

Experimental and Theoretical Study on the CH₄ Adsorption by Granular and Microporous Activated Carbon

A. Aleghafouri¹, M. Mahdyarfarm^{2*}, M. Mohsen-Nia¹, A. Mohajeri² and M. Asghari¹

1- Chemical Engineering Group, Department of Engineering, University of Kashan, Kashan, Iran

2- Gas Division, Research Institute of Petroleum Industry (R.I.P.I.), Tehran, Iran
mahdyarfarm@ripi.ir

Abstract

Adsorbed natural gas (ANG) by Granular Activated Carbon (GAC) has been widely investigated as an alternative to CNG and LNG technologies for storage and transportation of natural gas. In the present work, a theoretical and experimental study was conducted to accurately determine the amount of adsorption of CH₄ by GAC. To carry out the experiments, the volumetric method was used up to 4 MPa at constant temperature of 298 K. Also, various adsorption isotherm models were used to model the experimental data collected from the experiments. The accuracy of the results obtained from the adsorption isotherm models was compared and the values for the regressed parameters were reported. The results shows that the amount of CH₄ adsorbed is dependent on the physical characteristics of activated carbons. Moreover, the Toth, two term TVFM and Sips isotherm models show good agreement with the experimental data.

Key words: Adsorbed Natural Gas, Activated Carbon, Adsorption Isotherm

Introduction

One of the main drawbacks of natural gas (NG) as a fuel is its low density. For example, 1 L of NG at normal temperature and pressure (NTP) will yield 0.04 MJ on combustion while 1 L of gasoline will yield 34.8 MJ [1]. Whereas natural gas is a cheap and readily available source of fuel, its suitability for a particular application depends on the ability to store an adequate amount of it. This is a particularly acute problem in the design of gas driven vehicles. Storage is also a problem in the gas supply industry. NG needs to be stored at periods of low demand to meet peak requirements and it needs to be transported in containers by road, rail, and sea to regions not connected by pipeline. The principle constituent of NG is methane, which has a critical temperature of 191 K. Thus, NG cannot be liquefied by pressure alone. Liquefied natural gas (LNG) is usually stored as a boiling liquid at about 113 K in a cryogenic tank at a pressure of about 1 atm (0.103 MPa). Alternatively, the gas is stored as a compressed supercritical fluid known as compressed natural gas (CNG) at room temperature and about 200 MPa. LNG has a density of about 600 times greater than that at NTP (denoted 600 v/v) while CNG is about 220 v/v [1].

ANG by GAC has been widely investigated as an alternative to CNG and LNG technologies for storage and transportation of natural gases [2-8]. The physical characteristics of adsorbent, *i.e.*, activated carbon can significantly affect the amount of gas adsorbed and desorbed by GAC. Extensive investigations have been directed to study such effect [9-11].

In this study, theoretical and experimental investigations were performed to determine the adsorption of CH₄ by commercial microporous GACs up to 4 MPa at 298 K and to study different adsorption isotherm models to correlate the adsorption data.

Experimental Materials

Two commercial granular microporous activated carbons were used in this study:

The sample AC1 was purchased from Silcarbon Company and sample AC2 was supplied by Norit Company. It should be mentioned that except for the work of Mohammadi et al. [12] in which a study of CH₄ adsorption at pressures lower than 1 MPa has been carried out, experimental and theoretical studies on the CH₄ adsorption up to 4 MPa by these adsorbents have not been previously done.

Table 1- Physical specification of AC samples used

Sample	BET surface area(m ² /gr)	Micropores volume (cm ³ /gr)	Average pore diameter (Å)
AC1	1170	0.48	10.3
AC2	1117	0.45	11.5

Table 1 contains the physical specifications of tow samples obtained by applying N₂ adsorption using ASAP2010 (Micromeritics Co.) apparatus.

CH₄ Adsorption measurement

To obtain the adsorption isotherms of CH₄ on activated carbons a volumetric based apparatus was used in this study. A schematic diagram of the apparatus is shown in Fig. 1. This set up also has a pressure transducer to measure the equilibrium pressure with the accuracy of ±1 mbar. Prior to measurement, the samples are degassed at 300 °C for approximately 2 h at low pressure.

