

ADSORBED NATURAL GAS STORAGE SYSTEM – A PROMISING TECHNOLOGY IN STORING ENERGY AND TRANSPORTATION SECTORS

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Abstract- In recent years, Adsorbed Natural Gas (ANG) storage technology has attracted considerable attention as a possible alternative compared to the conventional methods, such as Compressed Natural Gas (CNG) and Liquefied Natural Gas (LNG) for energy storage and transportation purposes. The ANG storage system provides high energy density but operates at much lower pressure (usually 2 to 4 MPa) than the CNG method as well as it does not require huge cold energy to store gas in liquid phase like LNG. In ANG storage system, natural gas is pressurized and stored in a vessel which is compacted with suitable adsorbent material and hitherto, the activated carbon has been proven to be the most appropriate adsorbent for this application. The adsorption characteristics of adsorbent-adsorbate pairs, which are important information for uptake capacity and thermal management of the adsorptive gas storage, are presented in this article. The experimental uptake values are regressed with the Dubinin-Ashtakov adsorption isotherm model. The results are also compared for the storage capacity of the ANG system which is about four times higher than that of the CNG method for similar operating conditions. The heat of adsorption, which is concentration and temperature dependent, has also been calculated from the measured data.

Keywords: Adsorbed natural gas, Energy storage, Activated carbon, Adsorption uptake.

1. INTRODUCTION

Natural gas (NG) has long been consuming as an alternative energy source in transportation technology as it provides better combustion and minimizes exhaust pollutants. It is mostly composed of methane, CH₄ and has the highest heating value per unit mass (55.2 MJ/kg) of the hydrocarbon fuels (e.g. butane, diesel fuel, gasoline, etc.) [1]. Moreover, its lower price and copious availability makes NG a fungible commodity in energy sectors. According to the U.S. Energy Information Administration (EIA), the consumption of dry NG is about 25 % of the total primary energy consumptions for recent years. More than half of the world's reserve of natural gas is found in the Persian Gulf and Russia. The conventional method of storing and supplying NG is either in the compressed form of natural gas (CNG) or the liquefied natural gas (LNG). Although these techniques are widely used for gas storage and transportation purposes, they are being criticized because of their operational complexity. For example, the CNG vessel stores gas at very high pressure (20 to 30 MPa) that incurs high manufacturing and filling costs and also represents a safety concern. On the other hand, the LNG method requires huge energy for cryogenic cooling of the gas at a temperature of -163 °C and needs specialized equipment for re-gasification. However, the ANG vessel

can be designed to store NG at relatively low pressure (2 to 4 MPa) in a lightweight cylinder filled with porous adsorbent which allows good design flexibility in tank configuration and also the storage tank can be filled with an inexpensive single-stage compressor [2–4]. These attractive features of the ANG storage system over the conventional storage methods are the motivating factors for the ongoing developments of this technology.

In this paper, an ANG storage system up to 3.0 MPa is proposed to analyze the performance using two types of activated carbon namely, Maxsorb III and ACF (A-20). The uptake values are experimentally measured at temperatures ranging from 5 to 65 °C and pressures up to 2.5 MPa using volumetric apparatus. The adsorption parameters are evaluated through regressions to fit with the Dubinin-Ashtakov (D-A) adsorption isotherm model. The results are found in good accordance with the previous studies [5–6] for comparable adsorbent - adsorbate combinations. The results are also compared for the storage capacity with the CNG method for similar operating conditions of the ANG system. The heat of adsorption is extracted from the isotherm data which is functional for the thermal management of the adsorptive gas storage system during charging and discharging.

2. THEORY

In adsorbed natural gas storage system, the gas is pressurized and stored in a vessel which is compacted with suitable adsorbent materials. According to adsorption principles, the gas (adsorbate) molecules are captured in the pores of the adsorbent due to the strong attractive surface forces known as van der Waals forces. The molecular distances inside the pores of the adsorbent are much shorter than in the gaseous phase for similar pressure and temperature conditions and thus the adsorbate density in adsorbed phase becomes liquid-like [7]. In this way, NG can be stored in an adsorbent storage with high energy density but at much lower pressure compared to that of the compressed gas method. To provide a better understanding of the adsorbate density in the adsorbent pores, a typical illustration is given in Fig. 1 where the adsorbate molecules in the adsorbent pores are denser than in the gaseous phase.

