Preparation of powdered activated carbon from rice husk and its methane adsorption properties

Marriyappan Sivagnanam Balathanigaimani, Hyun-Chul Kang, Wang-Geun Shim, Chan Kim, Jae-Wook Lee* and Hee Moon[†]

Faculty of Applied Chemical Engineering, Chonnam National University, Gwangju 500-757, Korea
*Department of Environmental and Chemical Engineering, Seonam University, Namwon 590-170, Korea
(Received 18 January 2006 • accepted 2 March 2006)

Abstract−Success of adsorbed natural gas (ANG) storage process is mainly based on the characteristics of the adsorbent, so various synthesized adsorbents were analyzed for methane adsorption on a thermodynamic basis. Activated carbon from rice husk (AC-RH) was synthesized and its methane adsorption capacities were compared with phenol based activated carbons (AC-PH$_2$O and AC-PKOH). The adsorption experiments were conducted by volumetric method under various constant temperatures (293.15, 303.15, 313.15 and 323.15 K) and pressure up to 3.5 MPa. Maximum methane adsorption was observed in AC-RH as its surface area is higher than the other two adsorbents. The experimental data were correlated well with Langmuir-Fruendlich isotherms. In addition, isosteric heat of adsorption was calculated by using Clausius-Clapeyron equation.

Key words: Adsorbed Natural Gas, Activated Carbon, High Pressure Adsorption, Isosteric Heat of Adsorption

INTRODUCTION

Natural gas that satisfies environmental and economical concerns is one of the most desired fuels now in energy field compared to liquid fuels such as gasoline and diesel. Natural gas is an abundant and the cleanest burning alternative transportation fuel today. Natural gas vehicles (NGVs) have surpassed all other competitors in delivering superior emissions performance. Moreover, NGVs have been certified to the most demanding environmental emission standards. Although it is more convenient than liquid fuel, due to its low energy density at standard temperature and pressure (STP) conditions, storing huge amounts of methane in a given volume is very difficult. Thus, it has become the perfect challenge for active researchers [Perrin et al., 2005]. Also, the development of natural gas storage and transportation technologies is very important for the future. Well known conventional methods (e.g., liquefied natural gas (LNG) and compressed natural gas (CNG)) may be the solution for storage purposes even though they have some problems in both safety and cost wise [Lozano-Castello et al., 2002; Menon and Komarneni, 1998; Basumatary et al., 2005]. For example, storing high density methane in LNG vehicles is possible at cryogenic temperature. However, the specialized container design and refueling procedure required are undesirable for vehicular fuel application. In CNG due to low energy density compared to gasoline, multi stage compression increases the cost of the process and a relatively huge tank is required [Burchell, 1999]. Adsorbed natural gas (ANG) is one of the best alternatives for natural gas storage and inevitable technology to store the natural gas at 3.5 MPa under room temperature compared to CNG and LNG processes [Quinn and MacDonald, 1992; Burchell and Rogers, 2000; Wegrzyn and Gurevich, 1996]. Because of its low capital and operating cost compared with CNG, the ANG process is being considered as an on-board technology for NGVs [Jian

sun et al., 1996]. One of the most important problems in the ANG process is the development and evaluation of adsorbents [Quinn and MacDonald, 1992]. The majority of carbon adsorbents are granular, powder, or fibers. Clearly, an adsorbent with high pore volume and high surface area is important for adsorption in mass basis [Sircar et al., 1996]. Activated carbon exhibits the largest adsorption capacity and highest ANG energy [Cracknell et al., 1993]. Highly micro porous carbons are the most promising adsorbents for natural gas storage [Mota, 1999]. Large internal area and chemically inert graphite surface area of the activated carbon are the basic reason for its strong adsorption of non-polar and weakly polar molecules [Kim et al., 2003]. Microporosity in activated carbon adsorbent is basically formed by removal of carbon atoms by an activation process. To improve the adsorption capacity of the activated carbon, selected precursors and opt processing technologies have been employed [MacDonald and Quinn, 1998; Lozano-Castello et al., 2001]. Volumetric method is an important and widely accepted one for the adsorption amount measurement in high pressure absorption experiments [Belmabkhout et al., 2004]. Isosteric heat of adsorption is used to explain the nature of the surface. Adsorbents' surface structure can be elucidated by the relationships between isosteric enthalpy and coverage [Hill, 1949].

