AJChE 2016, Vol. 16, No. 2, 08 – 20

Thermodynamics Analysis on Methane Hydrate Formation in Porous Carbon

Wibiana W. Nandari *,1
Imam Prasetyo 2
Moh. Fahrurrozi 2
1 Chemical Engineering Department, UPN "Veteran" Yogyakarta, Jl. SWK 104 (Lingkar Utara), Condongcatur, Yogyakarta
2 Chemical Engineering Department, Universitas Gadjah Mada, Jl. Grafika no.2 Kampus UGM Yogyakarta
*e-mail: wibianawulan@upnyk.ac.id

Methane is a potential alternative energy source which is abundant and produces lower CO_2 emissions when it is used as fuel due to the content of C in the methane molecule is much lesser than its H content. Besides in a form of gas, methane in nature can also be in the form of methane hydrates. The formation process of methane hydrates in nature can be adopted as a method of storage of methane. In this study, a thermodynamics review will be studied related to temperature and pressure in a phase equilibrium system of methane hydrate . Thermodynamic model aims to predict the stability of methane hydrates for effective storage of methane. Each volume of methane hydrate contains as 164 volumes of methane gas under standard conditions (STP). The study was conducted by adsorbing methane on a wet porous carbon with the method of static volumetric.. The experimental results show that at the temperature of 274 K methane hydrates was formed at a pressure of 2.75 MPa; at a temperature of 275 K, pressure of 3.16 MPa; at a temperature of 276 K, pressure of 3.44 MPa, while at a temperature of 277 K, pressure of 3.67 MPa. Temperatures and pressures data are used to calculate the parameters of Langmuir equation constants modeled by the Van der Waals - Platteeuw for the chemical potential of water in the hydrate phase, Holder et al for the chemical potential of water in the liquid phase, as well as for the Gibbs-Thomson effect of porous carbon media.

Keywords : methane hydrate , modeling thermodynamics , Langmuir constants, porous carbon, mechanism of hydrate formation, methane storage

INTRODUCTION

Gas hydrate is non-stoichiometric crystal structure consist of host molecule such as water and chlarated guest molecules that are bounded to each other by hydrogen bonds. It has been confirmed the existence of abundant gas hydrate reserve on the sea floors so that methane hydrate has been believed as a very potential energy source to replace the depleting oil (Sloan 2008). Beside a high energy content, methane has also has higher octane number and burns cleaner than conventional petroleum based motor vehicle fuels.

Methane hydrate is a solid chlarated where a umber of guest molecule trapped within a crystal structure of host molecules that are formed a cage through hydrogen bounding. Methane hydrate is stable under low temperature and high pressures. One cubic meter of methane hydrate will release 164 m^3 of natural gas at 25 ^{o}C and atmospheric pressure. It is estimated that the current reserve of methane hydrate will not be depleted until 800 years with the current rate of gas production (Soesilo 2008). For each of 1 m^3 of column, there will be 0.2 m^3 of methane, while the rest ill be filled with the water (Makogon 2007).

Methane hydrate formation phenomena can be adopted as a safer methane storage technology compared to the existing ones. Currently, Methane is stored at room temperature under high pressure ranging from 200 to 250 bar or under low pressure (close to atmospheric pressure) under cryogenic temperature around -162 ^{o}C. High pressure storage necessitate the use multistage compressors which consumed significant energy and also very thick storage vessel. Additionally, high pressure methane may potentially cause explosion. Same wise, cryogenic gas storages also need relatively energy consuming process and special material for the storage vessel. This research proposes alternative methane storage based on hydrate formation on porous material (Prasetyo et al. 2011).

Previous studies show that methane storage in the form of adsorbed molecules on porous material is a promising technology from safety and energy consumption point of view (Dai 2009). Porous carbon is an attractive material for as an adsorbent for this purpose due to the a high surface area and low price (Talu 1992). In addition, carbon possesses an advantage of being hydrophobic and chemical resistant toward acids and alkaline, and stable structure at high temperatures and having non-polar surface (Yang 2003). Previous work by Yunanto (2012) shows that adsorption capacity of wet carbon toward methane is higher that of the dry one. Hydropobic nature of carbon is positive for hydrate formation. This may cause by the hydrophobic nature of the carbon surface that cause the water droplet formation that can enhance the contact surface. The higher the contact surface area, the more hydrate will form.

This research is aimed to study thermodynamics behavior of methane hydrate formation in porous carbon. Thermodynamics will enable to predict response of methane hydrate system toward system condition such as changes in system pressure and temperature.

RESEARCH METODOLOGY

Materials

This study used methane with purity 99.9 %, demineralized water, porous carbon specifically prepared from polymeric materials synthesized from formaldehyde and ethylene glycol (hence named RPF-EG2).

