for a monolithic carbon and a pelletized carbon, respectively (Biloé *et al.,* 2002). Monolithic carbon adsorbent used in non-cylindrical vessels have made possible to store the same capacity of methane as CNG tanks at much lower pressure (Vasiliev *et al.,* 2000). Although monolithic carbon is an ideal adsorbent for vehicle applications that exhibits small inter-particle space and maximum volumetric adsorption capacity, granular carbon involves

simpler and cheaper preparation procedures. Therefore, granular carbon is of great interest in large scale applications such as gas transportation (Prauchner and Rodríguez-Reinoso, 2008). The carbon precursors used to prepare activated carbons can also affect the adsorption capacity of methane. However, coconut shells were used as the carbon precursor to prepare activated carbon that owned higher $CO_2$ and $CH_4$ adsorption capacity than other precursors (Yang et al., 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).

Henry's Law selectivity at 30 °C displayed that the strength of adsorption of gases on the activated carbon increases in the order $CO_2 > CH_4 > N_2$. Hence, higher selectivity of adsorption of $CO_2$ over $CH_4$, and $N_2$. The selective permeation of the gases through the activated carbon (from the mixture) increases in the order $C_1 > C_2 > C_3 > C_4$, which is also the order of relative strengths of adsorption of these gases in the carbon (Sircar *et al.*, 1996).

Carbon dioxide more strongly adsorbs on activated carbon and has the heat of adsorption slightly larger than that of methane. The adsorption time scale for carbon dioxide is longer due to the combined effect of three factors: (i) the equilibrium capacity of carbon dioxide is higher; hence, it takes longer time to equilibrate the surface, (ii) carbon dioxide has higher molecular weight; hence, the mobility of carbon dioxide in the gas space is slower, and (iii) the surface diffusivity of carbon dioxide is smaller; hence, the mobility of the adsorbed carbon dioxide molecules is slower. The smaller surface diffusivity of carbon dioxide is associated with its higher affinity towards the carbon surface. The adsorbed methane molecule has smaller energy barrier than carbon dioxide does, and this could be due to the quadrupole moment of carbon dioxide compared to the non-polar nature of the methane molecule (Prasetyo and Do, 1998). The adsorption isotherms can reflect the adsorption capacity of the adsorbent. The $CO_2$ adsorption capacity increased rapidly with the change of pressure at 25 °C. However, the behavior of $CH_4$ adsorption was not same as that of $CO_2$ adsorption. The $CO_2$ and $CH_4$ adsorption capacity over the activated carbon were no more than 0.7 and 0.3 mmol/g, respectively, at 25 °C and 15 psi (Yang *et al.*, 2011).

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 $CH_4$, $C_2H_6$, $C_3H_8$, $C_4H_{10}$, $CO_2$, and $N_2$ 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 $C_1$-$C_4$ alkanes, $CO_2$ and $N_2$, were measured using a standard static gravimetric procedure. Briefly, the

method consists 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 are continuously monitored until equilibrium is reached, which is assumed to be attained when the rate of the measured mass change approaches zero. The procedure is repeated until there are enough points to generate the isotherms (Esteves *et al.*, 2008). Figures 2.8 and 2.9 show single-component adsorption isotherms for the n-alkanes $C_1$-$C_4$ and for $CO_2$ and $N_2$, 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.
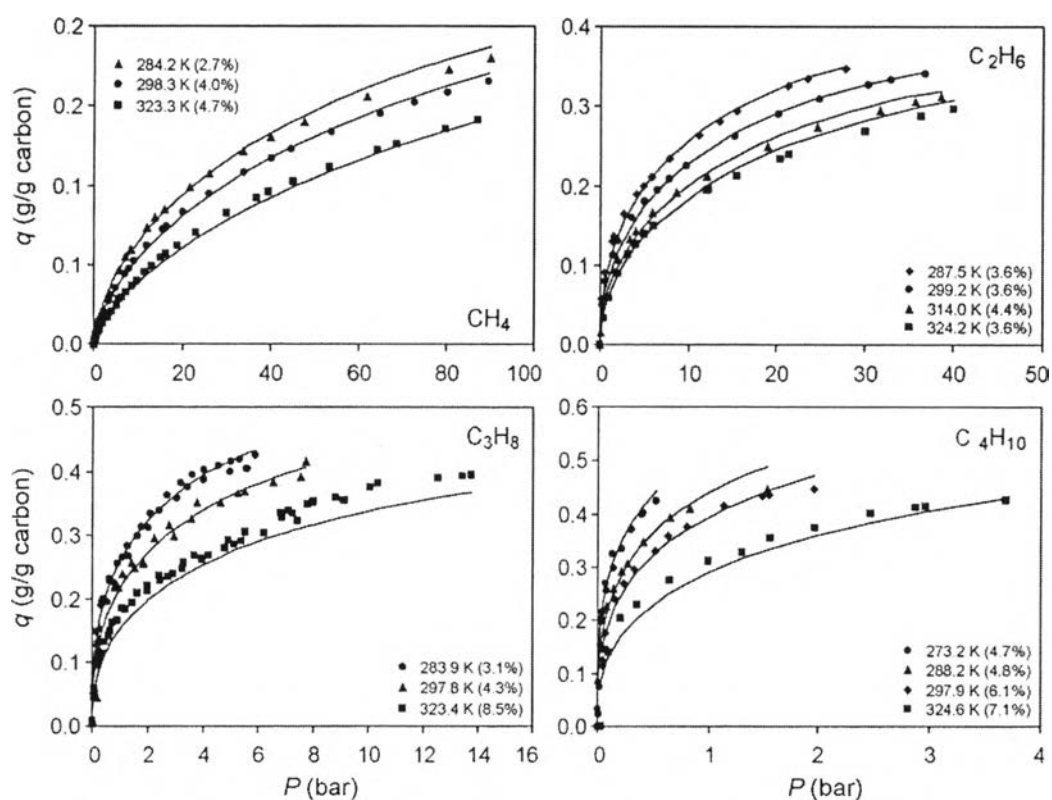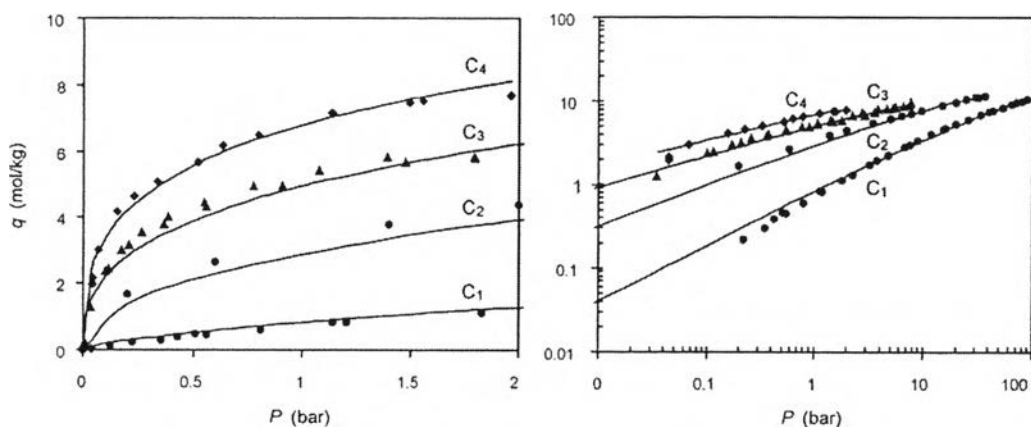