In this study, the preparation and characterization of activated carbon from rice husk (AC-RH) were investigated for methane storage. Methane adsorption on prepared carbon samples was conducted under various constant temperatures (293.15, 303.15, 313.15 and 323.15 K) and pressure up to 3.5 MPa to select the suitable adsorbents for the methane adsorption in mass basis. In addition, isosteric heat of adsorption was determined by employing the Clausius-Clapeyron equation.

EXPERIMENTAL

1. Porous Materials Preparations

For this methane adsorption we used activated carbon derived

[†]To whom correspondence should be addressed.
E-mail: hmoon@chonnam.ac.kr

from rice husk (AC-RH), Phenol based activated carbons such as steam activated phenol based carbon (AC-PH$_2$O) and potassium hydroxide activated phenol based carbon (AC-PKOH). By the contribution of suitable precursors and activation processes, these adsorbents were synthesized and characterized at the Carbon Materials Laboratory in Chonnam National University.

AC-RH was prepared from rice husk by the consecutive processes of sealed dry distillation and activation. Before processing the rice husk was washed and dried. Dried rice husk was carbonized at 1,000 °C in the presence of nitrogen. Then the carbonized product crushed by milling equipment. KOH was mixed with the crushed material at 4/1 ratio and heated to 800 °C for 2 hours in nitrogen. The activated product was consequently washed with 0.3 M HCl and distilled water. Finally, the washed product was dried at 120 °C in vacuum condition to form the porous carbon.

Novolac type Phenol resin was used as the precursor for the preparation of AC-PH$_2$O and AC-PKOH. The product formation steps for AC-PKOH and AC-PH$_2$O were the same up to the carbonization step. The only difference in AC-PKOH and AC-PH$_2$O product formation was the activation processes. Initially, 10% cross linking agent (hexa methylene diamine (HMDA)) was mixed with Novolac type phenol resin and heated at 150 °C. The resulting product was carbonized at 1,000 °C in nitrogen. For AC-PH$_2$O product formation, the carbonized material was activated in the presence of saturated steam up to 800 °C for 2 hours. In AC-PKOH formation, KOH was mixed with the carbonized product at 4/1 ratio and heated to 800 °C for 2 hours in the presence of nitrogen. Then the activated product was consequently washed with 0.3 M HCl and distilled water (pH 7). Finally, the washed product was dried at 120 °C in vacuum condition to form the porous carbon.

2. Experimental Set-up and Procedure

The static volumetric method was used for the indirect measurement of the adsorbed amount [Choi et al., 2004]. Loading cell and adsorption cell were the two important parts in experimental setup, with 1/8 in. tubes and 1/8 in. valves to minimize dead volume as much as possible. Fig. 1 shows the experimental setup for the volumetric method. With the help of novel helium gas, the volume of the loading cell (506.96 mL), the volume of adsorption cell (505.33 mL) and volume of the dead cell were measured. The temperature of each cell was measured by K-type thermocouples operated within

Fig. 1. Schematic diagram of the adsorption set-up.

±0.01 K. The temperature was maintained throughout the process by using a constant temperature water bath (BS-21, Jeio tech). A pressure transducer was also incorporated for the measurement of pressure in each cell. The adsorbents were kept in a high vacuum oven for more than 12 hours at 423.15 K to remove the moisture content before being put into the adsorption cell. A vacuum pump was attached to the experimental set-up to remove traces of impurities in adsorbents. The adsorption experiments were conducted at various constant temperatures. The experiments were started by introducing adsorbate in loading cell after reaching the requirement temperature in each cell. Meanwhile, the adsorption cell was closed to reach the equilibrium state in loading cell. After equilibrium was attained in the loading cell, the adsorbate was allowed to enter into the adsorption cell. The equilibrium state of adsorption in each cell was considered at constant temperatures and pressures. A recorder (MV 100, Yokogawa Co.) was used to record the temperatures and pressures before and after adsorption. The high pressure adsorption experiments were conducted by increasing the pressure up to 3.5 MPa at various constant temperatures. The amount adsorbed was calculated from the mass balance equation using the experimental data of the temperatures and pressures (before and after adsorption equilibrium state).