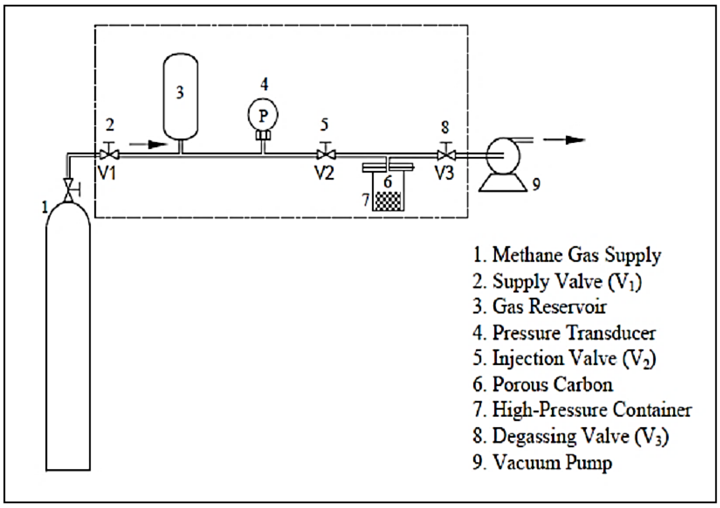

Fig. 1: . Schematic diagram of Methane Hydrate Formation Experiment

Research Tools

Experimental set-up is depicted in **Figure 1**.

Experimental Procedure

Experimental set-up for methane hydrate formation in porous carbon is shown in Figure1. The set up is basically an adsorption messurement apparatus assembled by using ultra high vacuum fitting and valve VCR$^{®}$ type from Swagelok$^{®}$ Prior to adsorption experiment, a specified amount of porous carbon sample was placed inside the sample cell, followed by degassing process to remove contaminants and moisture from the system. Subsequently, porous material was taken from the cell and then was weighed. The sample was returned to the cell and added with demineralized water with mass ratio = 1:1 gram water per gram of porous carbon.

During adsorption experiments, system temperature was varied to 174 K, 275, K, 276 K, and 277 K. By injecting methane gas under varied system pressure, adsorption data were obtained. Equilibrium conditions were indicated by the stabilized system pressures which were normally achieved for varied time ranging from 10 up to 120 minutes. The data obtained is presented as an adsorption isotherm curve.

The following measures must be taken prior to the adsorption test: regulator had been set at the maximum test pressure, assuring the vacuum pump work properly, the system pressure reach absolute vacuum 0 bar, and no leaking was found. Subsequently, valves V_2 and V_3 were then closed. To fill the cell, valve V1 was gradually opened until the desired pressure was reached (P1). Once the required pressure is reached valve V1 was then closed. Adsorption experiment was conducted by opening valve V2 and then observing the cell pressure changes until the equilibium pressure (P2). To obtain different equilibium pressure, the previous experimental procedure should be repeated for different initial pressure (P1) until the allowable maximum pressure was reached (4.0 MPa).

The mole of adsorbed gas can be determined by the following equation:

$$n_{ads} = \frac{P_1 V_1}{zRT} - \frac{P_2 V_2}{zRT} \quad (1)$$

Van der Waals and Platteeuw (1959) thermodynamically modeled methane hydrate formation similar to Langmuir model for adsorption. This was modeled as cages formation by water molecules wherein gas molecules enter into the cage structures. Upon equilibrium during methane hydrate formation, the water chemical potential difference in hydrate phase is equal to the chemical potential difference in liquid phase as shown by Eq (1).

$$\Delta\mu_w^H = \Delta\mu_w^\beta - \Delta\mu_w^H = \Delta\mu_w^\beta - \Delta\mu_w^L = \Delta\mu_w^L \quad (2)$$

Where μ_w^H is water chemical potential in the hydrate phase, μ_w^β is water chemical potential in an empty lattice at the system's temperature and pressure and μ_w^L is water chemical potential in the liquid phase.

$\Delta\mu_w^H$ can be computed through the mechanism modeled by Van der Waals and Platteew (1959) as:

$$\Delta\mu_w^H(T,P) = -RT\sum_{i=1}^{2} v_i ln\left(1 - \sum_{j=1}^{N_c}\theta_{ij}\right) \quad (3)$$

For type I hydrate, the number of small cavities is 1/23, and the large cavities is 3/23. θ_{ij} can be calculated by equation:

$$\theta_{ij} = \frac{C_{ij}.f_j}{1 + \sum_{j=1}^{N_c} C_{ij}.f_j} \quad (4)$$

On equilibrium among hydrate-liquid-vapor phases, fugacity of CH_4 on all phases are equal, hence:

$$f_{CH_4}^H = f_{CH_4}^L = f_{CH_4}^V \quad (5)$$

Where superscripts H, L, and V are for hydrate, liquid, and vapor respectively. Fugacity of CH_4 in vapor phase can be computed using EOS that was developed by Duan et al. (1992). By modifying Lee and Kesler EOS, that can be written in the form:

$$Z = \frac{PV}{R_g T} = \frac{P_r V_r}{T_r} = 1 + \frac{B}{V_r} + \frac{C}{{V_r}^2} + \frac{D}{{V_r}^4} + \frac{E}{{V_r}^5} + \frac{F}{{V_r}^2}\left(\beta + \frac{\gamma}{{V_r}^2}\right) exp\left(-\frac{\gamma}{{V_r}^2}\right) \quad (6)$$

