CHAPTER II
THEORETICAL BACKGROUND AND LITERATURE REVIEW

2.1 Natural Gas

Animals and plants deposit in the sediment at intense heat and pressure over thousands years can form fossil fuels such as crude oil and natural gas. Natural gas is the mixture of gases consists of ethane, propane, nitrogen, helium, sulfur compounds, water vapor, and mostly methane. It is colorless and odorless in its pure form. Natural gas is non-renewable energy that is often used for heating, cooking, power generation and fuel in vehicles. It is one of the cleanest energy because it is cleaner burning and emits lower levels of pollutions compare to other fossil fuels (naturalgas.org).

2.2 Natural Gas Storage

The storage of natural gas is required for supplying natural gas to use natural gas in the future or transport to other locations that expects to meets demand of consumers. There are three technologies to store natural gas (www.afsglobal.com).

2.2.1 Compressed Natural Gas (CNG)

Natural gas is stored in high-pressure tanks about 20 to 25 MPa (200 to 250 bar, or 3,000 to 3,600 psi). CNG is an economic solution for long distant offshore gas with small and medium reserves. It is usually used in small fueling location, and on vehicle. However, CNG requires greater space for gas storage in the same amount of gas compares to others technologies.

2.2.2 Liquefied Natural Gas (LNG)

LNG stores natural gas as cryogenic liquid at very low temperature to condense natural gas to be liquid. It is typically between -120 and -170°C (-184 and –274°F). The disadvantage is high cost of cryogenic storage. LNG is applied for long distance gas transportation and for local distribution like ship and truck. This technology also provides the opportunity to store fuel in the area which not suitable for underground storage. The advantage of LNG is it can reduce costs for port facilities and reduce time that is needed to build the plant.

2.2.3 Adsorbed Natural Gas (ANG).

ANG stores natural gas in porous medium as adsorbents at standard temperature and pressure. It is the process that the gas molecules adhere to the pore and surface of porous medium. Porous medium requires low costs and high gas storage capacities like activated carbon. Therefore, addition of porous medium in gas storage can improve volume of natural gas in the same container at the same pressure and temperature (energtek.com).

The cost of ANG is cheaper than CNG and LNG because it neither needs compression to high pressure nor refrigeration methods nor requires less energy. ANG also has higher storage capacity in equivalent volumes than others storage technologies.

2.3 Adsorption

Adsorption is a process of one or more molecules of gas or liquid approach to the solid surface. The solid surface is called adsorbent, and the adsorbed fluid is called adsorbate. Surface of adsorbent plays an important role for adsorption phenomenon. The reverse of adsorption is a desorption process. Adsorption is different from absorption. In the absorption process, the fluid molecules are dissolved by liquid or solid. Adsorption phenomenon has high concentration molecules of fluids on the surface of adsorbent, while absorption phenomenon has uniform distribution. The adsorption process is used in many applications such as heterogeneous catalysis, creating vacuum by adsorbing gases on activated charcoal, adsorbs poison gas in refinery and ANG technique for transport and storage gas (amrita.vlab.co.in).

2.3.1 Types of Adsorption

1. Physical adsorption

The attraction between adsorbent and adsorbate are Van der waal's force. This force is very weak because it can easily break the attraction by heating or decreasing the pressure.

2. Chemical adsorption

The attraction between adsorbent and adsorbate are almost same strength as chemical bonds. It is very strong and hard to reverse.

2.3.2 Adsorption Isotherm

Adsorption isotherm is the relation between the adsorbed amount on the adsorbent and the pressure or concentration at constant temperature. The different types of isotherm are directly related to the characteristics of the solid, which depend on types of solid and intermolecular between fluids and solid surfaces. The first systematic interpreting adsorption isotherm for gas-solid equilibria is Brunauer, Deming, Deming and Teller or BDDT. This systematic, the isotherm is classified into five types (www.chemistrylearning.com).

1. Type I Adsorption Isotherm

Figure 2.1 shows the type I adsorption isotherm that explains monolayer adsorption. It is typical of microporous solids and chemisorption isotherms. The axis Y (x/m) is adsorption per gram of adsorbent, which is obtained by dividing the amount of adsorbate (x) by the weight of the adsorbent (m). The axis X (P) is Pressure and P_s is saturation pressure.

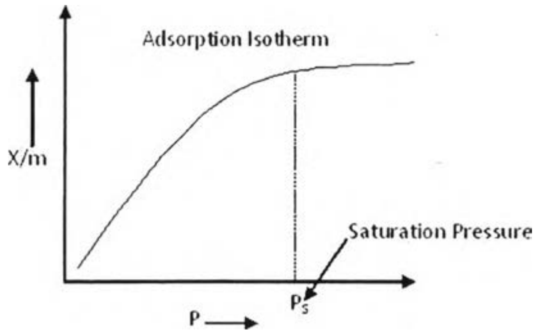

Figure 2.1 Type I of adsorption isotherm (www.chemistrylearning.com).

