# CHAPTER II

# LITERATURE REVIEW

## 2.1 Natural Gas

Natural gas is a type of fossil fuel originated from the decomposition of organic matter (naturalgas.org). It occurs in reservoirs under the surface of the earth. These underground organic matters are often found in combination with petroleum deposit. Natural gas is composed primarily of methane ($CH_4$), and also ethane ($C_2H_6$), propane ($C_3H_8$), butane ($C_4H_{10}$), pentane ($C_5H_{12}$). It often has nitrogen and carbon dioxide impurities are shown in Table 2.1.

Methane is colorless, odorless, and tasteless thus it is one of the cleanest, safest, and most useful of all energy sources. Unlike other fossil fuels, natural gas is an environmentally friendly due to its clean burning and emits lower levels of harmful byproducts (60-90% less smog-producing pollutants and 30-40% less greenhouse gas emissions).

**Table 2.1** Typical composition of Natural Gas (naturalgas.org)

| Component | Chemical Formula | Composition (% wt) |
|---|---|---|
| Methane | $CH_4$ | 70-90% |
| Ethane | $C_2H_6$ | 0-20% |
| Propane | $C_3H_8$ | |
| Butane | $C_4H_{10}$ | |
| Carbon Dioxide | $CO_2$ | 0-8% |
| Oxygen | $O_2$ | 0-0.2% |
| Nitrogen | $N_2$ | 0-5% |
| Hydrogen sulphide | $H_2S$ | 0-5% |
| Rare gases | A, He, Ne, Xe | trace |

Currently, natural gas is cheaper than conventional fuels (gasoline and diesel). Therefore, consumption of natural gas as a fuel for vehicle is rapidly increasing. However, natural gas has lower energy density than conventional and other alternative fuels at ambient conditions, which causes the driving range of natural gas based-fuels vehicle to be less than conventional vehicle.

The combustion of methane is shown as chemical equation 2.1. One molecule of methane is reacted with two molecules of oxygen, which in gaseous form to form one molecule of carbon dioxide in gaseous form which is low level emit, two molecules of water in liquid form, because of it is an exothermic reaction, the water released is usually in steam form and the energy released from the reaction is -891 kJ to drive the car engine.

$$CH_4[g] + 2O_2[g] \rightarrow CO_2[g] + 2H_2O[l] + 891kJ \qquad (2.1)$$

## 2.2 Natural Gas Storage

When natural gas is used as a fuel, the storage method needs to be safe and effective. Scientists have tried to develop technologies to stored large amounts of natural gas for transportation. Several ways to store natural gas are proposed and being implemented such as Compressed Natural Gas (CNG), Liquefied Natural Gas (LNG), and Adsorbed Natural Gas (ANG).

### 2.2.1 Compressed Natural Gas (CNG)

Compressed Natural Gas is a widely used method to increase the energy density of natural gas by compressing and storing it at high pressure (over 3,600 psi). Therefore, high pressure facilities and costly of cylinders are required. Furthermore, the CNG cylinder needs to be filled up more often than the gasoline or diesel tank (Solar *et al.*, 2010). Currently, the natural gas cylinder is produced mainly from steel, aluminum, and composite materials. To find the right type of cylinder for different vehicles, it depends on the duty cycle of the vehicle. Nevertheless, the cylinders are too heavy weigh and use up a large amount of space.

### 2.2.2 Liquefied Natural Gas (LNG)

Natural gas can be stored as liquefied natural gas (LNG at the boiling point (-161°C) in a cryogenic tank under pressure around 14.5 psi. The volumetric energy density is approximately 72% of the total gasoline, which means that 1 volume of LNG corresponds to 600 volume of natural gas under STP (600 v/v) conditions, while CNG is about 220 v/v (Solar *et al.*, 2010). However, this storage method shows many inconveniences including the use of complex and high liquefaction equipment. When pressure increases, it may result in a dangerous situation. Furthermore, the filling of the tank must be performed by a professional trained in cryogenic liquids handling. The shape of LNG storage tanks typically are cylinder or spherical. This storage method is applied to support the massive use in vehicles. For example, the cost of the on-board tank of a small vehicle is almost the same to the cost of heavy vehicle tank and it comes with even less net volumetric storage efficiency. Therefore, the cost of LNG vehicle refueling infrastructure is higher than CNG infrastructure (Solar *et al.*, 2010 and pttlng.com).