To determine the amount of CH₄ adsorbed on the activated carbon, at first stage, the adsorption cell is filled up with the degassed AC, the dead volume inside the cell is then determined with helium injection from the reference cell, which has been previously filled with helium gas up to the initial pressure and the adsorption cell reaches the thermodynamic equilibrium condition by opening valve 2. The total volume of the reference and adsorption cells and connecting lines is assumed to be V₂, where helium can be penetrated into and it can be calculated using P₁, the initial pressure of the reference cell, P₂ the equilibrium pressure of the whole adsorption system (the reference cell and the adsorption cell), and V₁, the volume between valves 1 and 2. Therefore, it is possible to determine the dead volume (V_{void}) inside the adsorption section (between valves 2 and 3) using the following relation:

$$V_{void} = V_2 - V_1 \quad (1)$$

To inject CH₄, the reference cell is filled with CH₄ at a known pressure. Then, gas from the reference cell is injected to the adsorption cell by opening the connecting

valve. Having reached equilibrium, the connecting valve between the adsorption and reference cells is closed and this procedure is repeated for further pressures of adsorption isotherm. To determine the amount of CH₄ adsorbed at any equilibrium pressure, the following equation was employed:

$$P_{1,i} V_1 = Z_{1,i} n_{1,i} RT \quad (2)$$

$$P_{2,i} V_2 = Z_{2,i} n_{2,i} RT \quad (3)$$

$$P_{2,i-1} V_{void} = Z_{2,i-1} n_{void,i} RT \quad (4)$$

Where P_{1,i} and P_{2,i} are the initial pressure of the reference cell and the equilibrium pressure of the adsorption and reference cells for a defined point (for example i) of CH₄ adsorption isotherm, respectively, and n_{1,i}, n_{2,i} and n_{void} represent the mole numbers of CH₄ before and after equilibrium in the V₁, V₂ and V_{void} volumes, respectively. Also, Z is the compressibility-factor of CH₄, which can be determined at a defined pressure using the simple form of the virial expansion [13]:

$$Z = 1 + \frac{BP}{RT} = 1 + \left(\frac{BP_C}{RT_C} \right) \left(\frac{P_r}{T_r} \right) \quad (5)$$

In which

$$\frac{BP_C}{RT_C} = B^0 + \omega B^1 = B^0 + 0.0104B^1 \quad (6)$$

Where

$$B^0 = 0.083 - \frac{0.422}{T_r^{1.6}} \quad (7)$$

$$B^1 = 0.139 - \frac{0.172}{T_r^{4.2}} \quad (8)$$

Finally, the mole numbers of CH₄ adsorbed on the activated carbon at this pressure is determined as shown below:

$$n_{adsorbed,i} = n_{1,i} + n_{void,i-1} - n_{2,i} \quad (9)$$

Therefore, the amount of adsorption (the mass ratio of adsorbed CH₄ (g) to activated carbon (g)) at a defined pressure is calculated by dividing the weight of adsorbed CH₄ (n_{adsorbed} × 16.034) by that of the activated carbons filled in the adsorption cell.

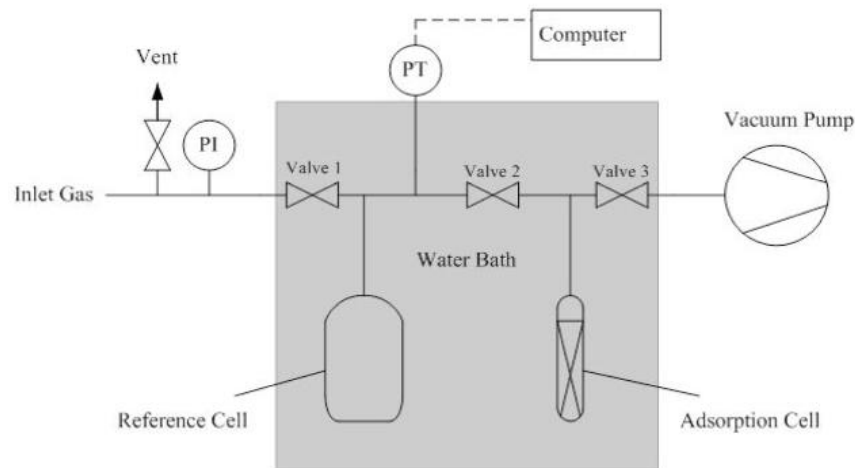


Figure 1- Schematic diagram of the volumetric based apparatus used to CH₄ adsorption measurements

