

## CHAPTER II

### THEORETICAL BACKGROUND AND LITERATURE REVIEW

#### 2.1 Natural Gas

Natural gas is mixture of hydrocarbon gases. In its purified form, it is colorless and odorless because of its combustion-complete combustion and release low emission when burned. The emission level is less than harmful level. In case of completely combustion comparing between the natural gas and other fossil-fuel, the natural gas is considerable to be clean energy and good choice for using, because the other fossil-fuels have chemically complicated so when it is burned it emits complicated chemicals. Whereas, the natural gas has methane as its major component gas which is normally around 90 to 99% of natural gas and when it is burned the carbon dioxide is only harmful chemical which emitted. From table below, it shows that methane is major component in natural gas, following by ethane, propane, and butane.

**Table 2.1** Typical composition of natural gas

Methane	CH <sub>4</sub>	70-90%
Ethane	C <sub>2</sub> H <sub>6</sub>	0-20%
Propane	C <sub>3</sub> H <sub>8</sub>	
Butane	C <sub>4</sub> H <sub>10</sub>	
Carbon Dioxide	CO <sub>2</sub>	0-8%
Oxygen	O <sub>2</sub>	0-0.2%
Nitrogen	N <sub>2</sub>	0-5%
Hydrogen sulphide	H <sub>2</sub> S	0-5%
Rare gases	A, He, Ne, Xe	trace

The natural gas is always filled up with mercaptan compounds which is odorant compound because the safety reason. Mercaptan compounds (such as methyl mercaptan, ethyl mercaptan, etc.) will give the odor-rotten egg smell to detected when the natural gas leak.

The combustion of methane is following by the equation below. According to the equation below, one molecule of methane is reacted with two molecules of oxygen to get one molecule of carbon dioxide which is low level emit, two molecule for water but because it is exothermic reaction so the water released is usually be in stream form and energy is released from the reaction-891 kilojoules (kJ) to drive the car engine.



In 2004, Kavalov *et al.*, studied on Techno-economic analysis of Natural Gas application as an energy source for road transport in the EU. The results indicated 3 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 the natural gas was is abundant and accessible.

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

3. A multi-optional fuel technology

Over these 3 advantages, natural gas-based fuels have also many strong points which interested on the automotive fuel market.

1. The cost is cheapest comparing to conventional fuel, such as diesel, gasoline, etc. and other alternative fuels such as solar cell.

2. Natural gas,based fuel is good environmental because it is completely combustion.

3. Compared to conventional fuels, most natural gas-derived fuels demonstrate acceptable performance when employed in current internal combustion engine (ICE).

On the other hand, there is an important drawback that could prevent the successful market implementation of natural gas-based fuels. At the present, most of these fuels are cheaper than conventional fuels, due to the price itself and the government subsidization. Therefore the consumption of the natural gas-based fuel is rapidly increased. Nevertheless, maintaining of the tax treatment is difficult as it has the effects on the automotive fuel market competition and the tax income flow. If the government decided to lift off the tax exemptions from natural gas-derived fuels, this would cause the reversion on the preferred choice of fuel and the consumption of conventional fuels would be increased. Furthermore, the 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, 1 cubic meter of natural gas would correspond to 1.0 liter of gasoline or 1.1 liter of diesel. Also, with the limitation of the car space, a storage technology requires to have 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**

When the natural gas is used as a fuel, the proper natural storage is needed to store natural gas safely and effectively. The natural gas mainly consists of small molecules called methane which makes it difficult to store in a high density. Therefore, the scientists tried to develop the technologies which would the transportation of the high amount of natural gas. The following are describing how the natural gas gets store in different ways.

### 2.2.1 Compressed Natural Gas (CNG)

Compressed natural gas or CNG is a common natural gas storage method used in vehicle. It is a developed technology which used to store the natural gas under the high pressure condition of 20-25 MPa (200-250 bars). Therefore, the high pressure facilities and expensive vessels are required to work under this condition. CNG storage vessels are normally supplied by manufactures and also get certified by the range of agencies.