### 2.2.3 Adsorbed Natural Gas (ANG)

Adsorbed natural gas or ANG is another method of natural gas storage that can store natural gas at a low pressure. Pressures are relatively low, in the range of 290 to 580 psi at room temperature, which represents an interesting in both transportation and large scale applications. ANG works by using an adsorption agent or adsorbent which could be an inexpensive activated carbon material and molecular sieve in cylinder. Thus, ANG technology can support a greater storage volume of natural gas in the same container and at the same pressure than other technology or even in the same storage volume in the same container at a much lower pressure (Solar *et al.*, 2010).

## 2.3 Adsorption

Adsorption is a process that any substance accumulates on the surface of solid without penetrate into the bulk, in a concentration which is higher than in the bulk of substance. Adsorption can take place at any solid – fluid interface for gas –

solid interface and liquid – solid interface. Adsorption process creates a film of the adsorbate (the molecules or atoms being adsorbed) on the surface of the adsorbent. It is different from absorption process by which the fluid molecules or atoms are diffuses into a liquid or solid to form a solution. The term "sorption" includes both adsorption and absoption process, while "desorption" is the reverse of adsorption (chemvironcarbon.com).

Currently, adsorption is used and applied in many applications and systems. For example, the transportation system uses the adsorption agents such as, active carbon, carbon nanotube, molecular sieve or MOFs (Metal Organic Frameworks) in vehicle cylinder tank to maximize the capacity by enlarging the surface area of adsorbing gas molecules and also minimize the repulsion of molecules in gas phase. The experiment was carried out by using unmodified activated carbon and carbon nanotube agents under high condition over 3,600 psi to prove the agents abilities. Later, there are more studies and experiments to confirm this principle which brought in the improvement of CNG by using ANG, thus CNG can function at much lower pressure than non-adsorption system. The new discovered adsorption agent can fulfill this vision and allow CNG to function under pressure of 580 psi. However, there is none of the adsorption agent system used for vehicle storage in Thailand.

The adsorption is generally classified as physisorption and chemisorption. Physisorption or physical adsorption is based on the Van der Waals, dipole-dipole or London forces interactions between the adsorbed molecules and between the adsorbate and the substrate. The enthalpy is approximately 20 kJ/mol. Physisorption is a reversible process. Physisorption occurs mostly at low temperatures and occur as a preliminary state to chemisorption. The other type of adsorption is Chemisorption, it occurs when there is the formation of a chemical (often covalent) linkage between adsorbate and substrate. The enthalpy is approximately 200 kJ/mol. Chemisorption is almost always exothermic and usually an irreversible process.

Physisorption is a process in which adsorbate molecules are transferred from the fluid phase on to the solid surface, while some are released again to the fluid state (Monocha, 2003) When the rates of adsorption and desorption process are equal, *adsorption equilibrium* will be obtained.

### 2.3.1  Adsorption Isotherms

When a gas comes into contact with a solid surface, atoms or molecules of the gas will adsorb to the surface as a function of their partial pressure in the bulk. Adsorption isotherm is the measurement of gas adsorbed as a function of partial pressures at a constant temperature. The amount adsorbed is nearly always normalized by the mass (or specific surface area) of the adsorbent to comparison of different materials. Many different types of isotherm can be observed by their characteristics which depend on types of adsorbate, types of adsorbent and intermolecular interactions between the gas and the surface.