Table 2- Different isotherm models

Isotherm model	Equation
Langmuir	$W = W_0 \frac{bP}{1 + bP}$
Freundlich	$W = KP^{1/n}$
Sips	$W = W_0 \frac{(bP)^{1/n}}{1 + (bP)^{1/n}}$
Toth	$W = W_0 \frac{bP}{(1 + (bP)^r)^{1/r}}$
Dubinin - Radushkevich (DR)	$W = W_0 \exp\left(-\left(\frac{A}{E}\right)^2\right)$
Two-Term TVFM	$W = W_{01} \exp\left(-\left(\frac{A}{E_1}\right)^2\right) + W_{02} \exp\left(-\left(\frac{A}{E_2}\right)^2\right)$

Where $A = RT \ln(P_s/P)$, P : operation pressure, P_s : saturation pressure

Modeling

To reduce the experimental data, different adsorption isotherm models were used. The adsorption isotherm models used in this study are rendered in Table 2. As observed, each adsorption isotherm model is based on its own physical and theoretical concept and contains several adjustable parameters. The details of the assumptions made for each adsorption isotherm models are given elsewhere [14-16].

The parameters for the adsorption isotherm models were obtained by the least square fit of the adsorption models to the experimental data collected in this study using the *Sigma plot ver. 11.0* software. It is noteworthy that the coefficient of determinations (R^2_{adj}) was used to

obtain the regressed parameters of the models.

Results and discussion

To determine the CH₄ adsorption isotherms, the experimental data obtained were used at twelve equilibrium pressures up to nearly 4 MPa and temperature of 298 K for each GAC sample. Figure 2 shows the adsorption isotherms of CH₄ for the GAC samples used in this study. It can be seen that amounts of CH₄ adsorbed increases by pressure rising, but the increasing trend is not significant at higher pressures. Also, the results show that sample AC1 has the higher adsorption in comparison with sample AC2, and this is because of the higher micropore volume and BET surface area.

