

Experimental Evaluation of Methane Adsorption on Granular Activated Carbon (GAC) and Determination of Model Isotherm

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Abstract—This study investigates the capacity of granular activated carbon (GAC) for the storage of methane through the equilibrium adsorption. An experimental apparatus consist of a dual adsorption vessel was set up for the measurement of equilibrium adsorption of methane on GAC using volumetric technique (pressure decay). Experimental isotherms of methane adsorption were determined by the measurement of equilibrium uptake of methane in different pressures (0-50 bar) and temperatures (285.15-328.15°K). The experimental data was fitted to Freundlich and Langmuir equations to determine the model isotherm. The results show that the experimental data is equally well fitted by the both model isotherms. Using the experimental data obtained in different temperatures the isosteric heat of methane adsorption was also calculated by the Clausius-Clapeyron equation from the Sips isotherm model. Results of isosteric heat of adsorption show that decreasing temperature or increasing methane uptake by GAC decrease the isosteric heat of methane adsorption.

Keywords—Methane adsorption, Activated carbon, Model isotherm, Isosteric heat

I. INTRODUCTION

ACTIVATED carbons are the adsorbents with the most favorable characteristics for ANG storage, because they have a large microporous volume, are efficiently compacted into a packed bed, and can be cheaply manufactured in large quantities [1]. The enhanced storage results from gas adsorption into the micropores. Activated carbon plays an important role in the technology of adsorbed natural gas. Methane is weakly adsorbed on the micropores of the carbon as compressed gas since the room temperature is much higher than the critical temperature. Consequently, the amount adsorbed increases with pressure as a function of micropore volume (space available for adsorption) and the micropore size [2,3]. Interactions between the methane molecules and the surface of carbon increase the density of adsorbed methane in respect to the density of compressed gas, this permitting to reduce the pressure in the cylinder from around 20-30 MPa to about 4 MPa, without loss of storage capacity [4].

Therefore natural gas can be stored as an adsorbed phase in porous materials so that this option can be an interesting

alternative to overcome the problems of CNG. The use of adsorbent materials in a storage vessel for storing natural gas, at relatively low pressure and at room temperature is a possibility for making natural gas vehicles competitive with the other types of vehicles. In this application, the maximum gas storage density became the ultimate requirement, in order to store and deliver the maximum gas storage capacity. Depending on the adsorbent characteristics, the volumetric adsorption capacity and delivery would be different as well as the volumetric energy density [5].

The gas storage capacity through adsorption is enhanced when the overall storage density is increased more than the normal gas density at a given pressure. Consequently, there is an enhancement in the storage system of the fixed volume, because a greater gas amount is adsorbed with respect to the gas volume displaced by the adsorbent volume. Accordingly, it has been concluded that the requirements for an ANG adsorbents are high adsorption/desorption rates and high adsorption capacity. Therefore, it has to be predominantly microporous to maximize the deliverability at ambient pressure, a high packing density to ensure that the storage capacity and the energy density on a volumetric basis will be high, a low adsorption heat and high heat capacity to minimize the changes in the vessel temperature during the adsorption and desorption processes, good mass transfer properties, it must be extremely hydrophobic and it should be inexpensive for the final user. The coals are commonly used as starting materials for the AC construction. Recently, numerous attempts have also been made to prepare activated carbon from solid waste [6]. Many studies have been conducted for the AC production by chemical activation for methane storage [7]. Although some adsorption equilibrium data for hydrocarbon adsorption on activated carbon have been published [8-11], but the experimental data for adsorption equilibrium of methane on GAC in different operating conditions with theoretical investigations and determination of adsorption isosteric heat are scarce. In this study the potential capacity of granular activated carbons (GAC) for the storage of methane in different operating conditions was investigated through the measurement of equilibrium uptake by the volumetric method. The effect of variation in pressure and temperature on the amount of adsorption was also investigated and finally the model isotherm and the isosteric heat of adsorption were determined.