#### 2.3.1.1  Type of Adsorption Isotherm

The adsorption isotherms are classified according to the molecular interactions between adsorbent surface and gas. Brunauer *et al.*, 1940; refers to Brunauer, Deming, Deming, and Teller or well known as BDDT, and IUPAC (1985) classified the types of the adsorption isotherms into five types. These BDDT isotherms and an additional one introduced much later by Sing, 1982, which completes the IUPAC classification. Six types of isotherm are illustrated in Figure 2.1.

Type I isotherm characterize microporous adsorbents. Microporous solids for this isotherm having relatively small external surfaces such as activated carbons. These isotherms reach a maximum value of adsorption without inflections. This isotherm is limited to the completion of a single monolayer of adsorbate at the adsorbent surface. At the first part of this isotherm having a relative pressure ($p/p_0$) from 0 to about 0.05 is an indication for the dimensions of the micropores. The steeper the gradient the narrower the micropores.

Type II isotherm (sigmoid or S–shaped) describes adsorption on non-porous or macroporous adsorbents. This isotherm indicates the beginning of an unlimited multilayer after completion of the monolayer (the region of relative pressure ($p/p_0$) > 0.1 and $p/p_0$ > 0.9) and is found in adsorbents with a wide pore sizes distribution. At point B, a monolayer is completed and the adsorption occurs in successive layers at higher relative pressure.

Type III isotherm that is convex and describes adsorption with weak adsorbate-adsorbent interactions but strong interactions between adsorbate. This isotherm also describes the formation of multilayer and there is no flat region because the monolayer formation is disappeared.

Type IV isotherm is hysteresis loop, which is associated with capillary condensation occurring in mesopores. This isotherm is quite similar to type II at low relative pressure. The point of inflection indicates the completion of monolayer and the beginning of multilayer adsorption.

Type V isotherm represents mesoporous and microporous adsorbents and quite similar to type III but there is a capillary condensation in pores as the same pore size as type IV isotherm.

Finally, type VI isotherm describes stepwise multilayer adsorption on a uniform non-porous surface. Each step depends on the system and the temperature. These adsorption isotherms are for surfaces with an extremely homogeneous structure such as pyrolytic graphite that uses methane and argon as adsorbate but not $N_2$.
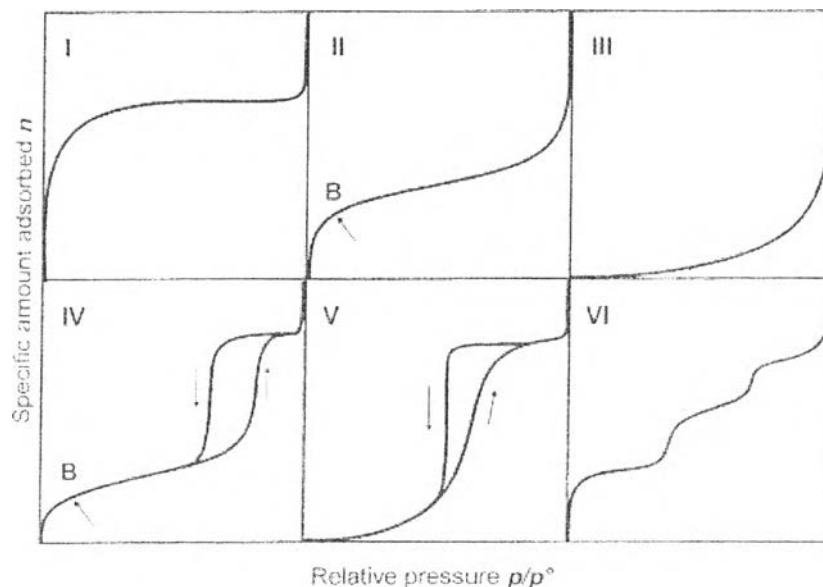


**Figure 2.1** The IUPAC classification for adsorption isotherms (Rouquerol *et al.*, 1999).

## 2.4 Activated Carbon

Activated carbon is a high porous material and widely used as an adsorbent because of its large amount of micropores and well-developed pore structures and the resulting in high surface area (Li *et al.*, 2008). The raw material of activated carbon are carbonaceous matter with high carbon content and low level of inorganic compounds, such as coconut shell (Azevedo *et al.*, 2007), corn cob, wood (both soft and hard) and coal (anthracite, lignite, and bituminous coals) or complex one like polymer (Méndez-Liñán *et al.*, 2010).

