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Experimental study and artificial neural network simulation of methane adsorption on activated carbon

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Abstract−The adsorption of methane on two activated carbons with different physical properties was measured. Adsorption isotherms were obtained by static volumetric method at different temperatures and pressures. The experimental results sow the best gas storage capacity was 113.5 V/V at temperature 280 K and pressure 8.5 MPa on an activated carbon with surface area 1,060 m^2/gr. An artificial neural network (ANN) based on genetic algorithm (GA) was used to predict amount of adsorption. The experimental data including input pressure, temperature and surface area of adsorbents as input parameters were used to create a GA-ANN simulation. The simulation results were compared with the experimental data and a good agreement was observed. The simulation was applied to calculate isosteric heat of adsorption by using the Clausius-Clapeyron equation. Comparison of the calculated adsorption heat showed different surface heterogeneity of the adsorbents.

Key words: Methane, Activated Carbon, Adsorption, Artificial Neural Network, Genetic Algorithm

INTRODUCTION

The worldwide energy demand shows a 1.7% average annual growth in the 2005-2020 periods. This growth concerns all energy sources, although fossil fuels will continue to rule of the energy scene for the next fifteen years. Natural gas demand will account for the highest growth rate and in 2020, and it will exceed that of coal which will be penalized by the increasing restrictions in pollutant emissions (especially in Europe) [1,2].

Methane, as a major component of natural gas, is receiving tremendous attention for consideration as the future clean and reliable fuel. Adsorbed natural gas technology (ANG) based on natural gas adsorption in porous materials at relatively low pressures (3.5-4 MPa) has been widely investigated as an alternative to compressed natural gas (CNG) and liquefied natural gas (LNG) technologies for storage and transportation of natural gases [3-8]. It has various operational and economical advantages. LNG technology needs very low temperature condition (around 108.5 K), and this condition is not suitable in the everyday usage of natural gas as a fuel, particularly for non-stationary uses. The main disadvantage of using CNG technology for transportation purposes is the necessity for expensive and heavy high pressure vessels designed in a specific shape.

In contrast, reduction in storage pressure allows using lighter, cheaper and safer onboard storage reservoirs and vehicles can refuel directly from a high pressure natural gas pipeline [9]. The best way to reduce the storage pressure is gas adsorption on a suitable adsorbent (ANG). Carbonaceous materials are promising adsorbents, since they have high surface area, good methane adsorption capacity. The best viable volumetric capacity in this technology is around 150 V/V of charging at 10 MPa [10]. The energy density as such is, however, less than CNG, whose volumetric capacity is 200 V/V at 20 MPa. Also, pelleting the activated carbon is usually a time consuming, thus inefficient, process. In fact, ANG technology isn't a commercial method and it should be improved [10,11].

In this study, the adsorption of methane on carbon adsorbents was investigated both experimentally and theoretically. Two different types of high surface area activated carbons as adsorbent were used in the experiments. Adsorption experiments were carried out in a high pressure setup at different temperatures and pressures. Artificial neural network modified with genetic algorithm (ANN-GA) was applied to simulate the process and to predict amount of adsorption at the other conditions. The simulation results data were used to predict isosteric heat of adsorption and adsorption amount at other conditions.

EXPERIMENTAL SECTION

1. Materials

Methane with the laboratory grade (purity 99.95%) was purchased from Air-Products Company. Two types of activated carbon as adsorbent (AC1 and AC2) were prepared as commercial samples. The AC1 sample was prepared from PJAC (Philippine-Japan Active Carbon) Corporation with surface area 1,060 m^2/gr, and the AC2 sample was prepared from SX Xinhui Activated Carbon company with surface area 850 m^2/gr. Bulk density of both samples is around 0.6 gr/cm^3 with the same particle size (average particle size 5 mm).

2. Apparatus and Procedures

Adsorption of methane on the adsorbent was measured in a laboratory scale setup designed based on volumetric method. A schematic diagram of the apparatus is shown in Fig. 1. The apparatus consists of two cylindrical cells: loading cell and adsorption cell. The first one with volume 270 cm^3 was used to measure amount of charged gas, and the second cell with volume 200 cm^3 was used to

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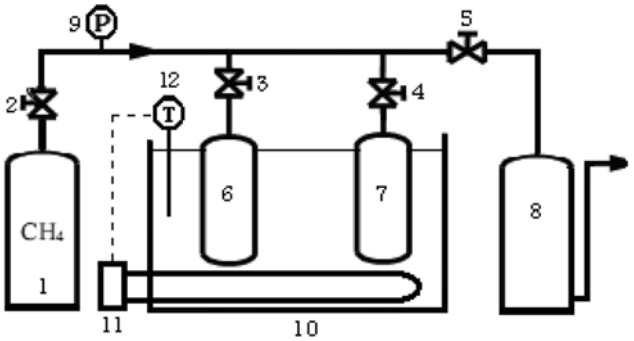

Fig. 1. Experimental apparatus.