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II. EXPERIMENTAL

A. Materials

The granular activated carbon used in this study is a coal-based, extruded carbon (2mm diameter tubes). It was purchased from AppliChem Company, (Germany). Methane used had a purity of 99.99% were purchased from Technical Gas Services Company. Surface characteristics and pore structure are very important properties of adsorbents, almost all applications about adsorption are associated with them. The BET analysis of GAC determined basing on the adsorption isotherm of N_2 at 77 °K measurement. Specific surface area of GAC was measured 907 m^2/g . Also apparent density of GAC was estimated 0.66 g/cm^3 GAC. Microscopic observation was conducted using SEM. Fig.1 shows the SEM image of GAC.

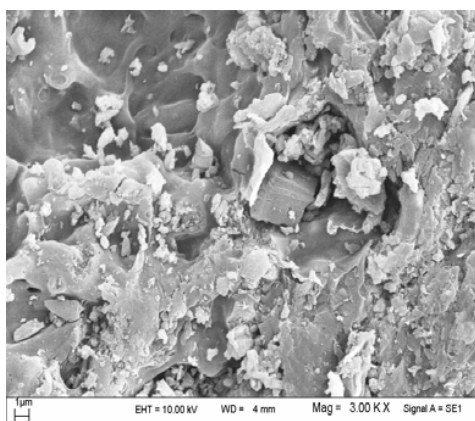


Fig. 1 SEM image of granular activated carbon

B. Methane storage test

The main goal in the experimental adsorption studies is the determination of the material adsorbed on the adsorbent in different equilibrium conditions. In this work in agreement with the volumetric method, the pressure drop due to adsorption was measured in a closed system. In this section, only a brief description of the volumetric apparatus (dual volume) that we have used in this study for the assessment of methane storage test by GAC is presented. The gas was admitted from the gas cylinder into the pressure cell through valve 1. The temperature of pressure cell was measured by a PT100 temperature probe located in the pressure cell. The pressure in pressure cell was measured by a pressure transducer located in the pressure cell. The gas was then expanded in the adsorption cell using valve 3 and valve 5. The pressure of adsorption cell was measured using the second pressure transducer located in the adsorption cell. The temperature of adsorption cell was measured by a second PT100 temperature probe located in the adsorbent. The whole installation is temperature controlled by a water bath. The whole system already vacuumed by a vacuum pump. The procedure was completely automated by a control unit and a computer. The maximum allowable pressure in the installation was 50 bar and its working temperature range was 283-343 °K.

The measurement of methane-storage capacity on GAC was carried out with an apparatus shown in Fig.2.

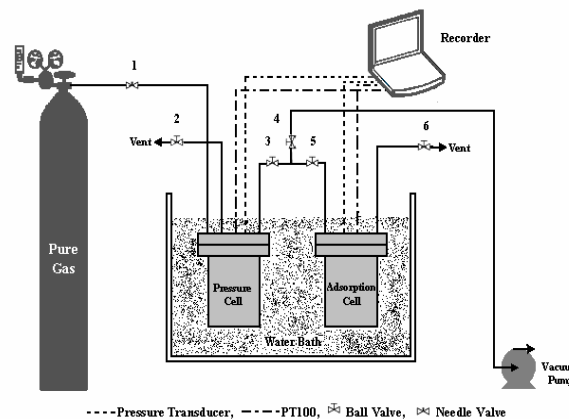


Fig. 2 Schematic diagram of the apparatus used to measure storage capacity

Because of the methane adsorption, the cell pressure reduced until the equilibrium condition was reached. The adsorbed gas amount was calculated by the suitable state equation (SRK in this study) in equilibrium conditions.

III. RESULTS AND DISCUSSIONS

A. Adsorption isotherms and isotherm models

Fig.3 shows the equilibrium uptake of methane by GAC versus pressure at different temperatures. As it is clear from the Fig.3, the amount of uptake increases with an increase in the pressure, but when the sorbent monolayer is saturated the amount of adsorption approaches to a limit gradually. Also shows that the amount of adsorption decreases with an increase in temperature. By isotherms test used for the simulation of adsorption of methane on activated carbon, it was found that the both model isotherms of Langmuir and Freundlich (equation 1 and 2 respectively) give a near perfect fit to the experimental adsorption data. Isotherms parameters obtained through a nonlinear fit of experimental data to the model equations using a Matlab software , version 7.5 (2007).

$$q = q_m \frac{bP}{1 + bP} \quad (1)$$

$$q = q_m kP^{(1/n)} \quad (2)$$

Where $b=K_a/K_b$, K_a and K_b are adsorption constant and desorption constant, respectively. q_m is the predicted maximum amount adsorbed on a monolayer of adsorbent and n characterizes the adsorbate/adsorbent interactions.