### 2.2.2 Liquefied Natural Gas (LNG)

Liquefied natural gas or LNG is another method used for natural gas storage. In this method, the natural gas get liquefied under pressure of 10-20 bars at -161.5 °C which requires the use of complex and high cost liquefaction equipment, thermos-like vessels and adequate energy consumption of about 25-35% of original energy gas content for liquefaction and degasification. The shape of LNG storage vessels are cylinder or spheres. This storage method is applied and used in marine transportation, but it is still advanced enough to support the massive use in vehicles. For example, the cost of the on-board vessel of a small vehicle is almost the same to the cost of heavy vehicle vessel and it comes with even less net volumetric storage efficiency. Therefore, the costs of LNG vehicle refuelling infrastructure are higher than CNG.

### 2.2.3 Adsorbed Natural Gas (ANG)

Adsorbed natural gas or ANG is another method of natural gas storage which can store the natural gas at much higher volumetric capacities than the pressurised storage at an equivalent pressure. ANG works by using the adsorption of gas on an adsorption agent or adsorbent which could be the cheap activated carbon material and molecular sieve in vessel. ANG technology can support a bigger 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.

## 2.3 Adsorption

Adsorption is a process by which a molecules or atoms in a gas or liquid phase attach to a solid surface. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the surface of the adsorbent. Distinguished from absorption process by which the fluid molecules or atoms are dissolved by a liquid or solid. The term sorption includes both processes, while desorption is the reverse of adsorption.

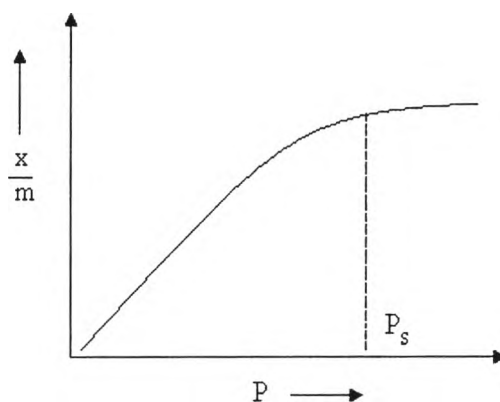
Nowadays, adsorption is used and applied in many applications and systems. For example, the transportation system uses the adsorption agents, such as, active carbon, carbon nanotube, molecular sieve or metal organic frameworks in vehicle vessel to maximize the capacity by enlarging the surface area of 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 of 20-25MPa 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, so 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 4MPa. However, there is none of the adsorption agent system used for vehicle storage in Thailand.

### 2.3.1 Adsorption Isotherms

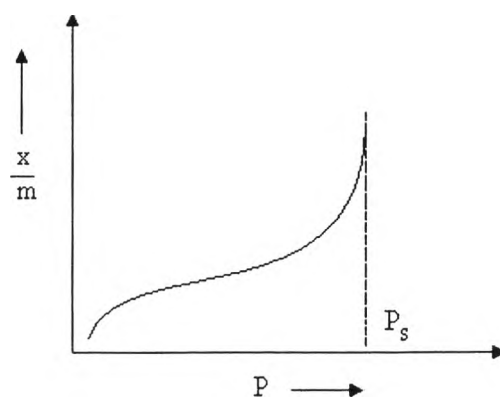
Adsorption is usually described through isotherms to determine the amount of adsorbate on the adsorbent as a function of its pressure (if gas) or concentration (if liquid) at constant temperature. The quantity adsorbed is nearly always normalized by the mass (or specific surface area) of the adsorbent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

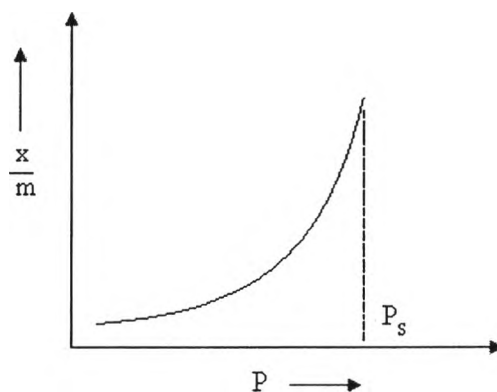
In 1940, Brunauer *et al.*, indicated the first systematic interpreting adsorption isotherm for gas-solid equilibria (Brunauer *et al.*, refers to Brunauer, Deming, Deming, and Teller or well known as BDDT). They classified isotherm into five types. These BDDT isotherms and additional one introduced much later by Sin, which completes the IUPAC classification. Five types of isotherm are illustrated in following figures. 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.