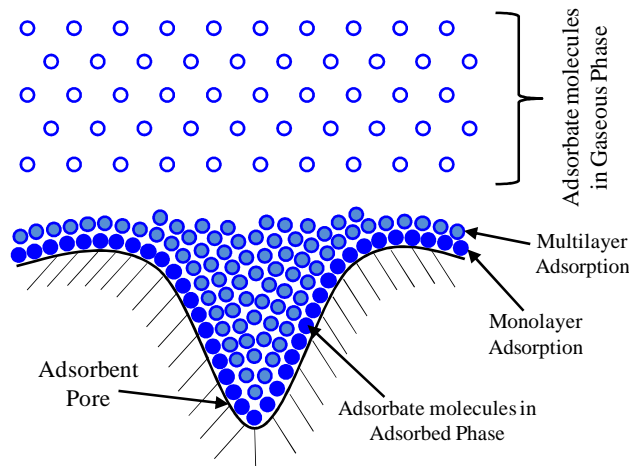


Fig. 1: A typical adsorption process providing relative comparison of the adsorbate density between the gaseous phase and the adsorbed phase.

Therefore, the storage capacity of the ANG storage system depends on the porous structure of the adsorbent material. A good porous adsorbent with larger pore volume and higher surface area is required for higher storage capacity of the ANG storage system and hitherto, the most promising adsorbents are the microporous activated carbons with relatively high packing densities [8–9] and higher specific surface area [10]. The carbon samples used in this study are with the highest surface area and pore volume among the available powdered and fibrous type activated carbons.

2.1 Adsorption isotherm

Dubinin and Astakhov proposed the following model for adsorption of vapors and gases onto non-homogeneous carbonaceous solids with wider pore size distribution [11]. This D-A model is allowed for the surface heterogeneity and also extended to high-pressure.

$$q = q_o \exp \left[- \left(\frac{A}{E} \right)^n \right] \quad (1)$$

where A is the adsorption potential and q is the amount of uptake in cm^3/g , q_o is the limiting uptake of adsorption space of the adsorbent in cm^3/g , E is the characteristic

energy of the adsorption system, and n is the structural heterogeneity parameter, which is typically varied from 1.2 to 1.8 for strongly activated carbon [11]. The adsorption potential, A is the specific work done in the isothermal compression of unit mass of vapor from any pressure P to the saturation vapor pressure, P_s and is given by

$$A = RT \ln \left(\frac{P_s}{P} \right) \quad (2)$$

Thus, Eq. (1) can be expressed as:

$$q = q_o \exp \left[- \left\{ \frac{RT}{E} \ln \left(\frac{P_s}{P} \right) \right\}^n \right] \quad (3)$$

The pseudo-vapor pressure, P_s at a given isotherm temperature is calculated by Dubinin's method [12].

$$P_s = \left(\frac{T}{T_c} \right)^2 P_c, (T > T_c) \quad (4)$$

where P_c and T_c are the critical pressure and the critical temperature of methane.

2.1 Isosteric Heat of Adsorption

The values of the heat of adsorption (Q_{st}) has been extracted from the isotherm data using the Clausius-Clayperon equation along with the correction term for the non-ideality of the gaseous phase, recently derived by Chakrabarty et al. [13] which is as follows

$$Q_{st} = RT^2 \left[\left(\frac{\partial(\ln P)}{\partial T} \right)_q \right] + T v_g \frac{dP}{dT}(P, T) \quad (5)$$

Here, the first term of the right hand side is derived from the Clausius-Clayperon equation and can be expanded by using the D-A isotherm model. A second term is introduced which defines the behavior of adsorbed mass with respect to both the pressure and the temperature changes during an adsorbate uptake, which occurs due to the non-ideality of the gaseous phase. Ultimately, Eq. (5) becomes

$$Q_{st} = 2RT + E \ln \left(\frac{\ln q_o}{q} \right)^{1/n} + T v_g \frac{dP}{dT}(P, T) \quad (6)$$

where v_g is the specific volume of the vapor phase, and

$\frac{dP}{dT}$ represents the gradient of the pressure with the temperature of the adsorbate.

3. RESULTS AND DISCUSSION

The equilibrium uptakes of methane on Maxsorb III and ACF (A-20) have been compared with the data cited from the literature [5–6] as shown in Fig. 2. The uptakes are slightly higher than the findings of Himeno et al. [5] for almost comparable physical characteristics of surface area and pore volume of Maxsorb sample. The reason could be the taking of bath temperature as the isotherm temperature whereas the adsorbent temperature has been recorded as isotherm temperature for the present study. Nevertheless, the present experimental data on ACF A-20 are fairly matched with the isotherm at 25 °C for the same sample which has been carried out in a DMT high-pressure microbalance by Lozano-Castelló et al. [6].