Lines in Fig.3(a) and Fig.3(b) show the Langmuir isotherm and Freundlich isotherm used to describe the adsorption values, respectively. For comparison, the experimental data were shown on the Fig.3 by symbols. The parameters of model isotherms of Langmuir and Freundlich recovered from a nonlinear fit to experimental data are shown in Tables 1 and 2 respectively.

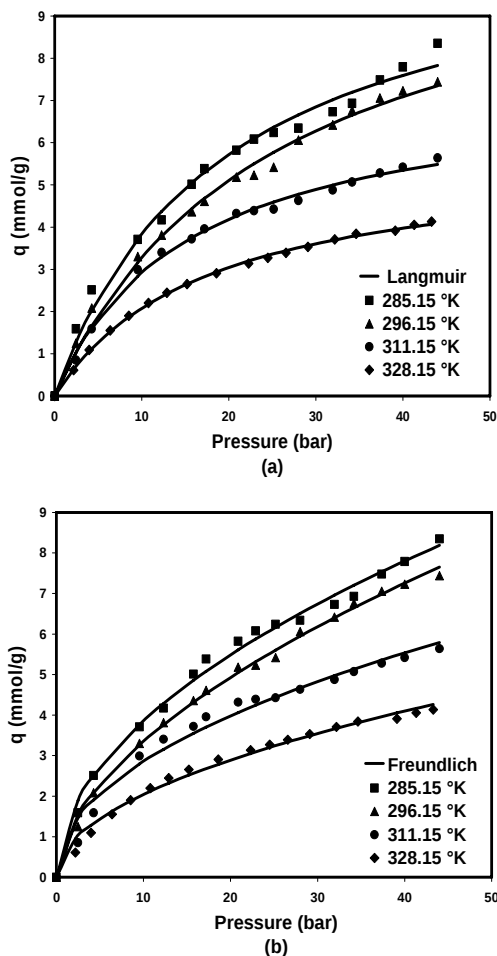


Fig.3 Methane adsorption on GAC in different temperatures. Symbols denote experimental data and lines in a and b, are predictions from the Langmuir and Freundlich isotherm models, respectively

TABLE I LANGMUIR ISOTHERM PARAMETERS FOR METHANE ADSORPTION ON GAC

Parameters	T=285.15°K	T=296.15°K	T=311.15°K	T=328.15°K
$q_{\max}$	11.3	11.6	7.408	5.715
B	0.05121	0.03931	0.06487	0.05699
R-square	0.9887	0.9938	0.9969	0.9998

TABLE II FREUNDLICH ISOTHERM PARAMETERS FOR METHANE ADSORPTION ON GAC

parameters	T=285.15°K	T=296.15°K	T=311.15°K	T=328.15°K
$q_{\max}$	11.511	10.801	8.402	5.88
K	0.1041	0.0858	0.1137	0.1088
N	1.968	1.793	2.1	1.986
R-square	0.9939	0.9969	0.9805	0.9893

B. Isosteric heat of adsorption

Knowledge of the adsorption equilibrium and heat of adsorption is essential for proper design and operation of any gas-phase adsorption process. The isosteric heat is an assessment of the interaction between adsorbent lattice atoms

and adsorbate molecules. The latter is usually estimated from the temperature dependence of the adsorption isotherm [12–14]. Therefore, correlations that capture the correct temperature dependence over a relatively wide range are essential for designing and operating gas-phase adsorption processes. The isosteric heat of adsorption, Q_{st} , is typically estimated using the Clausius–Clapeyron equation as [15]:

$$Q_{st} = RT^2 \left(\frac{\partial \ln P}{\partial T} \right)_q \quad (3)$$

The Sips adsorption isotherm model is the method with frequent applications for work on gas purification [16]. The advantages of this model are its ability to fit experimental data, its mathematical simplicity, and its straightforward extension to multicomponent adsorption. For these reasons, the Sips model is predominantly used in the modeling and design of adsorbents [17].