$$\left.\frac{PV}{ZRT}\right|_{L1} + \left.\frac{PV}{ZRT}\right|_{A1} = \left.\frac{PV}{ZRT}\right|_{L2} + \left.\frac{PV}{ZRT}\right|_{A2} + qM \tag{1}$$

where, P is the pressure, T is the temperature, R is the gas constant, M is the molecular weight, Z is the compressibility factor, and q is the amount adsorbed. Before adsorption equilibrium state conditions of the loading cell and adsorption cell are represented by the terms L1 and A1. The terms L2 and A2 indicate the after adsorption equilibrium state conditions of the loading cell and adsorption cell respectively.

RESULTS AND DISCUSSION

1. Adsorbents Characterizations

Nitrogen adsorption and desorption analysis for all adsorbents was carried out by volumetric sorption analyzer (Micromeritics type ASAP-2000). The Brunaur-Emmet-Teller (BET) surface area, pore size and micropore volume of AC-RH, AC-PKOH and AC-PH$_2$O samples were determined by applying the BET equation into the adsorption/desorption N$_2$ at 77 K. Such isotherms are shown in Fig. 2. The results show that all samples have Type I isotherm characteristics and negligible hysteresis between adsorption and desorption, which are a type representative of microporous solids. Although the samples show a microporous nature, their micropore size distributions are different. The nitrogen adsorption and desorption tests indicated that the BET surface area of AC-RH was higher than the other two adsorbents. The overall physical properties of the adsorbents are given in Table 1.

2. Methane Adsorption

A high pressure adsorption study by volumetric method is considered advantageous because of its simple configuration and its fabrication cost. The methane adsorption studies on AC-RH were conducted at three different temperatures (303.15 K, 313.15 K and 323.15 K) by increasing the pressure up to 3.5 MPa. On the other hand, AC-PKOH and AC-PH$_2$O were treated at 293.15 K, 303.15 K,
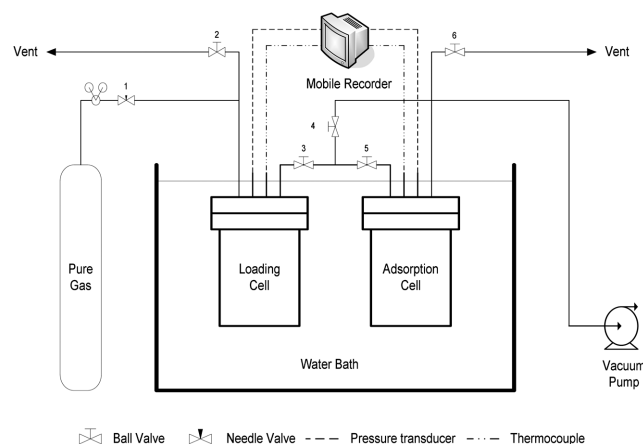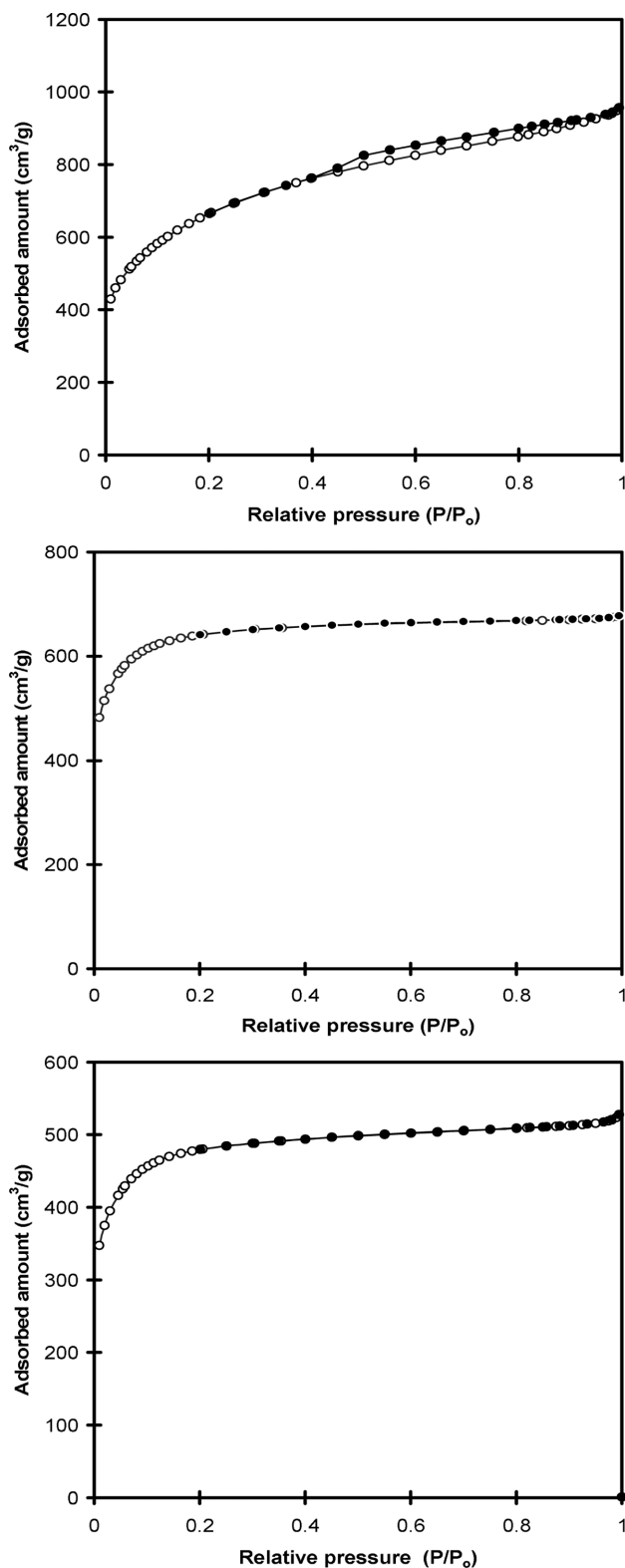
Fig. 2. Nitrogen adsorption and desorption isotherms for AC-RH, AC-PKOH and AC-PH₂O.