1. Methane tank	9. Pressure transducer
2, 3, 4, 5. Valves	10. Water bath
6. Loading cell	11. Heater
7. Adsorption cell	12. Temperature transducer
8. Water vessel	

accomplish adsorption process, both made of stainless steel. The adsorption experiments were carried out at temperatures 280, 290 and 300 K and pressure 1.5 to 8.5 MPa.

During the experiments, both cells were imbedded in a water bath with a temperature control system. A pressure indicator was used to show the pressure of the loading cell and adsorption step. Degassing of the adsorbents was performed at temperature 360 K for 3 hr. The adsorption cell was cleaned, dried and filled with about 60 gr adsorbent. Before entering methane into the adsorption cell, the pressure of loading cell was set at the required initial level for each adsorption measurement. After entering methane to the adsorption cell, the gas pressure was stabilized gradually and it approached the equilibrium state finally.

At first, the loading cell was charged with methane gas at initial pressure P_0 (KPa). Then valve 3 opened and both loading cell and adsorption cell (containing adsorbent) got to equilibrium pressure P_{eq} (KPa). In this state, the amount of adsorbed gas N′ (mol) can be evaluated with Eq. (1) as:

$$N' = \frac{P_0 V_l}{ZRT} - \frac{P_{eq}(V_l + V_a)}{Z'RT} \tag{1}$$

Where V_l and V_a (cm^3), are volume of loading and adsorption cells, respectively, T (K) is temperature, R is gas constant, and Z and Z′ are the compressibility factor at temperature T and pressure P_0 and P_{eq}, respectively. Repetition of the experiments at different P_0 gives different amount of parameters P_{eq} and N′. The intensive parameter, N, which shows the gas storage capacity of the system in dimension mol/kg, was calculated as follows:

$$N\left(\frac{\text{adsorbed gas mol}}{\text{adsorbent weight}}\right) = \frac{N'(\text{mol})}{\text{adsorbent weight (gr)}} \tag{2}$$

The parameter N in dimension V/V can be calculated by using Eq (3):

$$N\left(\frac{\text{adsorbed gas volume}}{\text{adsorbent volume}}\right) = \frac{N'(\text{mol})/\text{gas molar density}\left(\frac{\text{mol}}{\text{lit}}\right)}{\text{adsorbent weight (gr)}/\text{adsorbent density}\left(\frac{\text{gr}}{\text{lit}}\right)} \tag{3}$$

The curve N vs. P_{eq} at constant temperature is the adsorption isotherm. This curve was obtained at different temperatures. The adsorption isotherm is the most extensively used data for representing the equilibrium states of an adsorption system. It can give useful information regarding the adsorbate, adsorbent and the adsorption process. In addition, slope of ln P_{eq} vs. 1/T at constant adsorption amount gives the isosteric heat of adsorption (Q_{st}) based on the Clausius-Clapeyron equation (Eq. (4)) [11]. This parameter can be determined with regression of adsorption isotherm data [12].

$$Q_{st} = -R\left[\frac{\partial \ln P_{eq}}{\partial (1/T)}\right]_N \tag{4}$$

RESULTS AND DISCUSSION

1. Adsorption Isotherms

In this study, the experimental data of methane adsorption isotherm on two activated carbons were obtained and presented in Figs. 2 and 3. It can be seen in these figures that maximum methane adsorption is observed at a temperature of 280 K and pressure of 8.5 MPa, and the amounts are 5.07 and 3.2 mol/kg for AC1 and AC2, respectively. These amounts give adsorption capacities (parameter

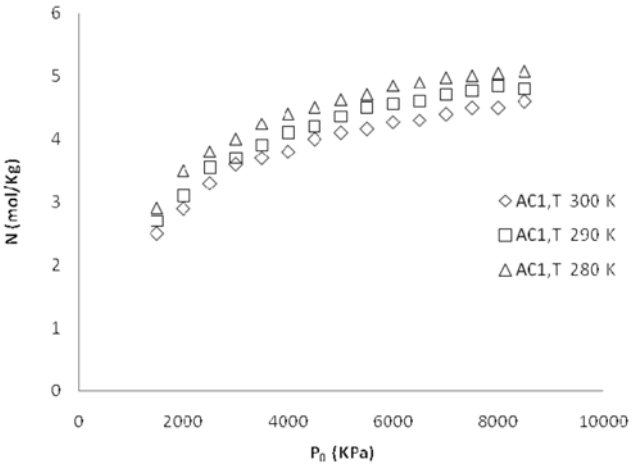

Fig. 2. Experimental isotherms of methane adsorption on AC1.