2. Type II Adsorption Isotherm

The intermediumte flat region in the isotherm corresponds to monolayer formation. This type is typical for non-porous solids.

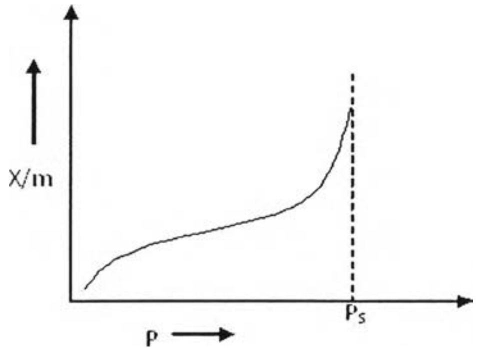

Figure 2.2 Type II of adsorption isotherm (www.chemistrylearning.com).

3. Type III Adsorption Isotherm

This isotherm explains the formation of multilayer. There is no flattish portion in the graph indicating that it has no formation of monolayer. It is typical for vapor adsorption.

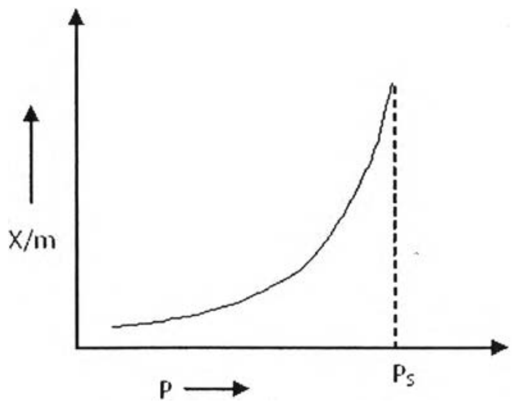

Figure 2.3 Type III of adsorption isotherm (www.chemistrylearning.com).

4. Type IV Adsorption Isotherm

Figure 2.4 shows type IV adsorption isotherm. The graph is similar to type II isotherm at low pressure and the intermediumte flat that explain the formation of monolayer. The saturation level reaches at a pressure below the saturation vapor pressures due to the gases may condense in the pores of adsorbent at pressure below the vapor pressure saturation.

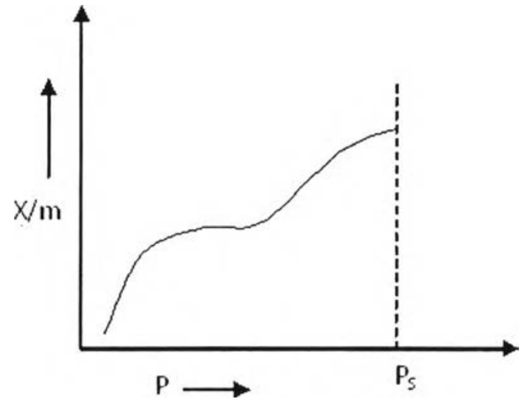

Figure 2.4 Type IV of adsorption isotherm (www.chemistrylearning.com).

5. Type V Adsorption Isotherm

The graph of type V is similar to type IV adsorption. Type IV and V show the phenomenon of condensed gas in capillary pores.

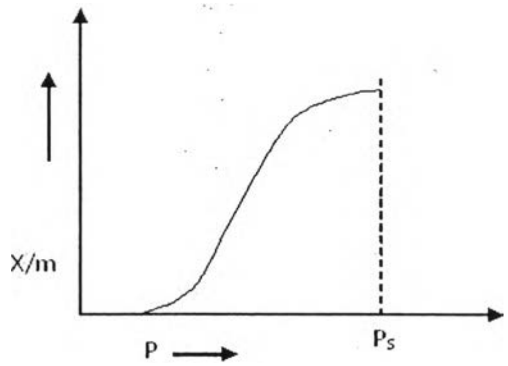

Figure 2.5 Type V of adsorption isotherm (www.chemistrylearning.com).

2.4 Gas Hydrates

Recently, natural gas hydrate technology has drawn much attention as a new technology in many processes such as gas separation process, gas storage, and transportation. Gas hydrates are ice-like crystalline solids, consisting of guest gas molecules inside water cage molecules. During hydrates formation, the liquid water is presented in terms of "Metastable liquid". Metastable liquid means liquid, at equilibrium, will exist as Hydrates (Henni, 2013). For natural gas hydrates, they have natural gas, where methane is the primary gas composition as guest molecules. Gas hydrates are classified by the size of guest molecules in three general structures (Demirbas, 2010a):

1. The structure I or sI gas hydrates contain 46 water molecules per 8 gas molecules consisting of 2 small and 6 large cages. It is usually formed by smaller gas molecules such as methane, ethane, and carbon dioxide.
2. The structure II or sII gas hydrates contain 136 water molecules per 24 gas molecules consisting of 16 small and 8 large cages. It is formed by larger molecules like propane and iso-butane as guest molecules.
3. The structure H or sH gas hydrates contain 34 water molecules per 6 gas molecules. It is occupied by larger gas molecules such as iso-pentane and methylcyclohexane.