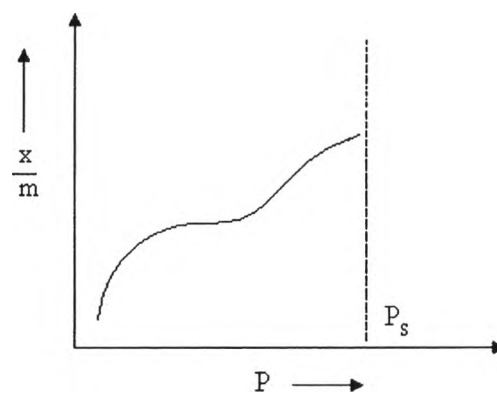
**Figure 2.1** Type I of adsorption isotherm: Typical of microporous solids and chemisorptions isotherms



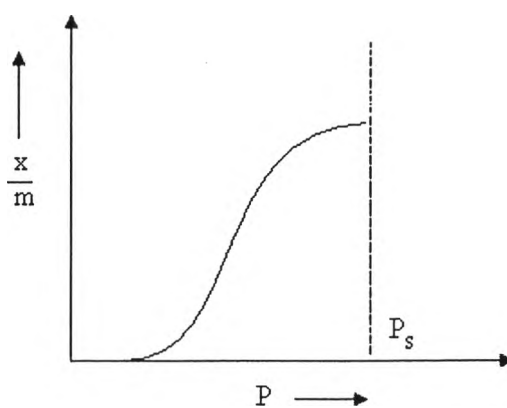
**Figure 2.2** Type II of adsorption isotherm: Finely divided non-porous solids.



**Figure 2.3** Type III of adsorption isotherm: Typical of vapor adsorption.



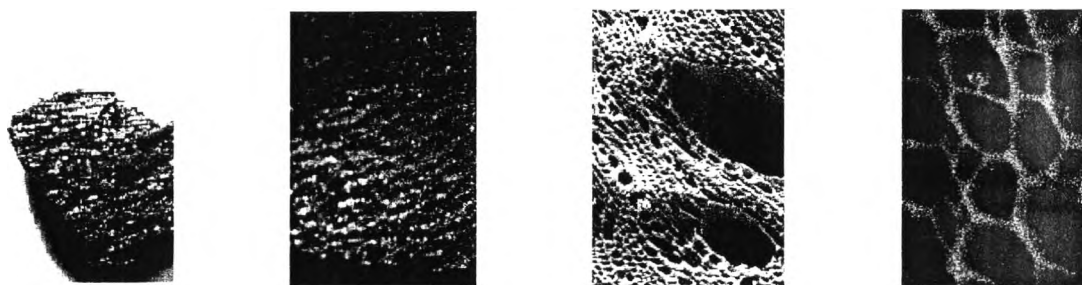
**Figure 2.4** Type IV of adsorption isotherm: The rare step-like isotherm type is shown by nitrogen adsorbed on special carbon.



**Figure 2.5** Type IV of adsorption isotherm: The capillary condensation of the adsorbate in the mesopores of the solid.

## 2.4 Activated Carbon

Activated carbon is used for the adsorption of organic substances and non-polar adsorbates and it is also usually used in waste gas or water treatment. 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. Highly porous, amorphous solid consisting of microcrystallites with a graphite lattice of activated carbon usually prepares in small pellets or a powder; therefore it is non-polar and cheap. The raw material for activated carbon are carbonaceous matter, such as coconut shell (Marcos *et al.*, 2007), corn cob and types of coal or complex one like polymer Anthracite and bituminous coals have been the major sources. Starting with initial pores present in the raw material, more pores with desired size distributions, are created by the so-called activation process. There are two types of activation used in producing activated carbon.



**Figure 2.6** Surface and pores of activated carbon, as viewed by an electron microscope (magnification increase from left to right).

### 2.4.1 Physical Activation

After initial treatment and pelletizing, one activation process involves carbonization at 400-500°C in oxygen-deficient condition to eliminate the bulk of volatile matter, and then partial treatment and partial gasification at 800-1,000°C to develop the porosity and surface area. A mild oxidizing gas such as CO<sub>2</sub>, steam, or flue gas is used in the activation step because the intrinsic surface reaction rate is much slower than the pore diffusion rate, thereby assuring the uniform development



of pores throughout the pellet. This activation step burns off the pore blocking structures created during the carbonization phase and so, they develop a porous, three-dimensional graphite lattice structure. The size of the pores developed during activation is a function of the time that they spend in this stage. Longer exposure times result in larger pore sizes.