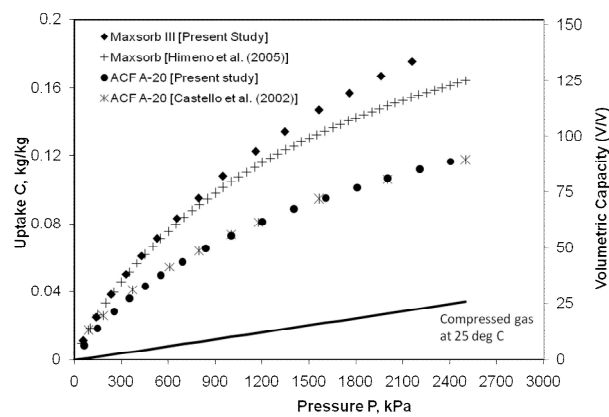


Fig. 2: Comparison of isotherm data at 25 °C from previous experimental methods.

The principle benefit of ANG storage can be observed in Fig. 2 that the volumetric capacity on the adsorbents (for packing density of 500 kg/m³) is considerably higher than the compressed natural gas (CNG) for the same vessel volume. The storage capacity of the ANG system is about four times higher than that of the CNG method in case of Maxsorb III sample. This higher volumetric energy density using sorption technique is the motivation for adsorbed natural gas (ANG) at lower pressure.

Figure 3 and 4 show the uptake data for the adsorption of methane on Maxsorb III and ACF (A-20) at the temperatures 5, 25, 45, and 65 °C and pressures up to 2.5 MPa. The experimental data have been regressed with both the D-A isotherm model as shown in Fig. 3 for Maxsorb III and Fig. 4 for ACF (A-20). The regressions agree to within 5% of experimental data. Table 1 shows the numerical value of the parameters q_o , E and n that have been regressed from the experimental data.

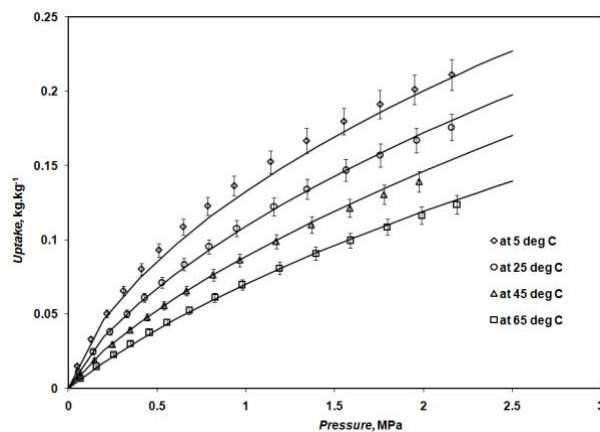


Fig. 3: Isotherm data on Maxsorb III (Solid lines are from D-A equation).

Table 1 The numerical value of the adsorption parameters (q_o , E and n)

Parameters	Maxsorb III	ACF (A-20)
q_o (kg/kg)	0.427	0.239
E (J/mol)	4632	5098
n	1.2	1.25
Error of regression (%)	3.8	4.4

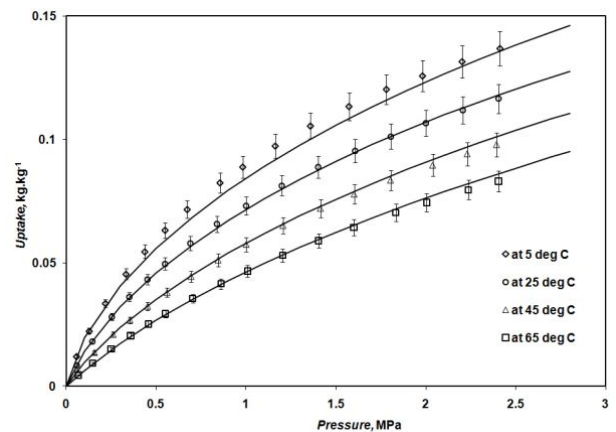


Fig. 4: Isotherm data on ACF A-20 (Solid lines are from D-A equation).

Figure 5 shows the uptake dependent heat of adsorption (Q_{st}) at different isothermal conditions for both Maxsorb III and ACF (A-20). It can be seen that the heat of adsorption (Q_{st}) varies with the adsorbate surface loading which confirms the surface heterogeneity for both the samples with wider pore size distribution. It indicates that an effective cooling/heating arrangement is to be installed to enhance the charging/discharging rate of adsorptive gas storage.