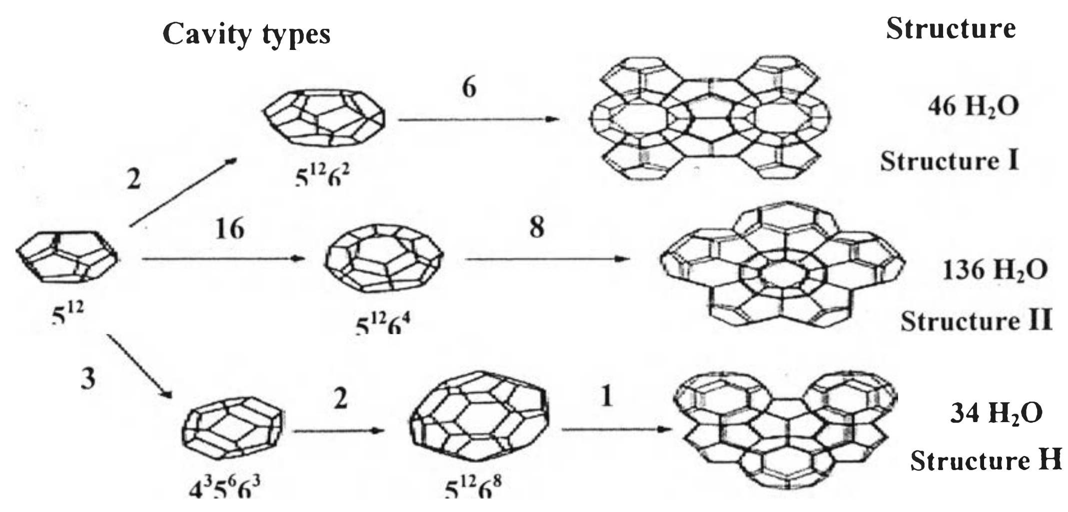

Figure 2.6 Structure types of gas hydrates (Perrin *et al.*, 2013) .

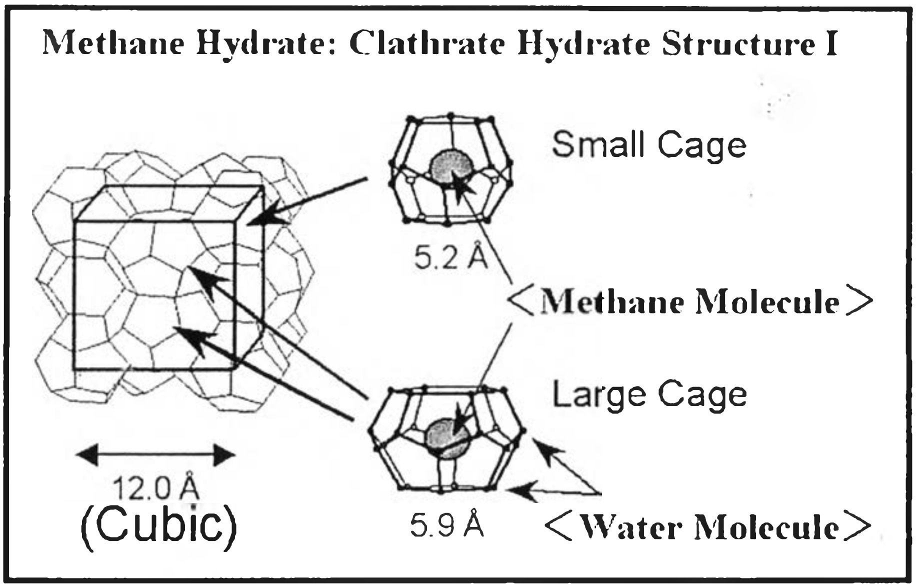

Figure 2.7 Crystal structure of methane hydrates (www-ner.office.kitami-it.ac.jp).