Coconut shell is suitable for production of coconut-based activated carbon because of its pore distribution with high amount of micropores, less amount of macropores, high carbon content, and low ash content (Mi *et al.*, 2012)

Most carbonaceous materials have an internal surface area approximately 10-15 $m^2/g$. The internal surface area is controlled by oxidation of carbon atoms during the activation process. The activated carbon after activation step will have an internal surface area approximately between 700 and 1,200 $m^2/g$, depending on the operating conditions. As a generalization, pore diameters are usually categorized as follows: micropores < 20 Angstroms, mesopores 20 - 500 Angstroms, and macropores ≥ 500 Angstroms (Duad, 2004).

Activated carbon has not only used for sorption and catalytic applications but also used in the specific industrial applications such as oil and natural gas, food, pharmaceuticals, water treatment, hydro metallurgy, gold recovery and carbon-in-pulp process. Because the activated carbon is produced from naturally occurring raw materials; its properties could be varied. In order to minimize variability it is necessary to be very selective in raw material source, quality and also practice a high level of manufacturing quality control.

### 2.4.1 Production of Activated Carbon

Activated carbon is usually produced by carbonization process and activation process of carbonaceous organic material.

*2.4.1.1 Carbonization process (or pyrolysis)*

This is one of the most important steps in the production activated carbon with oxygen-deficient condition (called pyrolysis) to eliminate the volatile matter and then partial treatment. The objective of carbonization is to enhance the carbon content and to create the initial porosity in the char (Li *et al.*, 2008). During carbonization, most of the non-carbon components, oxygen and hydrogen are first removed in gaseous form by pyrolytic decomposition (Wutthikun, 2001). There are three stages in the carbonization process follow:

i. Loss of water in the range of 30-200 °C.

ii. Form gases and tars in pyrolysis step within the range of 200-500 °C.

iii. Consolidate of char structure at 500-850 °C.

There are several parameters that would affect the structure of char such as carbonization temperature, carbonization time, heating rate, medium of reaction, and properties of raw material.

*2.4.1.2 Activation process*

Due to the starting with initial pores in the raw material from carbonization process, more pores with desired size distributions, are created by the activation process. There are two types of activation used in producing activated carbon including physical activation and chemical activation.

- Physical activation

Physical or thermal activation consists of two stages. First, eliminate of hydrogen and oxygen contents by carbonization at high temperature and in inert atmosphere. Second, activate the char at high temperature and flow oxidizing gases such as $CO_2$, steam, or flue gas passing it. Equation 2.2 and 2.3 represent the endothermic reaction of oxidizing gases with surface carbon atom (Arami-Niya *et al.*, 2011). The pore sizes developed by burns off the pore blocking structures which created during the carbonization process. Then, developed a porous and three-

dimensional graphite lattice structure. this activation process are depending on the activation time. Longer activation times result in larger pore sizes.

$$C + CO_2 \rightarrow 2CO \qquad (2.2)$$

$$C + H_2O \rightarrow CO + H_2 \qquad (2.3)$$

- Chemical activation

Chemical activation involves the impregnation of the char by mixing it with an excess amount of a given chemical, usually in the form of concentrated solution. The activating agent used in this process are potassium hydroxide (KOH), sodium hydroxide (NaOH), zinc chloride ($ZnCl_2$), phosphoric acid ($H_3PO_4$), sulfuric acid ($H_2SO_4$), and potassium carbonate ($K_2CO_3$) (Adinata *et al.*, 2007, and Wutthikun, 2001).