$\Delta\mu_w^L$ can be calculated the model proposed by Holder et al. (1980):

$$\frac{\Delta\mu_w^L(T,P)}{R.T} = \frac{\Delta\mu_w^0(T_0,0)}{R.T_0} - \int_{T_0}^{T}\left(\frac{\Delta {h_w}^{\beta-L}}{R.T^2}\right)dT + \int_0^P\left(\frac{\Delta {V_w}^{\beta-L}}{R.T}\right)dP - lna_w \quad (7)$$

Porous media influence the equilibrium on the liquid phase on which dissociation as described by Gibbs-Thomson developed by Dicharry et al. (2005) can be described as:

$$\Delta\mu_w^L(pore) = \Delta\mu_w^L(bulk) + V^\beta \frac{F.\sigma_{HW}.cos\alpha}{r} \quad (8)$$

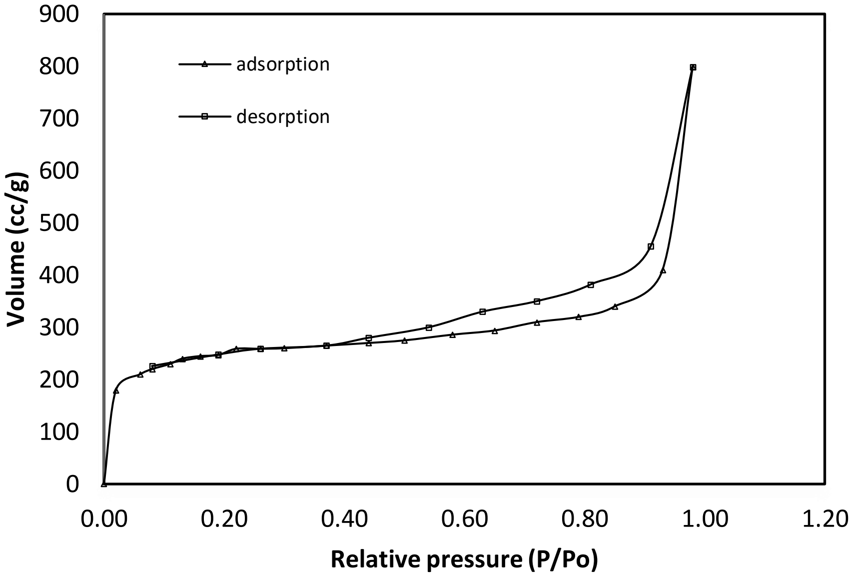

Fig. 2: . Nitrogen Adsorption-Desorption Isotherm on Porous Carbon

Langmuir constant is the key parameter to predict cage occupancy (cages that are filled with guest molecules). Value of Langmuir constant (C_{ij}) of j type gas on I type cavity depend on the temperature. According to Sun et al. (2007), Langmuir contestant of gas j on cavity type of c is defined as:

$$C_{ij} = \frac{z_{ij}}{kT} = \frac{1}{kT}\iint exp\left[-\frac{\Phi(r,\Omega)}{kT}\right] dr\, d\Omega \qquad (9)$$

In this work, equation to predict Langmuir constant is simplified as:

$$C_{ij,CH_4}(T) = \frac{1}{R_g T} exp\left(A + \frac{B}{T}\right) \qquad (10)$$

RESULT AND DISCUSSION

Porous Carbon Characterization

The study use mesoporous carbon material. Material characterization was performed using BET. Adsorption desorption characteristics of the material is shown in **Figure 2** while the pore structure is given in **Table 1**.

The isotherm curves on Figure 2 indicate that mesopore structure is more dominant than micropore structure. This is shown by the shape of the isotherm curves that that are steeper at relative pressure (P/P_0) close to 1.0 and similar to type IV of those IUPAC standards. Figure 2 also shows the hysteresis phenomena as indicated by the separation of desorption and adsorption curves. Hysteresis phenomenon occurs only for adsorbents with predominantly mesopore or macro pore structure.

Porous carbon structure that includes internal surface area, pore size distribution, mean pore diameter, and pore volume can be obtained from adsorption-desorption isotherm utilizing NOVA 2000 (No Void Analysis) apparatus. Characterization result of material use in this study is shown in Table 1.