2.4.1 Formation of Gas Hydrates

Many researches investigated the hydrate formation in bulk water system compared to porous medium system such as silica sand, silica gels, and bentonite. The crucial property of porous medium is high adsorption capacity due to high specific surface area. The solids, which have smaller size or rougher surfaces, have high specific surface area such as powder, and solids with small holes that can increase interaction between gas and water in the hydrate system. For example, a well-known porous medium in many processes is activated carbon. Activated carbon is carbon, which is activated by thermal decomposition with oxygen to create small pores between carbon atoms. The small pores increase surface area of activated carbon that is suitable for adsorption process. The potentials of gas-solids interaction are high at the wall or surface of solid. The porous solid, which is the gas molecules in the pores are surrounded by the walls of solids, is considered that it has very high interaction of gas and solid. Hence, porous medium is very attractive way to enhance gas hydrate formation.

In natural, hydrates can form in interstitial pore space or fractures between sediments under high pressure and low temperature conditions. Gas hydrates formation is dependent on pressure, temperature, phase composition, and interfacial contact area (Cha *et al.*, 1988). The formation of gas hydrates is similar to crystallization process. It has three stages. First, the gases dissolve into the water or dissolution. When it reaches super saturation, nucleation occurs. The final stage is the growth of hydrates (Babu *et al.*, 2013a).

Najibi *et al.* (2008) studied three different types of activated carbons; NC120, Picazin, Sigma, in dry and wet conditions on methane hydrate formation. In the wet activated carbons, water molecules were trapped inside the activated carbon so the available pores to adsorb gas were lower than the dry activated carbons. For NC120, at pressures greater than 4 MPa, the amounts of gas uptake was increased and higher than the dry activated carbon because of gas hydrates formation in the system. This result indicated that the formation of gas hydrates can increase the gas storage in porous medium. The similar results were reported by Zanota *et al.* (2005), as shown in Figure 2.8. At the pressure about 3.5 MPa, the amount of gas in the activated carbon, which had 73% water content, significantly increased due to the hydrate formation in the activated carbon. Hence, the gas hydrates become attractive for storage and transportation in industrial.

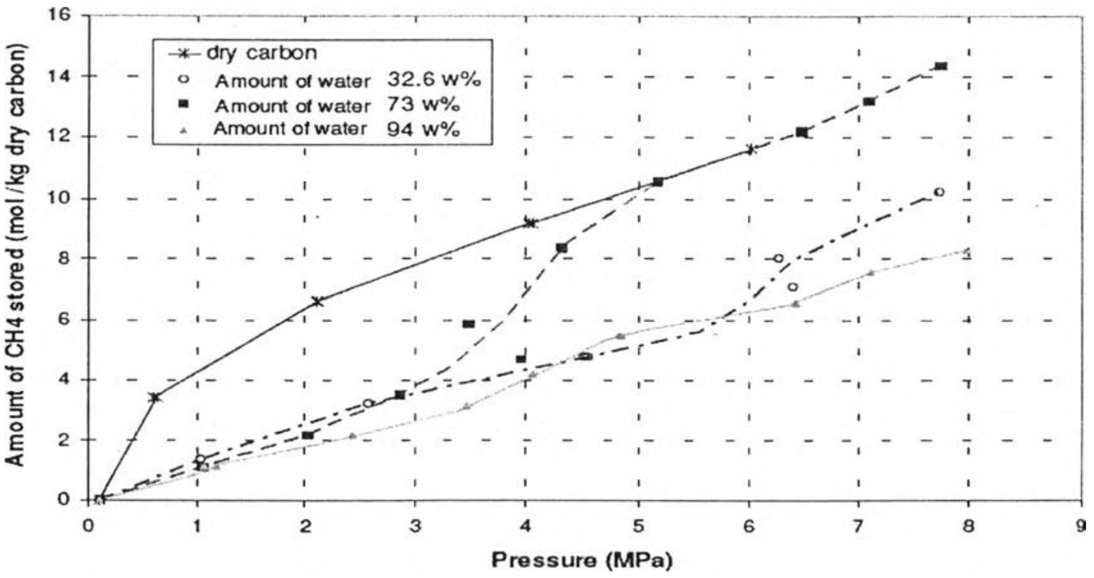

Figure 2.8 Effect of water content on the storage of methane gas in activated carbon (Zanota *et al.*, 2005).

The formation and dissociation of methane hydrates are shown in Figure 2.9. The figure shows the temperature and profile during the process. Point A is the equilibrium point, where hydrates start to form. The pressure gradually decreases when the temperature decreases because of the dissolution of gas to water. When reaching point B, the pressure drops rapidly at a constant temperature due to hydrates nucleation. The methane gas is consumed to form hydrates. Then, the pressure decreases continuously because of the hydrates growth. In the opposite way, the pressure in the system is increased when the hydrates start the dissociation. Figure 2.10 shows phase behavior of water/hydrocarbon system. Phase behavior equilibrium, also called hydrates formation curve, is usually used for prediction formation or dissociation of gas hydrates. The equilibrium curves are always based on the analysis of dissociation curve of hydrates in the P-T diagram (Zanota *et al.*, 2005). The right side of the line is no hydrates can form at that temperature and pressure. The hydrates can form on the left side of the line. In pure water system, the hydrates formation is low because the slow reaction between water and methane gas. Hydrate formation occurs at the interface between water and methane initially. Films of hydrates at interface will hinder diffusion of methane gas and mobility of water (Saw *et al.*, 2014). The rate of hydrate formation is affected by the combination of heat and mass transfer. Hydrate formation rate is enhanced by, for example, high driving force, mechanical mixing, surfactants (Hashemi *et al.*, 2012; Prasad *et al.*, 2014).