Chemical activation is usually carried out between 400 to 600 °C and can be up to 1,000 °C which is lower than physical activation. The char is impregnated with chemical then, heated up in an inert atmosphere. After that, the pyrolyzed product is cooled and washed with distilled water or by mild acid to eliminate the rest of the activating agent.

The main advantages of this process compare with physical activation are the higher yield, lower temperature of activation, less activation time and generally, higher development of microporosity, and better narrow micropore size distributions. Furthermore, a disadvantage of chemical activation such as the production process is more expensive and the product requires a washing step (Hernández-Montoya *et al.*, 2012).

## 2.5 Literature Review

- Production of activated carbon (carbonization and activation

process)

Tam *et al.*, (1999) studied the three-step process to prepared activated carbons from macadamia nut shell and coconut shell by air activation. To produced activated carbon, there are three-step process involving (i) carbonized. charcoal is

heated to a high temperature, (ii) oxygenated, charcoal is oxidized in air following a stepwise heating program from low (177°C) to high (387°C) temperatures, and (iii) activated, charcoal id heated in an inert environment to a high temperature. By use of this method activated carbons have surface area greater than 1,000 $m^2/g$ with an overall yield of 15% (base on the dry shell feed) and this yield was almost double commercial yield for coconut shell activated carbon. The results showed that macadamia nut shells were better for production of activated carbon by air oxidation than coconut shells. From both theoretical estimates of mass transfer limitations and experimental measurements of pore-size distributions indicated that surface area per gram increased by decreased the apparent density of the carbon. The decreased in density result from the development of mesopores and macropores which have little effect on the surface area of carbon. This increase in the surface area above 600 $m^2/g$ was not caused by the development of micropores. So, the surface area per gram of activated carbon can be represented by reverse the yield for burnoffs between 15 and 60%. Measured gasification rate with a kinetic model by Eley-Rideal type reaction of a surface oxide with oxygen in air. This reaction generates carbon dioxide with a new surface oxide over a temperature range of 277-387°C.

Duad and Ali (2004) compared the pore size distribution of micro-, meso-, and macropores in palm and coconut-based activated carbons produced from the same conditions. The experiment was carried out by fluidized bed reactor under temperature at 850 °C of carbonization and activation processes. The results indicated that higher fibrous structure content (halocellulose) materials like coconut shell char can easily be activated to produce activated carbon. The activation rate of coconut shell char is almost five times higher than palm shell char. They concluded that the high activation rate could be attributed to the high cellulose and hemicellullose content in the raw material. Moreover, at any burn-off, the micropore and mesopore volumes of palm-based activated carbons were always higher than activated carbon prepared from coconut shell. For macropore volume, the volume increased as an increased in burn-off and then decreased for palm-based activated carbon but the absolute macropore volume decreased with burn-off for coconut-based activated carbon.

Jia *et al.*, (2008) researched on effects of vacuum and nitrogen pyrolysis of oil-palm activated carbons used in aqueous phase phenol adsorption. The results indicated that the optimum pyrolysis conditions for preparing activated carbon to reach high surface area were vacuum pyrolysis under 675°C and hold time for 2 hours. The steam activation conditions were operated at 900°C and hold time for 1 hour. The conversion, physical characteristics, and surface morphology under vacuum pyrolysis were higher than nitrogen pyrolysis. The phenol adsorption capacity was 166 mg/g of activated carbon under optimum vacuum conditions. Moreover, there was a linear relationship between the amount of aqueous phase phenol adsorption and BET surface area.

Li *et al.*, (2008) prepared the coconut shell activated carbon to studied the effects of different carbonization temperatures (400, 600, 800 and 1,000°C) and different activation time (30, 60, 90 and 120 min) at constant activation temperature of 900°C. The results showed that the higher temperature of char and activated carbon result in higher of BET surface area, total volume, micropore volume and yield. Also, most of volatiles were removed and micropores were generated at high temperature. The BET surface area, total volume and micropore volume of coconut shell activated carbon with activation temperature at 1,000°C and 120 min of activation time were 1,926 $m^2$/g, 1.26 $cm^3$/g and 0.931$cm^3$/g, respectively.