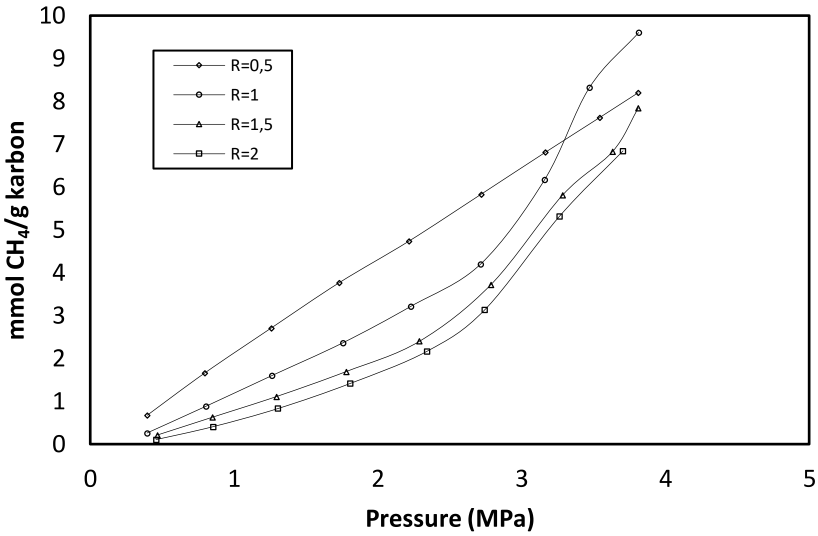

Fig. 3: . Influence of Water-Carbon Ratio on Methane Hydrate Formation

Table 1. Characteristics of the Mosepores Carbon

Specific internal surface ara (S_{BET})	770 m^2/g
Total pore volume	1.23 cm^3/g
Micropore volume (V_μ)	0.1149 cm^3/g
% V_μ	9.34 %
Mesopore volume (V_{me})	1.1151 cm^3/g
% V_{me}	90.66 %
Mean pore diameter	6.389 nm

Table 1 shows that volume of mesopores reaching 1.1151 cm^3/g is significantly higher that volume of micropores that amount only 0.1149 cm^3/g. The average pore diamater is 6.389 which is fall under the range of mesopore size (2 nm< D_{avg}< 50 nm). These results lead to the conclusion that the porous carbon material used in this study is mosopore carbon.

Determining Optimum Water-Porous Carbon Ratio for Methane Hydrate Formation

Water : carbon ratio (w/w) significantly influence the onset of methane hydrate formation. To find the optimum water: carbon ratio, study was performed under the water: carbon ratio variation of 0.5, 1.0, 1.5, and 2.0. Adsorption system was carefully controlled above the water freezing point temperature (275 K) to avoid the ice formation.

Figure 3 shows that water : carbon ratio of 1 gives the maximum methane hydrate. Under pressure below 31.6 MPa, methane gas was only dissolve into water. Once the pressure high enough to allow hydrate formation (31.6 MPa), the adsorb methane rise significantly. This indicates the hydrate formation. According to Carroll (2009) there are 3 requirement of the hydrate formation, i.e. the existence of guest molecules (methane gas), the existence of host molecule (sufficient water), and conducive operating condition. Hence, it can be concluded that under water : carbon ratio of 1, these requirement was met optimally.

Experimental results for water-carbon ratio of 0.5 show a straight linear trend without a steep change in the end. This

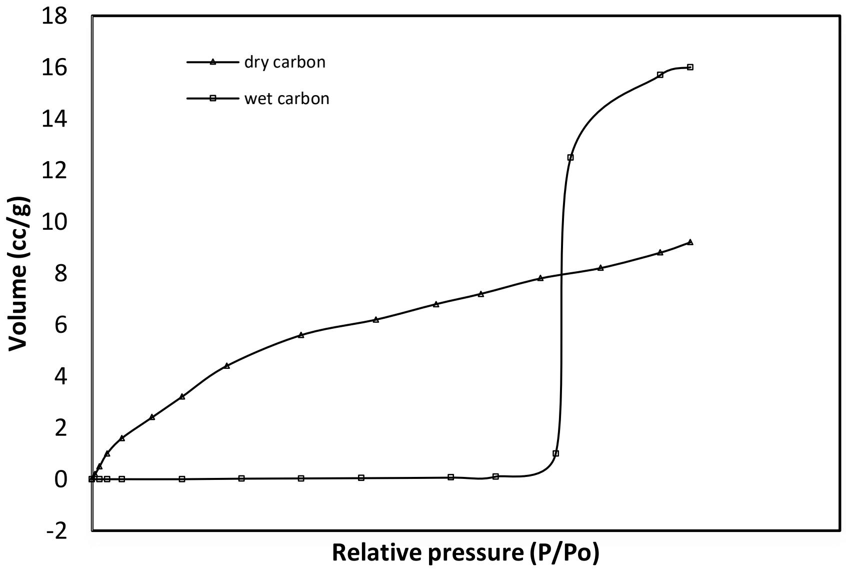

Fig. 4: . Comparison of Adsorption Isotherms of Methane Gas on Dry and Wet Mesoporous carbon (Yunanto 2012)

indicates that no methane hydrate was formed. Experimental results for carbon ratio of 1.5 and 2.0 show proper trends of hydrate formation by steep change in methane adsorption in the ends although the amount of adsorbed methane was lower than that of experiment with water carbon ratio 1.0. This lead to a conclusion that the existence of excess water is not beneficial in maximizing methane hydrate formation since the excess water may block pores of the mesoporous carbon and hence lower the available surface area to facilitate the contacts between water and methane molecules.