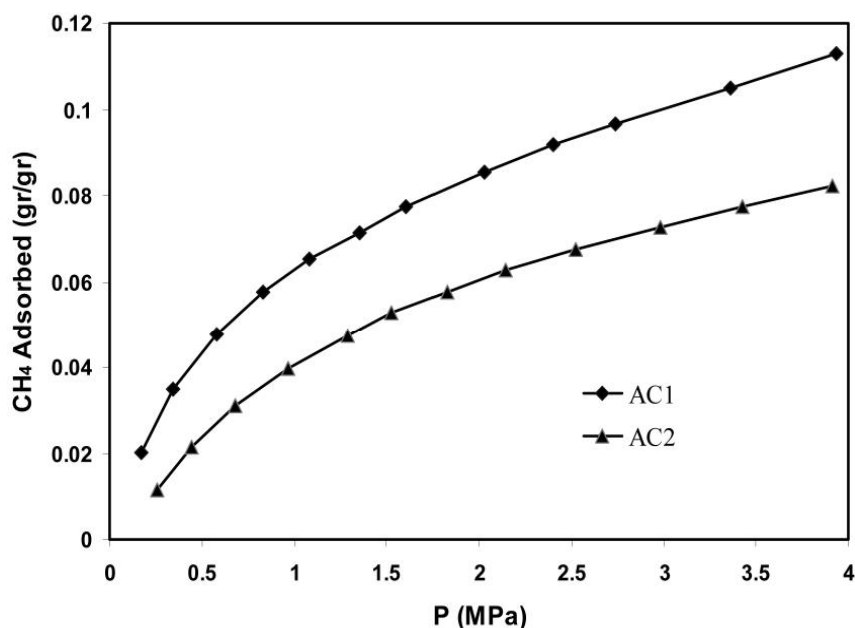


Figure 2- CH₄ adsorption isotherms for the GAC samples

To compare samples used in this study with wood based granulated carbon used by ADVANTICA technology, the values of STP volume of CH₄ adsorbed per volume of adsorbent (v/v) at 2.45 MPa and room temperature together with enhancement factor (ANG/CNG storage) are presented in table 3 [17]. It can be seen that the values for the samples used in this study are better than those of the sample used by ADVANTICA technology. Also, it should be mentioned that although v/v values for the sample used in this study at 3.5 MPa and room temperature are not high (75 v/v for AC1 and 55 v/v for AC2), the results reported from research in this area show that the target value of 150 v/v deliverable at 3.5 MPa and room temperature make the system commercially attractive [18] is still hardly reached.

Table 4 shows the obtained results including adjustable parameters and R^2_{adj} adjusting six isotherm models, presented in Table 2, with the experimental data of CH₄ adsorption isotherms obtained from two GAC samples.

As observed, it is concluded that the Toth, two term TVFM and Sips isotherms show better agreement with the experimental data for two GAC samples in comparison with the other isotherms, whereas the Freundlich equation shows inferior results compared with the experimental data.

The accuracy of the results obtained from the two-term

TVFM isotherm model in comparison with the other isotherm models having the same theoretical concept (such as DR) is related to the presumptions considered for this model. As seen in Table 2, two-term TVFM equation contains four adjustable parameters, *i.e.*, W_{01} , E_1 , W_{02} , and E_2 . For the homogeneous microporous structure adsorbents $W_{02} = 0$. The first term of the two-term TVFM model represents the adsorption of CH₄ onto micropores and the second term justifies the adsorption onto super-micropores. Therefore, the use of DR equation with one term cannot give superior results in the comparison of experimental data.

Conclusions

An experimental study was carried out to determine CH₄ adsorption capacities of two different types of GAC up to 4 MPa at 298 K and the results obtained are comparable with wood based granulated carbon used by ADVANTICA technology. Also, various adsorption isotherm models were used to model the experimental data obtained from those two GAC samples. The accuracy of the results obtained from the adsorption isotherm models was compared and the values for the regressed parameters were reported. The results showed that the physical characteristics of activated carbons such as BET surface area, micropore volume, and pore size

Table 3- Comparison of ANG capacity at 2.45 MPa and room temperature

Sample	CH ₄ Adsorbed (v/v)	ANG/CNG storage
AC1	61.1	2.83
AC2	40.4	1.87
Sample used by ADVANTICA	32.4	1.50

Table 4- Data reduction results

Isotherm model	AC1		AC2	
	Parameters	R^2_{adj}	Parameters	R^2_{adj}
Langmuir	$W_0 = 8.852$ $b = 8 \times 10^{-4}$	0.990	$W_0 = 7.876$ $b = 5 \times 10^{-4}$	0.999
Freundlich	$K = 0.151$ $n = 2.144$	0.992	$K = 0.047$ $n = 1.751$	0.982
Sips	$W_0 = 13.567$ $b = 0.003$ $n = 1.417$	0.998	$W_0 = 7.549$ $b = 0.0004$ $n = 0.964$	0.999
Toth	$W_0 = 20.029$ $b = 0.001$ $t = 0.419$	0.999	$W_0 = 7.639$ $b = 0.0005$ $t = 1.042$	0.999
Dubinin - Radushkevich (DR)	$W_0 = 7.558$ $E = 7473.874$	0.991	$W_0 = 5.890$ $E = 6484.589$	0.997
Two-Term TVFM	$W_{01} = 2.541$ $E_1 = 2531.671$ $W_{02} = 6.814$ $E_2 = 8033.606$	0.999	$W_{01} = 3.058$ $E_1 = 1595.040$ $W_{02} = 5.739$ $E_2 = 6597.726$	0.999

distribution have significant effects on the amount of CH₄ adsorbed and used in this study are better than those used in ADVANTICA technology. Also, it is concluded that the Toth, two-term TVFM and Sips isotherms show better agreement with the experimental data in comparison with the other isotherms.