Tsai *et al.*, (2001) prepared granular activated carbon from corn cob by potassium hydroxide (KOH) and potassium carbonate ($K_2CO_3$) and/or physical activation with $CO_2$. Potassium hydroxide (KOH) and potassium carbonate ($K_2CO_3$) were effective activating agents for chemical activation at a heating rate 10°C/min and physical activation at a soaking temperature of 800°C. The greater BET surface areas (>1,600 $m^2$/g) of activated carbons were prepared from the combined activation. Moreover, the porosity of acid unwashed carbon was less than acid-washed carbon products because potassium salts left in the pore structure.

Hayashi *et al.*, (2002) prepared several types of nutshells, such as almond shell (AM), coconut shell (CN) oil palm shell (OP), pistachio shell (PT), and walnut shell (WN) to produced activated carbon by chemical activation process with potassium carbonate ($K_2CO_3$). All of the nutshells had the maximum specific surface

area at carbonization temperature 800°C. The results showed that $K_2CO_3$ was efficiently worked as an activation agent but in different carbonization temperature for below 527°C and above 627°C. At the carbonization temperature range below 527°C, cellulose and hemi-cellulose were modified by $K_2CO_3$ and the weight losses of the nutshells were changed. While, in the carbonization temperature range above 627°C, CO was removed by the chars due to the reduction of $K_2CO_3$ as follows: $K_2CO_3 + 2C \rightarrow 2K + 3CO$; which result in high specific surface area and a high pore volume. Furthermore, the difference between in pore structure and specific surface areas corresponding the difference between weight losses during carbonization at temperature range above 627°C.

Sun *et al.*, (2011) researched on the production of activated carbon by $K_2CO_3$ activation process which prepared from furfural waste. The results indicated that the product was microporous due to the BET surface area 2218 $m^2/g$ and pore volume 1.04 $cm^3/g$ under activation temperature of 800°C for 60 min. The hydrogen adsorption of all the activated carbons showed a fast adsorption rate and the carbon activated at 800°C had the highest amount of hydrogen adsorption because of its greater specific surface area and micropore volume. The amount of hydrogen adsorption on carbon at activation temperature of 800°C was 1.7 wt % at -196°C 14.7 psi and 0.48 wt % at 25°C 870 psi, respectively. The isosteric heat of adsorption with zero loading of hydrogen on carbon with the highest specific surface area can be 5 kJ/mol which belongs to physisorption.

- Methane Adsorption by several types of adsorbents

Dreisbach *et al.*, (1999) studied the methane, nitrogen, carbon dioxide and their binary and ternary mixtures adsorption on activated carbon under high pressure. The adsorption was measured under the pressure up to 870 psi with the steady temperature 25°C by gravimetric method. Co-adsorption of the three mixtures $CH_4/CO_2$, $CH_4/N_2$, and $CO_2/N_2$ were measured by the volume-gravimetric method in the same range of pressure and at the constant temperature. Five ternary mixtures $CH_4/CO_2/N_2$ isotherms were measured under the same pressure and temperature by using the volume-chromatographic method for constant concentrations of the

adsorptive. In order to correct the measured data in volumetric or gravimetric experiments, the activated carbon so-called helium volume was used for adsorbed the surface excess amounts. The result of pure gas adsorption data are correlated with Langmuir isotherm which accounted in the adsorbent heterogeneity and fractal character of the internal microporous structure. Binary and ternary mixtures adsorption can be predicted by this model with the only pure gas adsorption parameters. There was a big success in this study as the predicted and experimental data were almost the same which suggested that prediction of the total amounts adsorbed came with deviation below 5%, the concentrations of the adsorbate of the binary mixtures with deviation below 9%, and the concentrations of the strongly adsorbed components of the ternary mixture in the adsorbate could be predicted from pure gas data with deviation below 15%.