These results are inline with results of the previous work from this group by Yunanto (2012). Yunanto (2012) compared methane adsorption on dry and wet mesoporous carbon. As shown in **Figure 4**, wet mesoporous carbon could not significantly adsorb methane under system pressure 0 – 3.0 MPa. This very dramatically changed when the system pressure reach the range of 3.0 – 4.0 MPa. Under 3.0 MPa, only physisorption occurs which is very limited due to the blocking some of the carbon pores by water (Celzard et al. 2005). When the system pressure reach 3.0 MPa, methane hydrate starts to form since all the requirement of methane hydrate formation are present. This is shown by the dramatic change in the amount of adsorbed methane to the extend far exceed the adsorbtion capacity of dry mesoporous carbon. Under 4.0 MPa pressure, adsorption capacity of wet mesoporous carbon reach almost twice of that dry mesoporous carbon.

Previous work by Celzard (2006) investigate the optimum water-carbon ratio for methane hydrate formation. The optimum ratio of 1.0 in this work, in fact, confirms the previous finding by Celzard (2006).

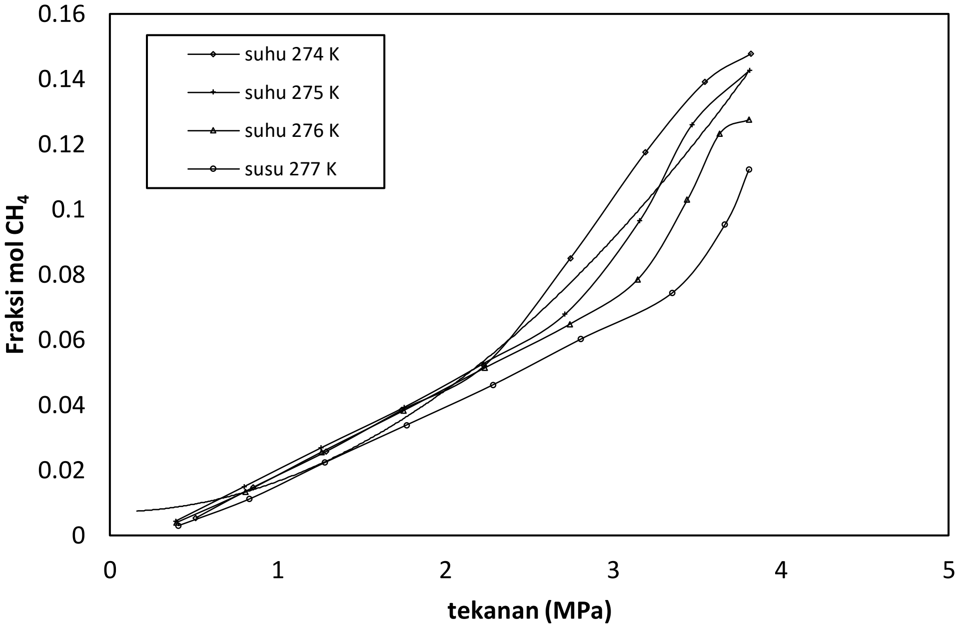

Fig. 5: Methane Hydrate Formation Curve at Various Temperatures

Table 2. Influence on System Condition to the Hydrate Number

Temperature (K)	Pressure (MPa)	Hydrate Number (n)
274	2.75	5.77
275	3.16	6.00
276	3.44	6.43
277	3.67	7.90

Influence on Temperature on Methane Hydrate Formation on Wet Mesoporous carbon

The experiment was performed by adsoprtion of methane gas on porous carbon with the method of static volumetric. The adsoprtion system was conditioned at various experimental temperatures (274 K, 275 K, 276 K, and 277 K) and vacumed prior to the injection of the the adsorbate (CH_4). The test gas (methane) was injected gradually under various pressure. The equilibrum was presumed when a stable system pressures are reached. This normally toke between 20- 120 minutes. Experimental results are shown in **Figure 5**.

The amount of water that form hydrate cages can be indicated by the hydrate number. Hydrate number is defined as ratio between the number of water molcule and the number of methane molecule in the hydrate. The minimum number hydrate is 5.75 which shows that all the water form hydrate. Experimental results show that as the system temperature is higher, the measured hydrate number is lower. This is shown in **Table 2.** This indicates that as the temperature is higher, the number of methane gas molecules in the hydrate is lower.

Thermodynamics Analysis of Methane Hydrate Formation on Porous Carbon Material

One of the objectives of this research is to determine the Langmuir constants for methane hydrate systems at equilibrium. The values of constants A and B for small and large cages were fitted to the experimental temperature and pressures data that fulfill the equilibrium criteria, e.i. the water chemical potentials in hydrate phase are equal to those in liquid phase. Measured temperature are compared with the calculated temperature that fulfilled Eq. (3).

$$\sum_{i=1}^{2} ln(1-\theta_{ij}) = \frac{\Delta\mu_w^0(T_0,0)}{R_g.T_0} - \int_{T_0}^{T}\left(\frac{\Delta h_w{}^{\beta-L}}{R.T^2}\right)dT - \int_0^P\left(\frac{\Delta V_w{}^{\beta-L}}{R.T}\right)dP - lna_w + V^{\beta}\frac{F.\sigma_{HW}.cos\alpha}{r} \quad (11)$$

The best fitted values of the contants are shown in **Table 3**.