References

- [1] Cracknell R.F., Gordon P. & Gubbins K.E., "Influence of pore geometry on the design of microporous materials for methane storage", *J. Phys. Chem.*, Vol. 97, No.2, pp. 494-499, 1993.
- [2] Brunauer S., Emmett P.H. & Teller E., "Adsorption of gases in multimolecular layers", *J. Am. Chem. Soc.*, Vol. 60, No. 2, pp. 309-319, 1938.
- [3] Lu X.C., Li F.C. & Watson A.T., "Adsorption measurements in Devonian shales", *Fuel*, Vol. 74, No. 4, pp. 599-603, 1995.
- [4] Inomata K., Kanatawa K., Urabe Y., Hosono H. & Araki T., "Natural gas storage in activated carbon pellets without a binder", *Carbon*, Vol. 40, No. 1, pp. 87-93, 2002.
- [5] Diamond W.P. & Schattel S.J., "Measuring the gas content of coal: a review", *Int. J. Coal. Geology*, Vol. 35, Nos. 1-4, pp. 311-331, 1998.
- [6] Jiang S.Y., Zollweg J.A. & Gubbins K.E., "Theory of Adsorption of Trace Components", *J. Phys. Chem.*, Vol. 98, No. 9, pp. 2403-2411, 1994.
- [7] Vasiliev L.L., Yanonchik L.E., Mishkinis D.A. & Rabetsky M.I., "Adsorbed natural gas storage and transportation vessels", *Int. J. Therm. Sci.*, Vol. 39, Nos. 9-11, pp. 1047-1055, 2000.
- [8] Zhang S.Y., Talu O. & Hayhant D.T., "High-pressure adsorption of methane in zeolites NaX, MgX, CaX, SrX and BaX", *J. Phys. Chem.*, Vol. 95, No. 4, pp. 1722-1726, 1991.
- [9] Bastos-Neto M., Canabrava D.V., Torres A.E.B. & Rodriguez-Castellon E., "Effects of textural and surface characteristics of microporous activated carbons on the methane adsorption capacity at high pressures", *Appl. Surf. Sci.*, Vol. 253, No. 13, pp. 5721-5725, 2007.
- [10] Shao X., Wang W. & Zhang X., "Experimental measurements and computer simulation of methane adsorption on activated carbon fibers", *Carbon*, Vol. 45, No. 1, pp. 188-195, 2007.
- [11] Quinn D.F. & Macdonald J.A., "Natural gas storage", *Carbon*, Vol. 30, No. 7, pp. 1097-1103, 1992.
- [12] Mohammadi T., Abedinzadegan Abdi M., Parvinpour A. & Mahdyarfar M., "Prediction of active carbon and carbon molecular sieve's adsorption behavior with the adsorption models", 7th Chemical Engineering Conference, Tehran University, Tehran, Iran, 2002.
- [13] Smith J.M., Van Ness H.V. & Abbott M.M., *Introduction to chemical engineering thermodynamics*, 6th ed., Ch. 3, pp. 97-98, McGraw-Hill Companies, Inc., 2001.
- [14] Toth J., *Adsorption, Theory, Modeling, and Analysis*, Vol. 107, Ch. 1, pp. 58-66, Marcel Dekker, Inc., 2001.
- [15] Do D.D., *Adsorption Analysis: Equilibria and Kinetics*, Vol. 2, Ch. 3, pp. 49-77, Imperial College Press, 1998.
- [16] Dubinin M.M., "Fundamentals of the theory of adsorption in micropores of carbon adsorbents: Characteristics of their adsorption properties and microporous structures", *Carbon*, Vol. 27, No. 3, pp. 457-467, 1989.
- [17] Dvorak K., Hodrien R.C., Judd R., Bates D., Allen M. & Ingram J., Internal Advantica Technology Co. Report, 2003.
- [18] Atlanta Gas Light Adsorbent Research Group (AGLARG). Report to US Department of Energy, Contract 466590, 1997.