The Sips isotherm can be written as:

$$q = \frac{q_m (bP)^{1/n}}{1 + (bP)^{1/n}} \quad (4)$$

$$b = b_0 \exp \left[\frac{Q}{RT_0} \left(\frac{T_0}{T} - 1 \right) \right], \quad \frac{1}{n} = \frac{1}{n_0} + \alpha \left(1 - \frac{T_0}{T} \right)$$

where q_m is the maximum adsorbed amount, $\gamma = Q/RT_0$ is the heat coefficient, n_0 and α are parameters, and Q is the isosteric heat of adsorption at half loading; n characterizes the adsorbate/adsorbent interactions. The n dependencies of temperature were incorporated into Sips isotherm model. The Sips isotherm model [18] was used here for evaluation of isosteric heat of adsorption. Applying Eq.(3) to the Sips isotherm model, defined by Eq.(4), gives:

$$Q_{st} = Q - \alpha n R T_0 \ln(bP) \quad (5)$$

Table 3 lists the optimal isotherm parameters obtained by simultaneously fitting all the adsorption equilibrium data at multiple temperatures for methane, assuming a temperature independent q_m value. In every case, the obtained regression coefficient, r^2 , is greater than 0.99. The excellent agreement between the fitting of Sips model and the experimental data demonstrates that this isotherm model can be confidently employed to accurately correlate the adsorption equilibria of the adsorbate as well. The methane amount adsorbed at saturation conditions, as predicted by the Sips isotherm model for GAC is equal to 12.84 mmol/g.

TABLE III SIPS ISOTHERM PARAMETERS FOR METHANE ADSORPTION ON GAC

q_s (mmol/g)	b_0 (bar ⁻¹)	α	n_0	Q(KJ/mol)	T_0 (°K)
12.84	0.0445	0.3739	0.0893	22.227	285.15

Fig.4 shows the variation of the isosteric heat of methane adsorption with pressure, as determined from the temperature dependence of Sips isotherm model. The selected

temperatures for plotting the curves are those at which the adsorption equilibria were measured. The values of Q_{st} are quite satisfactory when compared with the values reported in the literature [14].

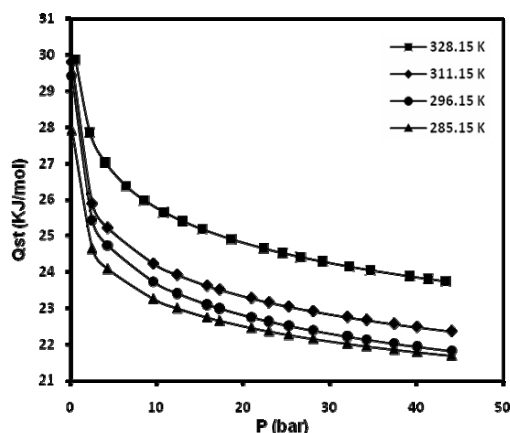


Fig. 4 Isosteric heats of methane adsorption on GAC as a function of equilibrium pressure as predicted from the temperature dependence of the Sips isotherm model

As it shown in Fig. 4, the value of Q_{st} decreases with decreasing temperature and increasing loading and this trend is showing that the carbon surface is energetically heterogeneous with regards to adsorption of methane as adsorbate. Most amorphous adsorbents, such as granular activated carbon, belong to this category.

IV. CONCLUSION

To investigate the potential ability of granular activated carbon (GAC) for storage of methane, an experimental apparatus was set up by which the equilibrium isotherms were determined using volumetric technique. Then the experimental data was fitted to a model isotherm for prediction purposes. Results show that the trend of variation in amount of methane uptake by GAC follows the Langmuir, Freundlich and Sips isotherms. A series of experiments was conducted at different temperatures and pressures to evaluate the effect of later variations on methane adsorption. Results revealed that increasing the pressure and decreasing the temperature increases the amount of adsorption. Evaluation of isosteric heat of methane adsorption on GAC from the Sips isotherm model shows that decreasing temperature or increasing methane uptake by GAC decreases the isosteric heat of adsorption that reveal that the GAC adsorbents have an actively heterogeneous surface.

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