Table 3. Langmuir Cosntants for Methane Hydrate System on Porous Carbon

Constants	Small Cages	Large Cages
A	7.5562	7.8734
B	18.9996	18.9986

Hence:

For small cage,

$$C_{i,CH_4}(T) = \frac{1}{R_g T}\exp\left(7,5562 + \frac{18,9996}{T}\right) \quad (12)$$

For large cage,

$$C_{i,CH_4}(T) = \frac{1}{R_g T}\exp\left(7,8734 + \frac{18,9986}{T}\right) \quad (13)$$

Figure 6 shows that the model can well fit the experimental data. This shows that equilibrium model well fit the experimental data. This shows that equlibrium model of Van der Waals

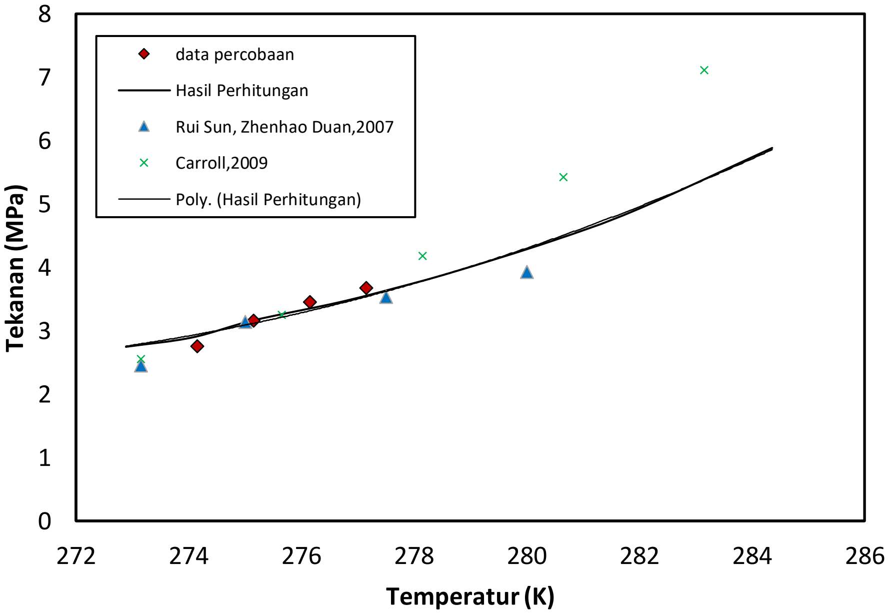

Fig. 6: Equilibrium model and the experimental data

Platteeuw and Gibbs-Thomson can be used to accurately model the formation of methane hydrate in porous carbon.

Allow it to air dry for some time and then spray 50% sulfuric acid, then heat for 10 minutes. The formations of colored spots were observed.

CONCLUSION

Several conclusions can be drawn from this study, they are :

1. Hydrophocity of the pore walls of porous carbon material caused the water absorbed on the carbon surface forms small clusters which act as nuclei for the crystallisation of methane hydrate. Therefore the formation of methane hydrate within porous material is easier than that in the bulk water.
2. At the equilibrium of Hydrate-Liquid-Vapor, the higher the temperature require greater pressure of hydrate formation and resulting bigger hydrate number.
3. Langmuir constants can be used to predict the equilibrium conditions of methane hydrate and cage filling fraction of methane molecules. In this study, the Langmuir constant values obtained are:

   For small cage,

   $$C_{i,CH_4}(T) = \frac{1}{R_g T}\exp\left(7,5562+\frac{18,9996}{T}\right)$$

   For big cage,

   $$C_{i,CH_4}(T) = \frac{1}{R_g T}\exp\left(7,8734+\frac{18,9986}{T}\right)$$
4. The mechanism of hydrate formation in porous media can be adopted as an effective method for methane storage.

REFERENCES

1. Aladko. E.Y., Dyadin, Y.A., Fenelonov, V.B., Larionov, E.G., Mel'gunov, M.S., Manakov, A.Y., Nesterov, A.N., Zhurko, F.V. (2004). *Dissociation conditions of methane hyydrate in mesoporous silica gels in wide ranges of pressure and water content*, J. Phys. Chem., B 108, 16540-16547. [Journal article]
2. Anderson, R., Llamedo, M., Tohidi, B., Burgass, R.W. (2003). *Characteristic of chlathrate hydrate equilibria in mesopores and interpretation of experimental data*, J.Phys.Chem., B 107, 3500-3506. [Journal article]
3. Baker, F. S. (1980). *Activated Carbon Adsorption Handbook Second Edition*, Michigan : Ann Arbor Science Pub Inc. [Books]
4. Benedict, W.S., Gailar, N., Plyler, E.K., J. (1956). *Chemical Physis.* [Books]
5. Bugge, T., Benderson, R.H., Kenyon, N.H. (1988). *Phil Trans Roy Soc Lond.* [Books]
6. Carroll, John (2009). *Natural Gas Hydrates*, Elsevier's Science and Technology Rights Departement in Oxford. [Books]
7. Celzard, A., Mareche, J. F. (2005). *Optimal Wetting of Active Carbons for Methane Hydrate Formation*, Universite Henry Poincare-Nancy, France. [Journal article]
8. Clarke, M.A., Pooladi-Darvish, M., Bishnoi, P.R. (1999). *A Method to Predict Equilibrium Conditions of Gas Hydrates Formation in Porous Media*,