**Figure 2.8** Single-component adsorption isotherms for the n-alkanes $C_1$-$C_4$ (Esteves *et al.*, 2008).
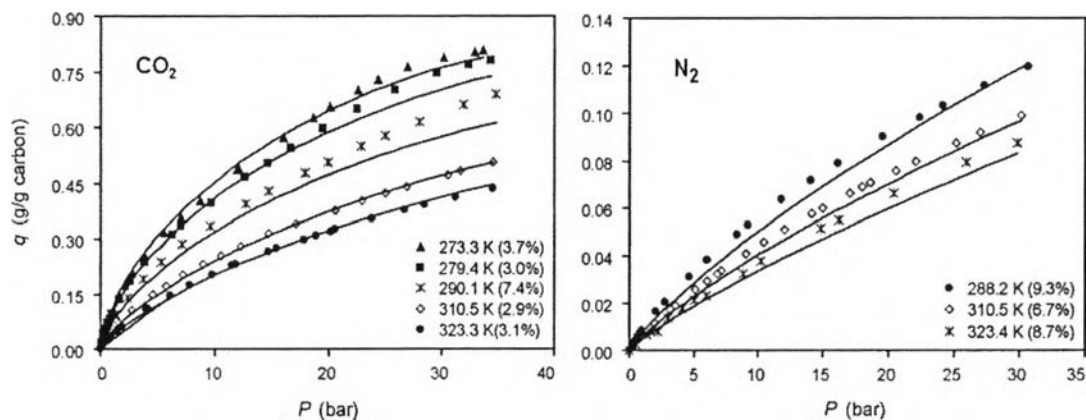
**Figure 2.9** Single-component adsorption isotherms for $CO_2$ and $N_2$ (Esteves *et al.*, 2008).

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 2.10 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 isotherms slope in the low-pressure region increase 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 2.10** Comparative of adsorption isotherms for the n-alkanes $C_1$-$C_4$ at 25 °C (Esteves *et al.*, 2008).

Figure 2.11 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.
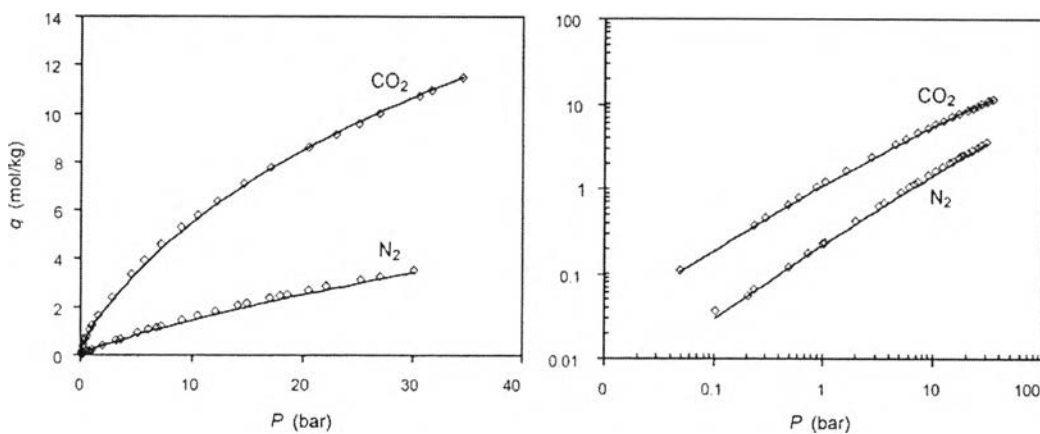


**Figure 2.11** Comparative of adsorption isotherms for $CO_2$ and $N_2$ at 37 °C (Esteves *et al.*, 2008).