Lozano-Castelló *et al.*, (2002) studied the methane storage applications by using different raw materials, activating agents, and preparation variables to compare the behavior of carbon materials with different morphologies. Activated carbons were prepared from chemical and physical process. Surface area and micropore size distribution (MPSD) were prepared on both types of materials. The results indicated that there was a direct relationship between the methane adsorption capacity of the adsorbent and micropore volume. Furthermore, the raw material and activation process method used for its preparation had no effect on adsorption capacity. Also, it showed that methane adsorption capacity depended on the MPSD.

Balathanigaimani *et al.*, (2006) studied the preparation and methane adsorption properties of powdered rice husk activated carbon. To achieve the storage natural gas by using adsorbed natural gas (ANG) was mainly based on the characteristics of the adsorbent. Thus the researchers focus on the different synthesized adsorbents including activated carbon from rice husk (AC-RH) compared with phenol based activated carbon (AC-PH$_2$O and AC-PKOH). The adsorption experiments were conducted by volumetric method under different constant temperatures (20, 30, 40, and 50°C) and pressure up to 507 psi. The adsorbed amounts of methane on adsorbents were calculated by using a mass balance equation. The results showed that maximum methane adsorption was observed in AC-RH as its higher surface area than the other two adsorbents. The experimental

data were correlated well with Langmuir-Fruendlich isotherms because of its flexibility and low percentage error. From Langmuir-Fruendlich isotherms indicate that AC-RH has heteroheneous surface while AC-PH₂O and AC-PKOH have homogeneous surfaces. Moreover, isosteric heat of adsorption was calculated by using Clausius-Clapeyron equation. The results from the Clausius-Clapeyron equation also confirmed the Langmuir-Fruendlich isothermn results.

Salehi *et al.*, (2007) studied the theoretical and experimental study to find out the accurate amount of methane adsorption and desorption by using four granular activated carbon or GAC samples under different physical conditions. The volumetric method was used to measure equilibrium of methane adsorption at temperature of 25°C and the pressure used up to 500 psia. Moreover, the different equilibrium pressures, a constant temperature, and various adsorption isotherm models were also studied. The results indicated that the physical characteristics of activated carbon which consisted of BET surface area, micropore volume, packing density, and pore size distribution were important factors in the amount of adsorption and desorption of methane.

Najibi *et al.*, (2008) studied the Methane/natural gas storage by measuring the capacity of three different activated carbons for both dry and wet conditions. The different of wet and dry conditions were only at before loading the activated carbon which was mixed with specific amounts of distilled water into the cell. This experiment used the water ratio (the ratio of the weight of water to the weight of dry activated carbon) at $R_w$ = 1. This work was maintained at constant temperature (-196°C) and pressure was up to 1450 psi. In all three types of activated carbons tested, the capacity of natural gas storage in dry condition was greater than in wet conditions, but the gas delivery was almost the same value. Hydrate might occurred in one of the activated carbon (NC120) at pressure greater than 580 psi while the amount of gas stored was less than in dry conditions overall the pressure. The study showed that the gas released from the activated carbons in each pressure in the dry conditions would change in composition. Moreover, it also indicated that the amount of heavy components were unable to come out of the bed even applied at very low pressures. Repeatability of the sorption/desorption processes–studying for industrial using, it found that the efficiency of repeatability was decreased for the

natural gas after only a few cycles, probably due to accumulation of heavier components in the natural gas.

Alcañiz-Monge *et al.*, (2009) researched fundamentals on methane adsorption on microporous carbons. Also, methane ($CH_4$) adsorption on a series of microporous activated carbons (AC), activated carbon fibers (ACF) and superactivated carbons (SAC), under supercritical conditions (25°C and 580 psi) were studied. The results showed that $CH_4$ adsorbed in narrow micropores which less than 0.7 nm and $CH_4$ adsorption data perfectly fitted in the characteristic curve with uniform micropore size distribution (MPSD). Conversely, carbons with heterogeneous MPSD, $CH_4$ adsorption data unable to fitted the characteristic curve. Pore size would affect on the adsorbed $CH_4$ density at supercritical conditions. Even though $CH_4$ could be adsorbed in the microporosity and filled it as a compressed gas, the methane adsorption was related to the specific BET surface area. A linear relationship was observed between the estimated BET surface areas obtained from both $CH_4$ and $N_2$.