and 313.15 K, respectively, under the same pressure conditions such as AC-RH. Adsorbed amount was predicted by substituting the experimental values in the mass balance equation (Eq. (1)). Maximum of 9.48 mmol/g methane was adsorbed by AC-RH at 25.15 atm pres-

sure under a constant isothermic condition (303.15 K). Even though AC-RH has low micropore volume compared to AC-PKOH, the methane adsorbed amount in the mass basis was higher than AC-PKOH because of its high surface area. It was found that at the maximum amount of 10.498 mmol/g methane adsorbed by AC-PKOH at 35.373 atm under constant temperature of 293.15 K and exactly 8.022 mmol/g of methane was adsorbed by AC-PH₂O at 35.371 atm under a constant isothermic condition of 293.15 K. Methane adsorption capacity of AC-PH₂O was less than the other adsorbents because of its low surface area and low micropore volume. Totally, it was observed that adsorption capacity of all adsorbents decreases with increases in temperature and indicated the physisorption relationship between adsorbents and adsorbate.

To correlate experimental equilibrium data, a number of equilibrium isotherm models can be utilized. Pure species isotherms such as Langmuir isotherm, Fruendlich isotherm, Langmuir-Fruendlich isotherm, Toth and Unilan isotherms equations were considered for the result correlations. Percentage error was introduced along with the isotherms because the volumetric method has some disadvantages such as the gas tightness and the inherent errors. The main sources of errors of this technique are the error in the determination of the pressure cell and adsorption cell volumes, the error in the pressure and temperature measurements, the error due to leakage at high pressure, the error in the sample mass and the error due to the equation of state [Belmabkhout et al., 2004]. The percentage error factor was calculated by,

$$E = \frac{1}{n}\sum_{i}^{n}\left|\frac{N_i^{obs} - N_i^{cal}}{N_i^{obs}}\right| \times 100 \qquad (2)$$

where, N_i^{obs} are the experimental data, N_i^{cal} are the correlation data and n is the number of data.