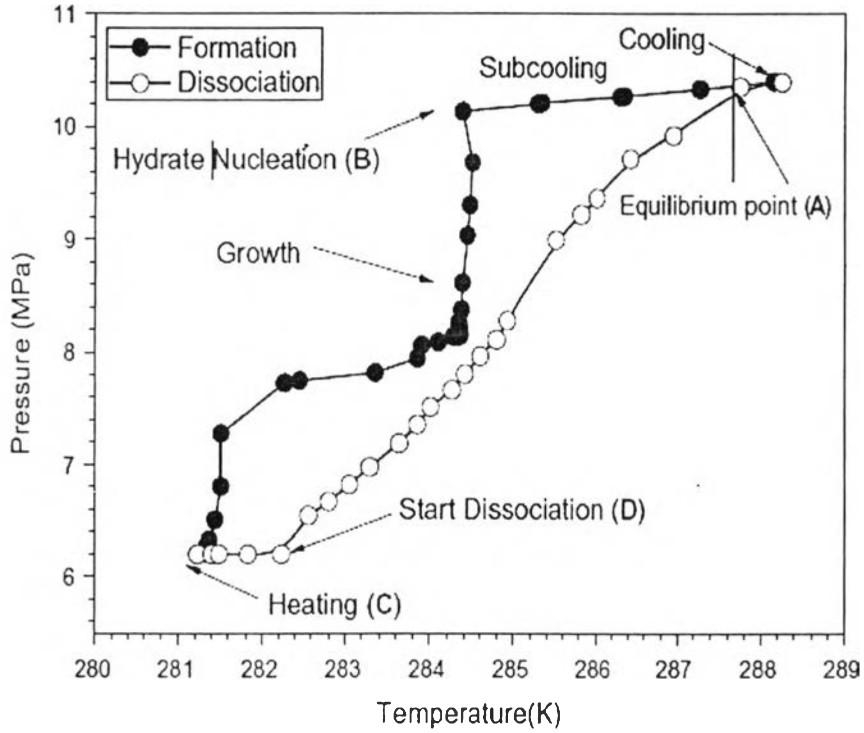

Figure 2.9 Temperature-pressure behavior of methane hydrate formation and dissociation in distilled water (Saw *et al.*, 2014).

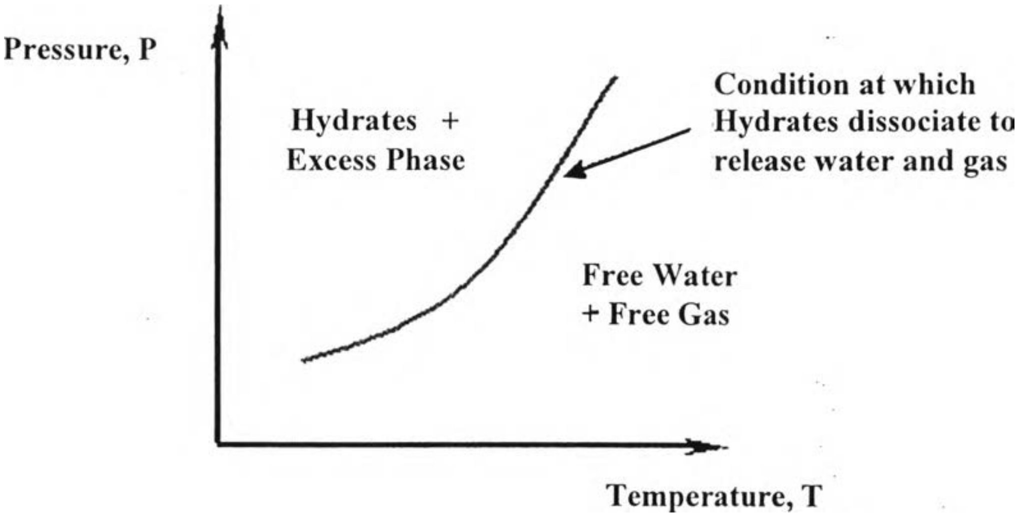

Figure 2.10 Phase behavior of water/hydrocarbon system (www.e-education.psu. edu.).