Delavar *et al.*, (2010) studied the experimental evaluation for methane storage by granular activated carbon (GAC) through the equilibrium adsorption. The volumetric apparatus (pressure decay) was used for methane adsorption on Granular activated carbon (GAC). The methane adsorption isotherms were determined by the measurement of equilibrium uptake of methane under pressures within range of 0-725 psi and at temperatures of 12-55°C. Freundlich and Langmuir equations were proper to determine the model isotherm. The results showed that the increase in pressure would increase in the amount of methane uptake. The isosteric heat of methane adsorption was calculated from Sips isotherm model by the Clausius-Clapeyron equation. It was showed that the isosteric heat of methane adsorption decrease with decreasing temperature or increasing amount of methane.

- Another high porous adsorbents for methane adsorption

Tranchemontagne *et al.*, (2008) synthesized four famous metal-organic frameworks (MOFs): MOF-5, MOF-74, MOF-177, and MOF-199 at room temperature. In addition, they also synthesized isoreticular metal framework

(IRMOF), IRMOF-0 which had the same cubic topology as MOF-5, and synthesized from acetylenedicarboxylic acid. This synthesized method was suitable for the thermal sensitivity of the linker. Although acetylenedicarboxylate was the shortest straight linker that can be produced into an IRMOF, IRMOF-0 forms as a doubly interpenetrating structure, because of the rod-like nature of the linker. The results showed that the pore apertures of IRMOF-0 were too small to allow for removal of trapped guest molecules or adsorption of gases. Both of FTIR and elemental analysis also indicated that guest molecules are trapped within the pores, so they preventing the porosity.

Li *et al.*, (2009) focused on the synthesis and hydrogen-storage behavior of metal-organic framework MOF-5. They were interested in MOF-5 ($Zn_4O(BDC)_3$) because of a high surface area and large pore volume then synthesized by three procedures: direct mixing of triethylamine (TEA), slow diffusion of TEA, and solvothermal synthesis. Characterization of MOF-5 by X-ray diffraction (XRD), scanning electron microscopy (SEM), thermogravimetric (TG) analysis, and nitrogen adsorption. Also measured hydrogen storage capacities at -196°C by P-C-T apparatus. The different methods to synthesized MOF-5 showed the different in the pore-structure parameters, morphologies, and the capacities of hydrogen storage. The result indicated that synthesized MOF-5 by solvothermal can reached a higher crystalline, higher surface area and larger pore volume than the other two procedures. In addition, the hydrogen storage capacities were related to the specific surface area and pore volume of MOF-5.

Jia *et al.*, (2011) studied densification of MOF-5 synthesized at ambient temperature for methane adsorption and also, solvothermal activation, preservation, and reactivation of MOF-5 under anhydrous conditions. In this work, they synthesized MOF-5 by starting with terephthalic acid and triethylamine were dissolved in N,N-dimethylformamide (DMF) to form organic solution. Zinc acetate dihydrate also dissolved in DMF to form zinc salt solution. After mixed organic solution and zinc salt solution, precipitate occurred. Then, they have done the activation process to complete the MOF-5 synthesized. XRD and $N_2$ adsorption isotherm measurements were used to characterize it. The effect of densification of MOF-5 on methane volumetric storage capability was measured by packing densities

of the samples mechanically pressed under different pressures. From their experiments, mechanical pressing could improve the packing density, but decrease the amount of methane gravimetric storage. The optimized effective of methane volumetric storage was 81 V(STP)/V at 535 psi for the sample pressed under 145 psi.