Positive points of the entire single component isotherms were considered and analyzed in various ways to select the suitable isotherm for our problem. Accuracy and mathematical simplicity are the two important parameters to analyze the importance of any isothermal model. Number of independent parameters in the model is directly proportional to the accuracy of an isothermal model. Number of independent parameters and mathematical simplicity are the main reasons for the popularity of any model [Malek and Farook, 1996]. High adjustable independent parameters compared with Langmuir and Fruendlich isotherms and also the mathematical simplicity of Langmuir-Fruendlich isotherm were more suitable for this high pressure adsorption study. In addition, the value of percentage error was very low. Meanwhile, Langmuir and Fruendlich isotherms have only two adjustable parameters and Toth and Unilan equations failed to predict the experimental data at high pressure [Yang, 1987; Choi et al., 2003]. Finally, based on these advantages, the Langmuir-Fruendlich isotherm was selected in the correlation of high pressure adsorption experimental results. The mathematical form of Langmuir-Fruendlich is as follows:

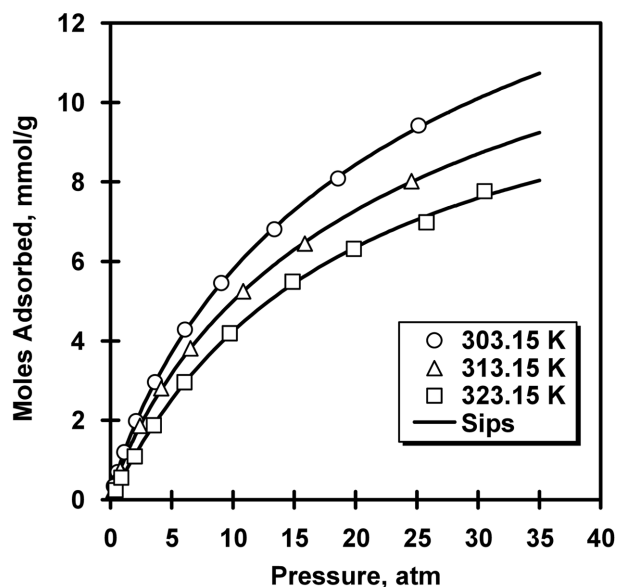$$q = \frac{q_m B P^{1/n}}{1 + B P^{1/n}} \qquad (3)$$

where, q is the amount adsorbed, P is the pressure and q_m, B, and n are isotherm parameters. The measured experimental data of all the adsorbents were correlated with the Langmuir-Fruendlich isotherm, and the parameters of Langmuir-Fruendlich isotherm along with

Table 1. Physical properties of adsorbents

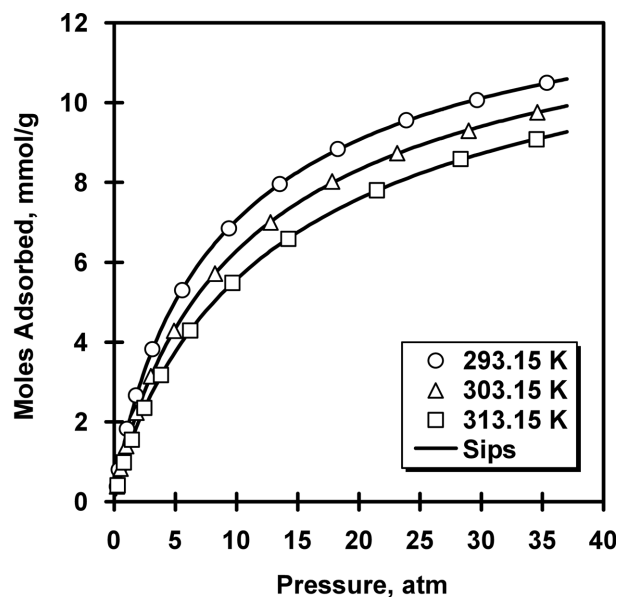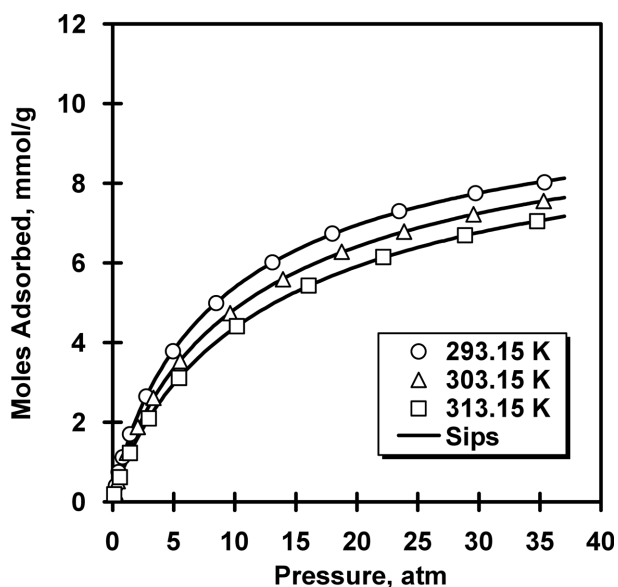| Adsorbent	Average particle size (μm)[a]	BET S.S.A/(m²/g)[b]	t-plot Micropore volume (cm³/g)	T.P.V (cm³/g)[c]	Average pore size (Å)
AC-RH	50	2350	0.95	1.48	24.90
AC-PKOH	7	2200	0.98	1.05	19.03
AC-PH₂O	5	1660	0.73	0.82	19.73