Cha *et al.* (1988) studied effect of bentonite as the third surface in the hydrate formation system compared to pure water system. The results indicated that the third surface may promote two important factors for hydrate formation: thermodynamic promotion and kinetics promotion. The third surface in the system may order the adsorption of water molecules in layer, which was easier to form hydrate cages for the thermodynamic promotion or may provide nucleation sites in the case of the kinetics promotion. Phase behavior equilibrium was changed due to the change in the liquid phase composition. The slope of the hydrate phase equilibrium is related to the heat of hydrate formation, which is the function of the type of hydrate structure formed or the condensed phase available (Sun *et al.*, 2008; Turner *et al.*, 2005; Wang *et al.*, 2008). The formation process of hydrates in porous medium is different from free water. In the free water system, the hydrates form at the gas/water interface initially. The formation in a porous medium like activated carbon, the water is adsorbed in the porous of activated carbon that have efficient contact area between gas and water that do not hinder further hydrate formation (Yan *et al.*, 2005). Hydrate nucleation occurs simultaneously in different locations in the porous medium, called multiple nucleation (Babu *et al.*, 2013b; Zhong *et al.*, 2013). Kumar *et al.* (2013) compared hydrate formation kinetics of quiescent water with silica gel. They found that the percent conversion of water to hydrates of silica gel was 8 times higher than quiescent water. The results suggested that larger surface area between gas and water in silica gel enhanced the conversion of water to hydrates.

Park *et al.* (2010) found the shift of equilibrium curve of 0.004 wt% multi-walled carbon nanotubes to a higher temperature at the same pressure and to lower pressure at the same temperature compared to the pure water system. The equilibrium curves are shown in Figure 2.11. Multi-walled carbon nanotubes also increased gas consumption indicating the increasing in amount of hydrates formation.

The change of equilibrium curves was also reported by Chari *et al.* (2013), Figure 2.12. The equilibrium curves of nano silica suspension were shifted into the lower pressure at the same temperature, and the slope of curves was changed. Pressure drop of pure water system was much lower than the nano silica suspension system indicating the lower amount of methane hydrates formation.

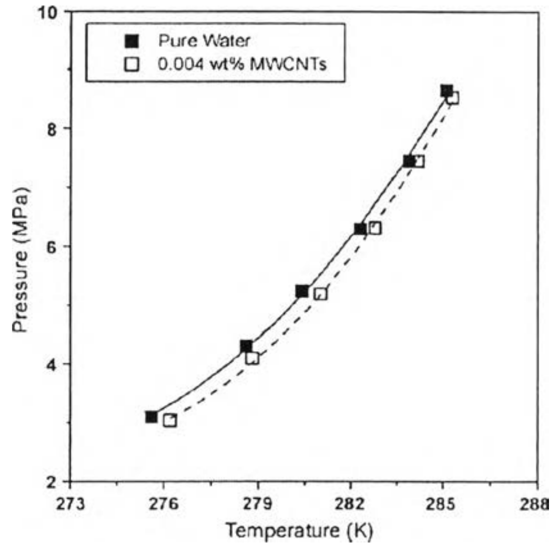

Figure 2.11 Equilibrium curve of 0.004 wt% multi-walled carbon nanotubes and pure water (Park *et al.*, 2010).

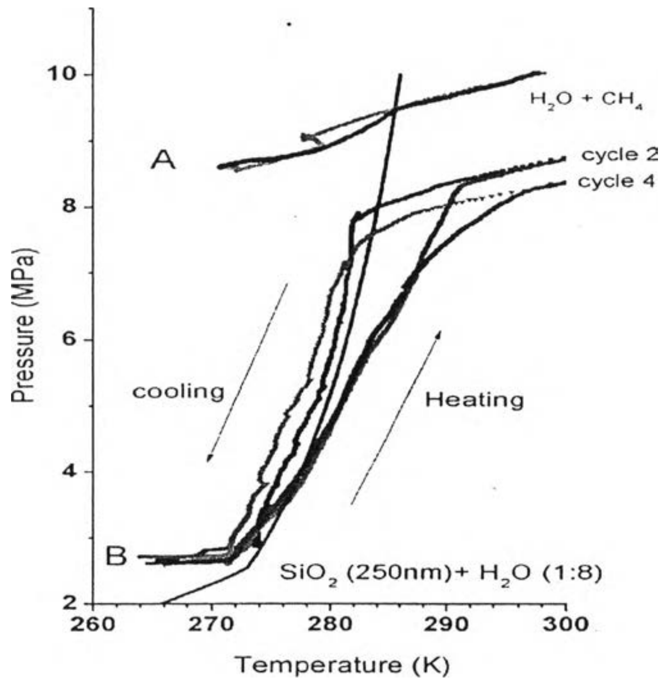

Figure 2.12 The pressure and temperature in methane hydrate systems. Curve A is with pure water system, while Curve B is for nano silica suspension system in two freezing-thawing cycles (Chari *et al.*, 2013a).