Ind. Eng. Chem. Res., 38, 2485-2490. [Journal article]

9. Clennell, M.B., Hovland, M., Booth, J.S., Henry, P., Winters, W.J. (1999). *Formation of Natural Gas Hydrates in Marine Sediments*, *Conceptual Model of Gas Hydrate Growth Conditioned by Host Sediment Properties*, J., Geophys, Res., 104(B10), 22985-23003. [Journal article]
10. Dai, X.D., Liu, X.M., Xing, W., Qian, L., Qiao, K., Yan, Z.F. (2009). *Natural Gas Storage on Activated Carbon Nodified by Metal Oxides*, J Porous Mater, vol.16, pp.27-32. [Books]
11. Davidson, D. W. (1983). *Natural Gas Hydrate*, Butterworths, London. [Books]
12. Dicharry, C., Gayet, P., Marion, G., Graciaa,A., Nesterov, A. N. (2005). *Modeling Heating Curve for Gas Hydrate Dissociation in Porous Media*, J. Phys. Chem., B109, 17205-17211. [Journal article]
13. Do, D. D. (1998). *Adsoprtion Analysis:Equilibria and Kinetics*, Imperial College Press, 203 Electrical Engineering Building, Imperial College, London SW 72 BT, pp.13-17; 50-59. [Books]
14. Fauzi, A. A. (2012). *Adsorpsi Gas* CO_2 *Menggunakan Karbon Mesopori dari Pirolisis Resin Resorcinol-Phenol-Formaldehyde dengan Penambahan Etylen Glycol*, Laporan Penelitian, Universitas Gadjah Mada, Yogyakarta. [Journal article]
15. Handa, Y. P., Stupin, D. (1992). *Thermodynamic properties and dissociation characteristics of methane and propane hydrates in 70-A-Radius silica gel pores*, J. Phys. Chem 96, 8599-8603. [Journal article]
16. Henry, P., Thomas, M., Clennell, M. B. (1999). *Formation of Natural Gas Hydrates in Marine Sediments*, J Geophys. [Journal article]
17. Klauda, J. B., Sandler, S.I. (2001). *Modeling Gas Hydrate Phase Equilibria in Laboratory and Natural Porous Media*, Ind. Eng. Chem. Res., 40, 4197-4280. [Journal article]
18. Klauda, J.B., Sandler, S.I. (2003). *Predictions of Gas Hydrate Phase Equilibria and Amounts in Natural Sediment Porous Media*, Mar Pet Geol, 20, 459-470. [Journal article]
19. Legget,J. (1990). *Global Warming : The Greenpeace Report,* Oxford University Press, Oxford. [Books]
20. Lysne, D. (1995). *An Experimentall Study of Hydrate Plug Dissociation by Pressure Reduction*, D.Ing, Thesis, Norwegian Institute of Technology. [Thesis]
21. Makogon, Y. F., Holditch, S.A. and Makogon, T.Y. (2007). *Natural gas Hydrate-A Potential Energy Source for 21th Century*, Journal Petrolleum Science and Engineering. [Journal article]
22. Manocha, S.M. (2003). *Porous Carbons*, Sadhana volume 28 part 1&2 pp 335-348, India. [Books]
23. McCelland, A. L. (1963). *Dipole Moment*, San Fransisco. [Books]
24. Mutiara, T. (2013). *Tinjauan Termodinamika Pembetukan Hidrat Metana pada Media Glass Beads*, Laporan Thesis, Universitas Gadjah Mada, Yogyakarta. [Thesis]
25. Penelitian tim BPPT
26. Pople, J.A. (1951). *Proc Royal Society.*

[Books]