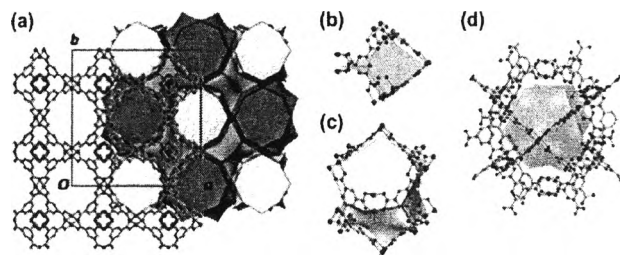
#### 2.4.2 Chemical Activation

The other commercial activation processes depend on the action of inorganic additives to degrade and dehydrate the cellulosic materials and, simultaneously, to prevent shrinkage during carbonization. Lignin can be used as a raw material by first blending with activators such as phosphoric acid, zinc chloride, potassium sulfide, or potassium thiocyanate, and then it is carbonized at temperatures up to 900°C. The product is usually in powder form and can be applied for both aqueous and gas phase adsorption.

### 2.5 **Metal Organic Framework (MOF)**

Metal organic framework is new kind of porous material which derived in mid'90ties (Moellmer *et al.*, 2011). It consisted of metal ions/cluster connected to organic linker. Type of metal and linker has strongly effects on the structure and properties such as pore size, shape of pore, surface area, etc. The MOF is interested due to its extremely high surface area. MOFs are used in many application such as gas purification, gas separation, gas storage, and heterogeneous catalysis. MOFs are interested on gas purification because of strong chemisorption that takes place between electron-rich, odor-generating molecules (such as amines, phosphines, oxygenates, alcohols, water, or sulfur-containing molecules) and the framework, allowing the desired gas to pass through the MOF. Gas separation can be performed with MOFs because they can allow certain molecules to pass through their pores based on size and kinetic diameter. This is particularly important for separating out carbon dioxide. Regarding gas storage, MOFs can store molecules such as carbon dioxide, carbon monoxide, methane, and oxygen due to their high adsorption enthalpies (similar to hydrogen). Finally, MOFs are used for catalysis because of

their shape and size selectivity and their accessible bulk volume. Also, because of their very porous architecture, mass transport in the pores is not hindered. It can be used for gas storage. Li et al. (2007) indicated that MOF is interested in storing hydrogen because it has high surface area and low densities.



**Figure 2.7** Structure of metal organic framework, basolite c300 (a) View on the structure of Cu<sub>3</sub>(btc)<sub>2</sub> along c; (b) small pores (S1) (eight per unit cell); (c) large pore (L2) (four per unit cell); (d) large pore (L3) (four per unit cell).

## 2.6 Isotherm Models

Langmuir isotherm model is used to describe the adsorption on the monolayer surface (Dung, 1998). Langmuir equation was derived from kinetic principle under 3 assumptions.

1. Homogeneous surface, *i.e.*, the adsorption energy is constant over all sites and no lateral interaction.
2. The adsorbed atoms or molecules are localised.
3. Each site is occupied by only one atom or molecule.

The Langmuir equation is

$$q = q_m \frac{b(T)P}{1 + b(T)P}$$

- where :
- $q$  = The amount of methane adsorption (mmol/g)
  - $q_m$  = The maximum amount of methane adsorption to complete monolayer coverage (mmol/g)
  - $b$  = Affinity constant or Langmuir constant which is a function of temperature
  - $P$  = Equilibrium pressure (psia)

From the Langmuir equation, Henry law isotherm will be used at very low pressure, thus the amount of methane adsorption increases linearly with pressure. At significantly high pressure, the amount of methane reaches the saturation point as shown in this experiment (monolayer coverage,  $\theta \rightarrow 1$ ). Langmuir cannot explain the results of this study because the adsorbents has heterogeneous surface.

Freundlich isotherm model is used to describe the adsorption of organic substances from aqueous stream on activated carbon and gas adsorption on heterogeneous surface (Dung, 1998). There are 2 assumptions in this isotherm.

1. The surface topology is patchwise.
2. The adsorption takes place on the heterogeneous surface, in term of distributed adsorption energy.