Different types of porous medium affect the gas hydrates formation, which depends on surface area, pore volume, pore size and pore distribution. Babu *et al.* (2013b) investigated different hydrate formation with the presence of silica gels and silica sand. The results showed that the gas uptake of silica sand was higher than silica gels because silica gels had internal pores, which affected the hydrate growth and hydrate formation. Kang *et al.* (2010) studied effects of pore sizes of silica gels to hydrate phase equilibrium. Figure 2.13 shows the shift of hydrate phase equilibrium to a higher pressure and a lower temperature when silica gels were added. The shift was increased as the pore size of silica gels decreased. Sun *et al.* (2014) investigated the hydrate formation in silica sand with different grain size. The results showed that the equilibrium curves of fined grain was shifted to a higher pressure and a lower temperature that means hydrate regions was decreased from the bulk system. The pore capillary force of fined-grain was greater than coarse-grain so the formation of hydrates in the fined grain silica sand was harder. The fined-grain has attraction at the surface more than the coarse-grain. The attraction of silica sand surface reduces activity of free water that decreases the free water to form hydrates. Siangsai *et al.* (2015) compared the methane hydrate formation and dissociation with different sizes of activated carbon (250 – 420 μm, 420 – 841 μm ,and 841 – 1680 μm). The results showed that the highest percentage of methane hydrate formation was conducted with 841 – 1680 μm or the larger size of activated carbon. The reason was the activated carbon size 841 – 1680 μm had interstitial space pores between particles which was preferred to form hydrate larger than other. On the whole, the above results indicate that the characteristics of porous medium significantly affect the hydrates formation (Zanjani *et al.*, 2012).

Hollow silica is silica grains, which have inner void. It has attractive unique properties such as permeable surface, large cavity, low density, high pore volume, high porosity, high specific area and good thermal insulation (Chen *et al.*, 2013). Prasad *et al.* (2014) studied gas hydrate formation in hollow silica matrix. The hydrates in pure water system formed at a high pressure, and the hydrate yield depended on driving force (pressure) of the system, while the hydrates in the hollow silica system formed at a moderate pressure (4-5 MPa) and gave higher hydrate yield. The result is shown in Figure 2.14. It also shows that the hydrate yield in the hollow silica increased rapidly at the moderate pressure but slowly increased at the high pressure, which was different from the pure water system. The hydrate yield was higher because effect of physi-sorption and methane hydrate formation. The hollow silica improved contact surface area between gas and water molecules to form hydrates, and another reason was the silica surfaces had lower polarity than water molecules so the methane hydrates formed easier on silica surfaces.

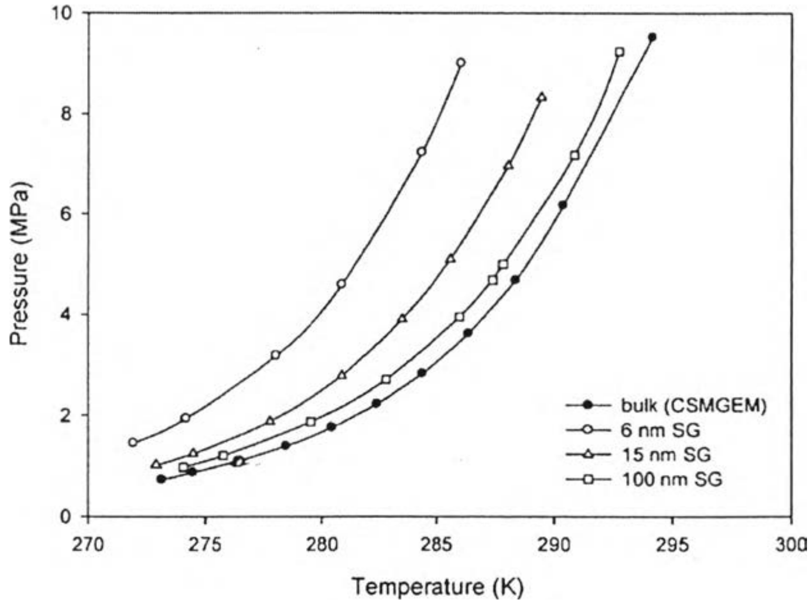

Figure 2.13 Hydrates phase equilibrium of natural gas hydrates in porous silica gels (Kang *et al.*, 2010).