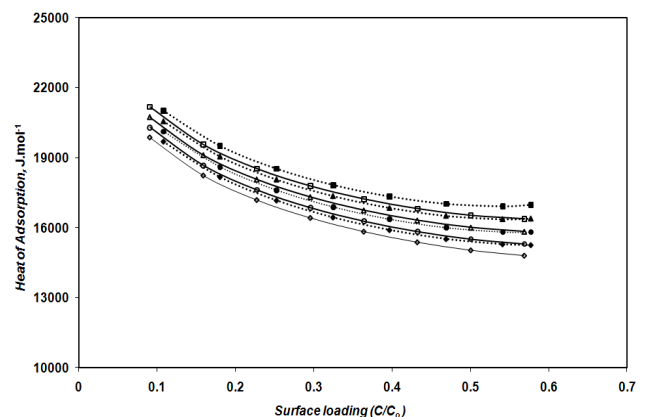


Fig. 5: Isothermic heat of adsorption calculated using D-A model for Maxsorb III (empty symbols) and ACF-A20 (solid symbols): \diamond/\bullet , 5 °C; \circ/\bullet , 25 °C; Δ/\blacktriangle , 45 °C; \square/\blacksquare , 65 °C.

4. CONCLUSIONS

The adsorption isotherm data, which are the basic information of adsorptive gas storage system, show the significantly higher storage capacity using pitch-based activated carbons. Among the samples experimented the Maxsorb III shows the higher uptake capacity due to its high specific pore volume than the ACF (A-20). Moreover, the heat of adsorption is lesser in case of the Maxsorb III sample which accelerates the adsorption rate and thus slows down the charging time. However, the charging and discharging rate can be enhanced with supplementary cooling and heating arrangements.

5. ACKNOWLEDGEMENT

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6. REFERENCES

- [1] O. Talu, "An overview of adsorptive storage of natural gas, Fundamentals of Adsorption", in *Proceedings of 4th International Conference on Fundamentals of Adsorption*, Kyoto, May, 1992, pp.17-22.
- [2] L. L. Vasiliev, L. E. Kanonchik, D. A. Mishkinis, and M. I. Rabetsky, "Adsorbed natural gas storage and transportation vessels", *International Journal of Thermal Sciences*, vol. 39, pp. 1047-1055, 2000.
- [3] M. Bastos-Neto, A. E. B. Torres, D. C. S. Azevedo, and C. L. Cavalcante Jr., "A theoretical and experimental study of charge and discharge cycles in a storage vessel for adsorbed natural gas", *Adsorption*, vol. 11, pp. 147-157, 2005.
- [4] J. P. B. Mota, "Adsorbed natural gas technology: Recent advances in adsorption processes for environmental protection and security", *Springer*, Netherlands, pp. 177-192, 2008.
- [5] S. Himeno, T. Komatsu, and S. Fujita, "High pressure adsorption equilibria of methane and carbon dioxide on several activated carbons," *J. Chem. Eng. Data*, vol. 50, pp. 369-376, 2005.
- [6] D. Lozano-Castelló, D. Cazorla-Amorós, and A. Linares-Solano, "Powdered Activated Carbons and Activated Carbon Fibers for Methane Storage: A Comparative Study," *Energy & Fuels*, vol. 16, pp. 1321-1328, 2002.
- [7] M. Suzuki, "Adsorption Engineering", *Elsevier Science Publishers*, Tokyo, 1990.
- [8] D. F. Quinn and J. A. MacDonald, "Natural Gas Storage", *Carbon*, vol. 30, no. 7, pp. 1097-1103, 1992.
- [9] J. Alcañiz-Monge, D. Lozano-Castelló, D. Cazorla-Amorós, and A. Linares-Solano, "Fundamentals of methane adsorption in microporous carbons", *Microporous and Mesoporous Materials*, vol. 124, pp. 110-116, 2009.
- [10] V. C. Menon and S. Komarneni, "Porous adsorbents for vehicular natural gas storage: A review", *Journal of Porous Materials*, vol. 5, pp. 43-58, 1998.
- [11] D. D. Do, "Adsorption Analysis: Equilibria and Kinetics". London: Imperial College Press, 1998.
- [12] M. M. Dubinin, "The potential theory of adsorption of gases and vapors for adsorbents with energetically nonuniform surfaces," *Chemical Review*, vol. 60, pp. 1-70, 1960.
- [13] A. Chakraborty, B. B. Saha, S. Koyama, and K. C. Ng, "On the thermodynamic modeling of the isosteric heat of adsorption and comparison with experiments," *Applied Physics Letter*, vol. 89, pp. 171901, 2006.

7. NOMENCLATURE

Symbol	Meaning	Unit
q	Amount of uptake	(cm ³ /g)
q_o	Limiting uptake of adsorption space of the adsorbent	(cm ³ /g)
A	Adsorption potential	(J/mol)
E	Characteristic energy	(J/mol)
n	Structural heterogeneity parameter	(-)
R	Gas Constant	(J/mol-K)
P	Pressure	(MPa)
T	Temperature	(K)
P_s	Saturation pressure	(MPa)
P_c	Critical pressure	(MPa)
T_c	Critical temperature	(K)
Q_{st}	Heat of adsorption	(J/mol)
v_g	Specific volume of gas	(cm ³ /g)