27. Ponnivalavan, Yee, D., Linga, P., Palmer, A., Cheong, B., Soon, T., Rangsunvigit, P. (2013). *Morphology of Methane Hydrate Formation in Porous Media.* [Journal article]
28. Prasetya, I., Budhijanto, Rochmadi, Yunanto, R., Ariyanto, T. (2011). *Methane Storage by Methane Hydrate Formation Within Water-Saturated Porous Carbon, The Effect of Mesoporosity.* [Journal article]
29. Qiu Jun-hong, Guo Tian-min, (2002). *Kinetics of Methane Hydrate Formation in Pure Water and Inhibitor Containing Systems*, Chin. J. Chem. Eng., 2002, V10(3):316-322. [Journal article]
30. Riestenberg, D., West, O., Lee, S.C., McCallum, S., Phelps, T.J. (2003). *Sediment surface effect of methane hydrate formation and dissociation*, Mar. Geol, 198,181-190. [Journal article]
31. Roadifer, R. D., Godbole, S.P., Kamath, V.A. (1987). *SPE California Regional Meeting,* Ventura. [Journal article]
32. Rodrigues, A.E., Leva, D., dan Tondeur, D. (1989). *Adsorption: Science and Technology*, Kluver, Dordrect. [Books]
33. Ruppel, C. (1997). *Anomalously cold temperatures observed at the base of the gas hydrate stability zone on the U.S. Atlantic passive margin*, Geology 25, 699-702. [Journal article]
34. Schmuck, E.A, Paull, C.K. (1993). Geo-Mar.Lett. [Journal article]
35. Seo. Y., Lee, H. (2003). *Hydrate phase equilibria of the ternary mixture in silica gel pores*, J. Phys. Chem., B 107, 889-894. [Journal article]
36. Seshandri, K., Wilder, J.W., Smith, D.H. (2001). *Measurement of Equilibrium Pressures and temperatures for propane Hydrate in Silica Gels with Different Pore-Size Distributions*, J. Phys. Chem., B 105, 2627-2631. [Journal article]
37. Sing, K. S. W., Everett, D. H., Haul, R. A. W., Moscoul, L., Pierotti, R.A., Rouqerol, J., Siemieniewska, T. (1985). *Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Source Area and Porosity*, Pure Appl, Chem., 57, pp. 603-619. [Journal article]
38. Sloan, E. D., Koh, C. A. (2008). *Chlatrate Hydrates of Nautral Gases*, 3rd Edition, Taylor and Francis Group, USA. [Books]
39. Smith, D.H., Wilder, J. W., Seshandri, K. (2002). *Methane Hydrate Equilibria in Silica Gels with Broad Pore-Size Distribution*, AIChE.J.48, 393-400. [Journal article]
40. Soesilo, (2008). *Gas Hidrat Metan (methane hydrate) Sumber Energi Alternatif Masa Depan Pengganti BBM*, http://komenindo.blogspot.com. [Journal article]
41. Sudibandriyo, M. (2003). *A Generalized Ono-Kondo Lattice Model for High Pressure on Carbon Adsorben*, Ph.D Disertation, Oklahoma State University. [Disertation]
42. Sun, R., Duan, Z. (2007). *Prediction of CH4 and CO2 Hydrate Phase Equilibrium and Cage Occupancy From ab Initio Intermolecular Potential*, Geochim Cosmochim. [Journal article]
43. Sung Chan Nam, Lingga, P., Haligva, C., Ripmeester, J.A., Englezos, P. (2008). *Kinetics of Hydrate Formation and Decomposition of Methane in Silica Sand*, Proceedings of the 6th

International Conference on Gas Hydrates, British Columbia, Canada. [Conference papers]

44. Talu, O. (1992). *An Overview of Adsorptive Storage of Natural Gas, Fundamentals of Adsorption*, Proc. 4th Int. Conf. On Fundamentals of Adsorption, Kyoto, May 17-22, pp.655-662. [Journal article]
45. Traufetter, Gerald, (2008). *Methane Hydrate China and India Exploit Icy Energy Reserves*, http://komenindo.blogspot.com. [Journal article]
46. Trehu, M. A., Bohrmann, G., Rack, R.F., Torres, M. E., Bargs, N. L., et al. (2006). in *Proc.ODP (Ocean Drilling Program)*, Initial Repts. 204, Texas A & M University, College Station. [Journal article]
47. Uchida, T., Takeya, S., Chuvilin, E.M., Ohmura. R.,Nagao, J., Yakushev, V.S., Istomin, V.A., Minagawa, H., Ebinuma, T., Narita, H. (2004). *Decomposition of methane hydrates in sand*, a=sandstone, clays, and glass beads, J., Geophys. Res. 109, B05206. [Journal article]
48. Van der Waals, J. H., Platteeuw, J. C. (1959). *Clathrate Solution*, In : Prigogine, I. (Ed), Advances in Chemical Physics, Interscience. [Journal article]
49. Waldeza, R. (2012). *Pengaruh Suhu Terhadap Pembuatan Karbon Aktif dari Proses Pirolisis Ploimer RPF dengan Aktivasi CO_2 Serta Pengaruhnya Terhadap Adsorpsi Butana*, Laporan Penelitian, Universitas Gadjah Mada, Yogyakarta. [Journal article]
50. Wilder, J. W., Seshandri, K., Smith, D. H. (2001). *Modeling Hydrate Formation in Media with Broad Pore Size Distribution*, Langmuir 17,6729-6735. [Journal article]
51. www.iea.org/publications, (2012).
52. www.bp.com/statisticalreview, (2012).
53. Yang, R. T. (2003). *Adsorbent Fundamentals and Applications*, University of Michigan, Michigan. [Journal article]
54. Yunanto, R. (2012). *Penjerapan Gas Rumah Kaca dengan Menggunakan Berbagai Karbon Berpori*, Laporan Thesis, Universitas Gadjah Mada, Yogyakarta. [Thesis]
55. Zhang. W., Wilder, J.W., Smith, D. H. (2002). *Interpretation of methane hydrate equilibrium data for porous media involving hydrate-ice euilibria*, AIChE.J.48, 2324-2331. [Journal article]
56. Zhou, Y.P., Dai, M., Zhou, L. (2004). *Storage of Methane on wet activated carbon*: Influence of pore size distribution. [Journal article]