The Freundlich equation is

$$q = q_m P^{\frac{1}{n}}$$

- where :
- $q$  = The amount of methane adsorption (mmol/g)
  - $q_m$  = The maximum amount of methane adsorption to complete monolayer coverage (mmol/g)
  - $n$  = A parameter which is a function of temperature
  - $P$  = Equilibrium pressure (psia)

Freunchlich's equation can only be used in a narrow range of pressure because it cannot explain the behavior at both low and high pressures.

Sips equation was created in order to eliminate the limitation of Freundlich equation (Dung, 1998). Sips equation is similar to Freundlich except it has a finite limit when reaches sufficiently high pressure. However, at low pressure, Sips equation cannot explain the adsorption behavior like Freundlich equation.

The Sips equation is

$$q = q_m \frac{(bP)^{\frac{1}{n}}}{1 + (bP)^{\frac{1}{n}}}$$

- where : q = The amount of methane adsorption (mmol/g)  
 $q_m$  = The maximum amount of methane adsorption to complete monolayer coverage (mmol/g)  
 n = A parameter which is a function of temperature  
 P = Equilibrium pressure (psia)

In general, Sips isotherm model is widely used in the adsorption of hydrocarbons on activated carbon.

While Sips equation was able to get rid of 1 limitation of Freundlich equation, Freundlich equation still has another limitation. In order to eliminate both limitations of Freundlich equation, Toth equation was developed (Dung, 1998).

The Toth equation is

$$q = q_m \frac{bP}{(1 + (bP)^r)^{\frac{1}{r}}}$$

where :  $q$  = The amount of methane adsorption (mmol/g)  
 $q_m$  = The maximum amount of methane adsorption to complete monolayer coverage (mmol/g)  
 $t$  = Parameter which specific for adsorbate - adsorbent pairs  
 $P$  = Equilibrium pressure (psia)

In general, Toth isotherm can well describe sub-monolayer coverage systems.

The last model in this study is Unilan equation. This equation is used to correlate the adsorption equilibrium data of many solids, such as activated carbon and zeolite (Dung, 1998). There are 3 assumptions in this isotherm.

1. The surface topology is patchwise.
2. Local Langmuir isotherm can describe on each patch.
3. The adsorption energy distribution is uniform.

The Unilan equation is

$$q = \frac{q_m}{2.5} \ln \left( \frac{1 + b e^{sP}}{1 + b e^{-sP}} \right)$$

where :  $q$  = The amount of methane adsorption (mmol/g)  
 $q_m$  = The maximum amount of methane adsorption to complete monolayer coverage (mmol/g).  
 $b$  = Affinity constant or Langmuir constant which is the function of temperature  
 $P$  = Equilibrium pressure (psia)  
 $S$  = Parameter which is charictestics the hetrogeneity of the system

## 2.6 Literature Reviews

In 2002, Lozano *et al.* studied by using different raw materials, activating agents, and preparation variables to compare the behavior of carbon materials with different morphologies in methane storage applications. Two different types of carbon materials were prepared which were chemically activated carbon and physically activated carbon. Wide range of surface area and micropore size distribution (MPSD) were prepared on both type of materials. The results showed that there was a direct relationship between the methane adsorption capacity of the adsorbent and its micropore volume. In addition, the raw material and activation method used for its preparation had no effect on adsorption capacity. Nevertheless, it showed that methane adsorption capacity also depended on the MPSD.

In 2003, Paul Chen *et al.* studied on the different physicochemical methods used to modify the surface of activated carbons. In the experiment, HCl, HNO<sub>3</sub> and NaOH were used to modify with activated carbons and studied the effect of surface modification on activated carbons properties, such as, the specific surface area (SSA), total acidity capacity, carbon pH and also by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The results of HCl, HNO<sub>3</sub> and NaOH treatment caused a significant change in the carbon chemical properties which included the carbon pH and total acidity capacity, however there was no change in the specific surface area of the carbon. According to the XPS and FTIR results, they showed that with the HNO<sub>3</sub> treatment, the activated carbon produced significantly large number of surface functional groups which included carbonyl, carboxyl, and nitrate groups, whereas, the NaOH treatment caused the increase of 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.