[a]Measured by particle size analyzer.
[b]BET specific surface area calculated by BET method.
[c]T.P.V.: Total pore volume 4V/A by BET.

Table 2. Langmuir-Freundlich isotherm parameters for methane on AC-RH, AC-PKOH, and AC-PH₂O

Adsorbent	Temperature K	q_m mmol/g	b atm⁻¹	n	Error %
AC-RH	303.15	19.35	0.060	1.171	0.014
	313.15	16.091	0.060	1.143	0.005
	323.15	12.146	0.050	0.969	0.047
AC-PKOH	293.15	13.906	0.141	1.157	0.018
	303.15	13.574	0.115	1.143	0.003
	313.15	13.473	0.095	1.150	0.001
AC-PH₂O	293.15	10.686	0.137	1.148	0.005
	303.15	10.508	0.115	1.149	0.003
	313.15	10.261	0.01	1.147	0.001

Fig. 3. Adsorption isotherms of methane on AC-RH.

Fig. 4. Adsorption isotherms of methane on AC-PKOH.

Fig. 5. Adsorption isotherms of methane on AC-PH₂O.

percentage errors are given in Table 2. Graphical representations of Langmuir-Fruendlich isotherms are shown in Fig. 3 to Fig. 5 by plotting the predicted values of pressure and adsorbed amount. These figures show the nonlinearity and indicate the heterogeneous characteristics of the adsorbents which are a very common nature of the activated carbons [Choi et al., 2003]. Maximum uptake of methane was achieved by AC-RH and the order of the adsorption capacities of activated carbons was almost the same order of the BET surface area.

The AC-RH adsorption equilibrium data of methane was compared with the literature data. Even though the nature of the materials was different, methane isotherms on AC-RH by volumetric meth-

Table 3. Comparison of physical parameters and adsorption capacity of various adsorbents

Adsorbent	Source	BET surface area (m^2/g)	HK pore size (Å)	$V_{DR} (N_2)$ Pore volume (cm^3/g)	Adsorption capacity (mmol/g)
Maxsorb-A*	Petroleum pitch	3100	9.14	1.38	10 (at 298.15 K under 2.5 MPa)
KUA41651*	Anthracite	2523	9.50	1.16	9 (at 298.15 K under 2.5 MPa)
CFC79*	Petroleum pitch	2370	9.27	1.13	8.27 (at 298.15 K under 2.5 MPa)
AC-RH	Rice Husk	2350	10.2	0.95	9.3 (at 303.15 K under 2.5 MPa)

*Cited in literature [Lozano-Castello et al., 2002].

od were compared with cited literatures based on its surface area. The higher surface area is found to be one of the important parameters for favorable methane adsorption. In addition to the surface area, micropore size and micropore volume of AC-RH were also compared with the adsorbents which were cited in the previous literatures [Lozano-castello et al., 2002; Shuji Himeno et al., 2005; Zhou et al., 2000]. The methane adsorption capacities and physical properties of adsorbents such as Maxsorb-A, KUA41651, and CFC79 from the previous literatures were compared with AC-RH and given in Table 3. Table 3 indicates that AC-RH has the largest pore size and lowest pore volume compared with other adsorbents. According to the previous results, the optimum pore size for methane storage was between 1-2 nm and this characteristic coincided with AC-RH pore size [Lozano-castello et al., 2002]. Interestingly, the quantity of methane uptake by adsorbent AC-RH was better than the data from previous literature on the mass basis. The adsorption activity of AC-RH might be due to its large pore size and low pore volume.