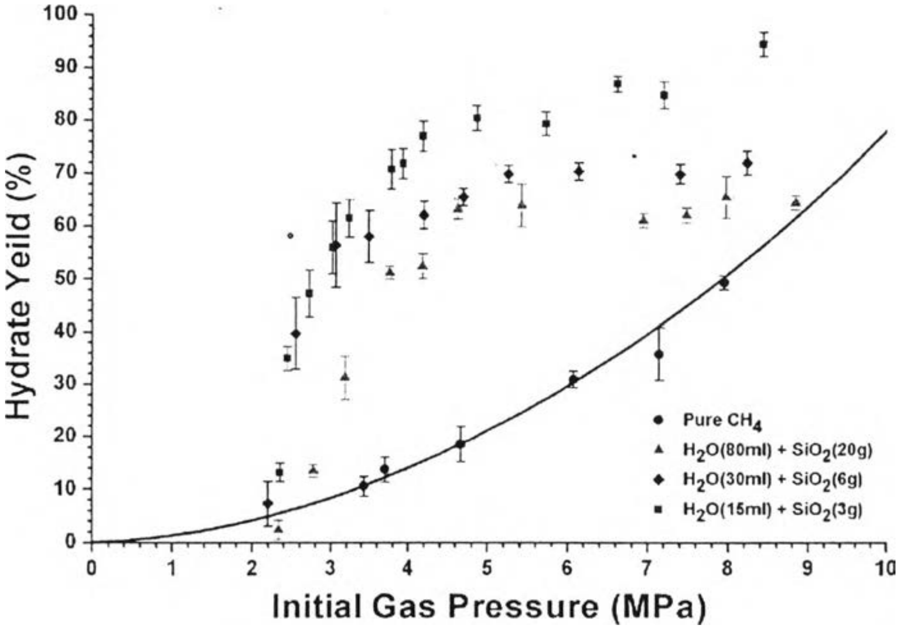

Figure 2.14 Gas hydrates yields at different pressures in methane-water-silica system (Prasad *et al.*, 2014).

2.4.2 Dissociation of Gas Hydrates

The dissociation of hydrates is an endothermic reaction. The production of natural gas from hydrates in sediment or permafrost is done by dissociation of the hydrates by changing the thermo-dynamic conditions in the system. The dissociation reaction is:

$$CH_4 \cdot 6H_2O(s) \rightarrow CH_4\,(g) + 6H_2O\,(l) \qquad (2.1)$$

There are three methods to dissociate gas hydrates: thermal stimulation depressurization and inhibitor injection (Demirbas, 2010b).

1. Thermal stimulation

Thermal stimulation is the process that addition of heat by raising temperature of system to higher than the hydrates dissociation temperature via injects steam, hot water or heated liquid to the system. The entire gas released by thermal stimulation is due to the hydrate dissociation and thermal expansion of gas in the crystallizer so the thermal expansion needs to be accounted to approach actual gas released from the hydrates dissociation (Babu *et al.*, 2013b). Nam *et al.* (2008) studied decomposition of methane hydrate by thermal stimulation at a constant pressure of 3.5 MPa and driving force 4°C in silica sand. The results showed that this method can achieve 95 to 98% of methane recovery.

2. Depressurization

Depressurization is process that decreased the pressure in the system to the free gas zone, where the hydrates is unstable, and it will decompose to gas and water. Haligava *et al.* (2010) investigated the decomposition of hydrates by depressurization in different volume of silica sand. They found that the required amount of heat to dissociate hydrates in smaller hydrates is less than the larger hydrates. When, the bed size of silica sand decreased, the rate of gas recovery increased meaning the duration of methane recovery was shorter. Xiong *et al.* (2012) indicated that depressurization in porous medium can divide in to three stages: free gas release at first, rapid hydrate dissociation, and slow hydrate dissociation. They also concluded that the lowering of dissociation pressure increases the dissociation rate. There are three important factors for depressurization: kinetics of dissociation, heat transfer and flow of fluids (Demirbas, 2010b).

3. Inhibitor injection

Inhibitor injection is the process that used the antifreeze or chemicals inhibitor such as glycol, methanol to shift the hydrates equilibrium, where the hydrates have no longer stable in that conditions.

The actual dissociation temperature of gas hydrates may be higher than the temperature of hydrates phase equlibrium because of self-preservation. Self-preservation is the condition, when the ice shield forms around gas hydrates. Dissociation of gas hydrates takes place after the ice shield melt. Hence, It can decrease the dissociation rate of gas hydrates or increase the stability of hydrates (Demirbas, 2010b).

Babu *et al.* (2013b) investigated the dissociation of hydrates in silca sand and silica gel. The dissociation characteristic, which was based on the dissociation curve, was similar even with different porous medium. They also suggested the combination of depressurization and thermal stimulation to decompose hydrates to achieve the complete gas recovery (99.6%).