In 2006, Shao *et al.* characterized and measured methane adsorption of the three activated carbon fibers which were different in their BET specific surface areas (SSA) by gravimetric analyzer at 258 and 298 K. The results of the isotherm testing suggested that the amount of adsorption would increase with the specific surface area of both temperatures. Therefore, specific surface area 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 methane storage capacity for the activated carbon fibers and the favorable temperature for methane adsorption is below 280 K.

In 2007, Bastos-Neto *et al.* studied on the relationship of textural and surface characteristics of selected microporous activated carbons produced from different raw materials to their methane storage capacity. In the experiment, the adsorption isotherms of several activated carbon samples were measured. 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 carbons produced from the same source, it was clearly recognized than methane adsorption properties which would be obtained for samples with higher surface area, higher micropore volume and narrower pore size distribution within the range of 8–15 Å. There was a common trend for BET surface area and micropore volume to be directly proportional to methane adsorption capacity. The study of surface chemistry of selected samples by XPS showed that the hydrophobic/hydrophilic nature of the carbon surface was a relevant aspect in determining the adsorption properties for non-polar sorbates, such as, methane. Samples with slightly more hydrophobic surfaces had superior methane adsorption properties in comparison to less hydrophobic samples with more favorable. Textural parameters were unable to unequivocally determine natural gas storage capacities. Surface chemistry and methane adsorption equilibria were subjects to be considered in the decision-making process when choosing the right adsorbent for gas storage.

In 2007, Danna *et al.* activated carbon adsorption characteristic prepared from coconut shells by applying chemical activation with zinc chloride and following with physical activation was studied. In experiment, nitrogen adsorption at 77 K was used to characterize the Textural of activated carbons. It showed that CAQF (chemical activation with  $ZnCl_2$  followed by physical activation) method was resulted in higher in BET area, total pore volume, micropore volume and microporosity. It also

indicated that the adsorption isotherm for excess adsorbed mass could exhibit type I isotherm which was the monolayer microporous adsorbent. In addition, the increase in temperature would decrease the amount of adsorption proves physisorption behavior on samples surface. Therefore, the best characterized sample was evaluated for methane adsorption at pressures between 0.1 MPa and 7 MPa and temperatures in the range of 283–333 K. At 298 K and 40 bar, the methane adsorption capacity of 122 mg of methane/g of carbon (80v/v) was found. In conclusion, the authors mentioned that the preparing activated carbons which were from coconut shell and firstly treating with chemical activation and then physical activation could be developed into the alternative adsorbents for natural gas storage applications.

In 2007, Najibi *et al.* studied on storage of Methane/natural gas by measuring the delivered capacity of three different activated carbons under dry and wet conditions. The wet and dry conditions were different only at before loading the activated carbon which was mixed with some specified amount of distilled water into the cell. The water ratio (the ratio of the weight of water to the weight of dry activated carbon) used in this work was  $R_w = 1$ . The cell temperature of all tests was maintained steady at 277.15 K and pressure was up to 10 MPa. In all three samples tested, the natural gas storage capacity in wet condition was less than methane storage capacity in dry conditions, but the gas delivery was almost the same value. The study also showed that the gas delivered from the activated carbons in each pressure step in the dry conditions would have a considerable change in composition. Furthermore, it also indicated that the significant amount of heavy components were unable to come out of the bed even applied at very low pressures in both dry and wet condition tests. Repeatability of the sorption/desorption processes—studying for industrial using, it found that the efficiency of repeatability was reduced considerably for the natural gas after only a few cycles, probably due to accumulation of heavier components in the natural gas.

In 2007, Salehi *et al.* carried out the theoretical and experimental study to figure out the accurate amount of methane adsorption and desorption by using many different type of granular activated carbon or GAC under different physical conditions. The experiments used the volumetric method to measure equilibrium of methane adsorption at temperature of 298 K and the maximum pressure of 500 psia.



In doing so, the adsorption and desorption capacities of four different GAC in the adsorption of methane at different equilibrium pressures and a constant temperature were studied. The results indicated that the activated carbon physical characteristics which included BET surface area, micropore volume, packing density, and pore size distribution were important factors in the adsorption and desorption the amount of methane.