3. Isoteric Heat of Adsorption

In this study, the isosteric enthalpies of adsorption were calculated by the Clausius-Clapeyron equation [Hill, 1949]. Usually, adsorption is a process that occurs through exothermic reaction. In the ANG process, adsorption with low heat of adsorption is the preferred one. Thermodynamics-based isosteric heat of adsorption was calculated

by using the Clausius-Claypeyron equation and the adsorption isotherms for at least three different temperatures.

$$\frac{q_{st}}{RT^2} = \left[\frac{\partial \ln P}{\partial T}\right]_q \tag{4}$$

where, P is the pressure, T is the temperature, R is the gas constant and q_{st} is the isosteric enthalpy. The value of isosteric enthalpy of adsorption was very high for AC-RH and low for AC-PH$_2$O. The isosteric adsorption at low surface coverage is related to the interaction between the adsorbent surfaces and adsorpative molecular forces [Nguyen et al., 1999]. A graph of the adsorbed amount and isosteric heat of adsorption is shown in Fig. 6. The isosteric enthalpies of AC-PKOH and AC-PH$_2$O increased slightly with an increased adsorbed amount. This indicates the homogeneous adsorption of the system. The results also show that the isosteric enthalpy of methane for AC-RH first decreased and then increased with a continuous adsorbed amount increment. Decreasing isosteric enthalpy with increasing adsorbed amount usually indicates the heterogeneous surface [Hill, 1949; Shuji Himeno et al., 2005]. Here, surface heterogeneity induces this kind of nonlinearity and it is a very common nature of the activated carbons [Jaroneic et al., 1990]. Although the isosteric heat adsorption for AC-RH was quite high compared to previous results [Shuji Himeno et al., 2005], its adsorption capacity was appreciable one in mass basis.

CONCLUSIONS

The adsorbed amounts of methane on adsorbents were calculated by using a mass balance equation. The adsorption capacities of adsorbents were ordered as AC-RH>AC-PKOH>AC-PH$_2$O, respectively, based on the experimental results. It was found that the higher surface area of AC-RH was the main reason for its superiority in methane adsorption. Predicted data successfully correlated with Langmuir-Fruendlich isotherm because of its flexibility and low percentage error. Graphical representations of the Langmuir-Fruendlich isotherm solid lines indicate the heterogeneous nature of all adsorbents. Clausius-Claypeyron equation was used for isosteric heat of adsorption calculation, resulting in the conclusion that the AC-RH has energetically heterogeneous surface whereas AC-PKOH and AC-PH$_2$O have homogeneous surfaces. Results from the Clausius-Claypeyron equation confirmed the Langmuir-Fruendlich isotherm results.

Fig. 6. Isosteric enthalpy of adsorption as a function of surface loading.

REFERENCES

Basumatary, R., Dutta, P., Prasad, B. and Srinivasan, K., "Thermal modeling of activated carbon based adsorpative natural gas storage system," *Carbon*, **43**, 541 (2005).

Belmabkhout, Y., Frere, M. and DeWeireld., "High-pressure adsorption measurements. A comparative study of the volumetric and gravimetric methods," *Meas. Sci. Technol.*, **15**, 848 (2004).

Burchell, T. D., *Carbon materials for advanced technologies*, Pergamon, Oxord (1999).

Burchell, T. and Rogers, M., SEA Paper No. 2000-01-2205, Pub. Society of Automotive Engineers, Inc. (2000).

Choi, B.-U., Choi, D.-K., Lee, Y.-W. and Lee, B.-K., "Adsorption equilibria of methane, ethane, ethylene, nitrogen, and hydrogen on to activated carbon," *J. Chem. Eng. Data*, **48**, 603 (2003).