In 2008, Marcos *et al.* studied on how the preparing carbons which were from the combination of chemical activation of coconut shell with  $\text{H}_3\text{PO}_4$  or  $\text{ZnCl}_2$  and then physical activating with  $\text{CO}_2$ , could give advantage in adsorption of natural gas. Using  $\text{H}_3\text{PO}_4$  or  $\text{ZnCl}_2$  in small amount could generate an incipient narrow microporosity without causing a significant reduction in bulk density in comparison to the sample that was carbonized alone without the chemicals. The following of physical activation allowed the primary pore structure which was generated by the chemicals to be further developed. The procedure showed the possibility of obtaining the materials with well developed porosity compatible and at high bulk density. Hence, the granular activated carbons which had the methane adsorption capacity of 95v/v were obtained and these can be used in multiple large scale applications like natural gas transportation in mobile pipelines. In addition, the agricultural by-product which included coconut shell could be used to synthesize the granular carbons by using the low cost and simple procedures and these factors are important in the large scale applications.

In 2009, Alcañiz-Monge *et al.* studied fundamental on adsorption of methane on microporous carbons.  $\text{CH}_4$  adsorption on a series of microporous activated carbons (AC), activated carbon fibers (ACF) and super activated carbons (SAC), at 298 K and 4 MPa (supercritical conditions) was studied. The results showed that  $\text{CH}_4$  adsorbed in narrow micropores which were less than 0.7 nm. For instance, with uniform micropore size distribution (MPSD),  $\text{CH}_4$  adsorption data perfectly fitted in the characteristic curve. On the other hand, samples with heterogeneous MPSD,  $\text{CH}_4$  adsorption data unable to fit on/in the characteristic curve. Pore size would affect on the adsorbed  $\text{CH}_4$  density at supercritical conditions, especially on samples with heterogeneous Pore size distribution (PSD). Even  $\text{CH}_4$  could be adsorbed in the microporosity and filled it as a compressed gas, the

adsorption data had been also related to the specific BET surface area. A linear relationship between the estimated BET areas obtained from both adsorptive ( $N_2$  and  $CH_4$ ) was observed.

In 2010, Delavar *et al.* studied on the capacity of granular activated carbon (GAC) for the storage of methane through the equilibrium adsorption. The volumetric technique (pressure decay) was used to measure equilibrium adsorption of methane on GAC. The isotherms of methane adsorption were determined by the measurement of equilibrium uptake of methane indifferent pressures of 0-50 bar and temperatures of 285.15-328.15°K. Freundlich and Langmuir equations were suitable to determine the model isotherm.

In 2011, Bao *et al.*, synthesize and characterize the magnesium-based metal organic framework (MOF or Mg-MOF-74) and evaluate adsorption equilibria and kinetics of methane and carbon dioxide. The volumetric technique was used to measure equilibrium adsorption at pressure up to 1 bar and 278, 298, 318 K. The results showed that the prepared Mg-MOF-74 has pore size width 10.2 Å and BET specific surface area 1175 m<sup>2</sup>/g. The methane and carbon dioxide uptake were 1.05 mmol/g (1.7 wt.%) and 8.61 mmol/g (37.8 wt.%), respectively, at 298 K and 1 bar. The initial heats of adsorption of  $CO_2$  and  $CH_4$  on the Mg-MOF-74 adsorbent were found to be -73.0 and -18.5 kJ/mol, respectively. To compare the diffusivity of methane and carbon dioxide on Mg-MOF-74, methane is adsorbed faster than carbon dioxide.

In 2011, Narges *et al.* studied on activated carbon which was prepared with corn cobs and potassium hydroxide under optimized variables. Due to their renewable origin, corn cobs could be the excellent initial material to produce nanoporous carbon for natural gas storage. Samples with different BET surface areas were chosen to perform methane adsorption experiments. The volumetric apparatus was measured for methane adsorptions on activated carbon at four different pressures which were at 500, 1000, 1500 and 2000 psi and two different temperatures of 298K and 323 K. The results showed that there was the direct correlation between the adsorption capacity of methane on the activated carbon and the surface area as the surface area increased the methane adsorption increased. In addition, the temperature and pressure level also affected the methane adsorption capacity. Furthermore, the

stored methane capacity is sensitive to the heat limitation. When the pressure constantly increased from 500 to 1500 psi, the stored methane capacity increased from 120 (v/v) to 160 (v/v) which was about 42% increase. When the temperature increased from 298 K to 323 K, this reduced the stored methane capacity from 120 (v/v) to 70 (v/v) which was the loss of about 72%. The applications could be used in the transportation of natural gas, natural gas based vehicles, and adsorption of gas from landfills.