Choi, B.-U., Nam, G.-M., Choi, D.-K., Lee, B.-K., Kim, S.-H. and Lee, C.-H., "Adsorption and regeneration dynamics characteristics of methane and hydrogen binary system," *Korean J. Chem. Eng.*, **21**, 821 (2004).

Cracknell, R. F., Gordon, P. and Gubbins, K. E., "Influence of pore geometry on the design of microporous materials for methane storage," *J. Phys. Chem.*, **97**, 494 (1993).

Dubinin, M. M., "The potential theory of adsorption of gases and vapors for adsorbents with energetically nonuniform surfaces," *Chem. Rev.*, **60**, 235 (1960).

Hill, T. L., "Statistical mechanics of adsorption. V. Thermodynamics and heat of adsorption," *J. Chem. Phys.*, **17**, 520 (1949).

Jaroneic, M., Lu, X. C. and Madey, R., "Use of polynomial equation for analysing low concentration adsorption measurements of ethane on activated carbon," *Sep. Sci. Tech.*, **24**, 1355 (1990).

Jian Sun, Mark, J. R., Massoud, R.-A. and Anthony, A. L., "Natural gas storage with activated carbon from a bituminous coal," *Gas. Sep. Purif.*, **10**, 91 (1996).

Linares-Solano, V., "Advances in the study of methane storage in porous carbonaceous materials," *Fuel*, **81**, 1777 (2002).

Lozano-Castello, D., Lillo-Rodenas, M. A., Cazorla-Amoros, D. and Linares-Solano, A., "Preparation of activated carbons from spanish anthracite. I. Activation by KOH," *Carbon*, **39**, 741 (2001).

Lozano-Castello, D., Cazorla-Amoros, D. and Linares-Solano, A., "Powdered activated carbons and activated carbon fibers for methane storage: A comparative study," *Energy & Fuels*, **16**, 1321 (2002).

Kim, B.-H., Kum, G.-H. and Seo, Y.-G., "Adsorption of methane and ethane into single-walled carbon nannotubes and slit-shaped carbonaceous pores," *Korean J. Chem. Eng.*, **20**, 104 (2003).

MacDonald, J. A. F. and Quinn, D. F., "Carbon adsorbents for natural gas storage," *Fuel*, **77**, 61 (1998).

Malek, A. and Farooq, S., "Comparison of isotherm models for hydrocarbon on activated carbon," *AIChE J.*, **42**, 3191 (1996).

Menon, V. and Kormarnei, S., "Porous adsorbents for vehicular natural gas storage: A review," *J. Porous. Mater.*, **5**, 43 (1998).

Perrin, A., Celzard, A., Albiniak, A., Jasienko-Halat, M., Mareche, J. F. and Furdin, G., "NaOH activation of anthracites: Effect of hydroxide content on pore textures and methane storage ability," *Micropor. Mesopor. Mater.*, **81**, 31 (2005).

Quinn, D. F. and MacDonald, J. A., "Natural gas storage," *Carbon*, **30**, 1097 (1992).

Mota, J. P. B., "Impact of gas composition on natural gas storage by adsorption," *AIChE J.*, **45**, 986 (1999).

Nguyen, D. M. and Do, D. D., "Adsorption of supercritical gases in porous media: determination of micropore size distribution," *J. Phys. Chem. B.*, **103**, 690 (1999).

Shuji, H., Toshiya, K. and Shoichi, F., "High-pressure adsorption equilibrium of methane and carbon dioxide on several activated carbons," *J. Chem. Eng. Data*, **50**, 369 (2005).

Sircar, S., Golden, T. C. and Rao, M. B., "Activated carbon for gas separation and storage," *Carbon*, **34**, 1 (1996).

Wegrzyn, J. and Gurevich, M., "Adsorbent storage of natural gas," *Applied Energy*, **55**, 71 (1996).

Yang, R. T., *Gas separation by adsorption processes*, Butterworths Publishers, Stoneham (1987).

Zhou, L., Zhou, Y., Ming, L. and Wang, Y., "Experimental and modeling study of the adsorption of supercritical methane on a high surface activated carbon," *Langmuir*, **16**, 5955 (2000).