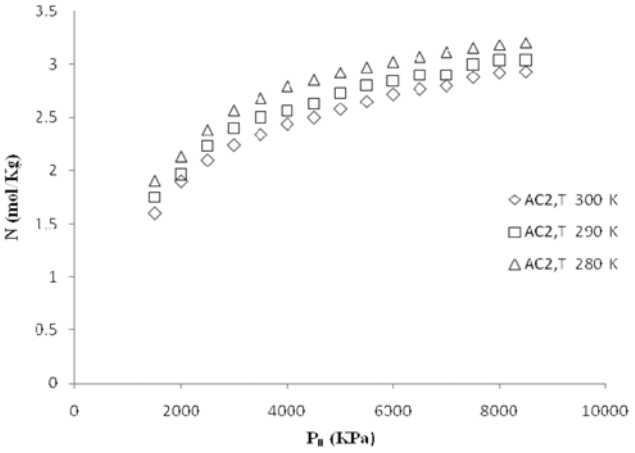

Fig. 3. Experimental isotherms of methane adsorption on AC2.

N) equal 113.5 and 71.6 V/V for two adsorbents, respectively.

Also, it can be observed that the amount of adsorbed gas increases with increasing in the pressure of adsorption. In fact, increasing the pressure causes an increase of the van der Waals attraction forces between the gas and adsorbent molecules [13]. In addition, adsorption at higher temperature reaches to lower adsorption capacity. This is because of the direct relation of adsorption equilibrium with temperature.

Comparison of Figs. 2 and 3 shows adsorption capacity of AC1 is better than on AC2. Adsorption capacity of an adsorbent is strongly a function of its surface area. Therefore, the adsorbent AC1 with higher surface area gives higher methane adsorbate amount than AC2.

2. Simulation

The complex relationship between the input and output of any process correlation irrespective of the physical features of the system can be done by artificial neural network (ANN). The genetic algorithm (GA) can be applied to ANN for determination and optimization of the ANN parameters. Today, ANNs are recognized as an excellent choice for solving types of complex adsorption problems. In addition, it has popular application to foresee in the adsorption equilibrium of solid-gas or liquid systems [14].

Neural networks are generally formed from a number of interconnected processing elements or neurons. How the inter-neuron connections are arranged and the structure of a network is determined by the nature of the connections. How the strengths of the connections are made appropriate or trained to obtain a desired general behavior of the network is controlled by its learning algorithm. Neural networks can be divided according to their structures and learning algorithms. On the basis of their structures, neural networks can be divided into two types: feed forward networks and recurrent networks. MLPs (multi-layer perceptron) are maybe the best known types of feed forward networks. MLP has three layers: an input layer, an output laye, and an intermediate or hidden layer.

Two most important types of learning algorithms train neural networks: supervised and unsupervised learning algorithms. A supervised learning algorithm makes appropriate the strengths or weights of the inter-neuron connections according to the difference between the desired and real network outputs related to a given input. An example of supervised learning algorithms is back propagation algorithm. Genetic algorithm is one of the learning algorithms acceptable for training MLPs.

In this study, the process of designing the networks was managed by NeuroSolutions for Excel Release 4.2 software, produced by NeuroDimension Incorporated, which incorporates ANN and GA. In this simulation, the adsorption equilibrium of methane onto activated carbon for different operating conditions was considered.

In describing the method of the work and the order in which the NeuroSolutions for Excel parts can be used to create and train a network, at least, only three operations are needed: tag data, create/open network and train network. These processes are often followed up by testing the model's performance (test network) and using the model to new input data where the output is unknown.

This simulation evaluated the applicability of the network in predicting the methane uptake at equilibrium condition for new conditions. The considered network was tested with the new data kept unaware of the neural network. In the simulation process, genetic algorithm was used to determine the number of neurons in the hidden layer, the momentum and the learning rates for minimizing the time and effort required to find the optimal architecture [15]. The design of ANNs is shown in Fig. 4.

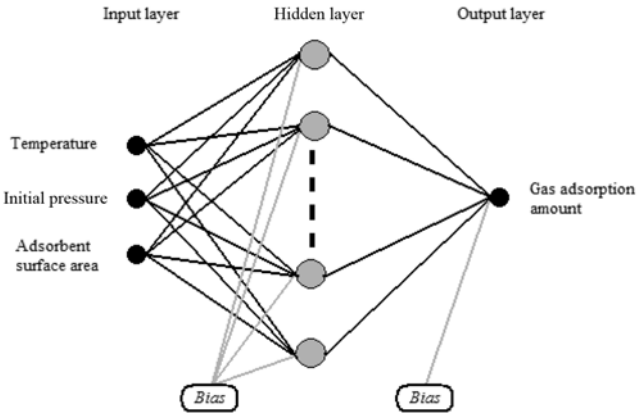

Fig. 4. The design of the Artificial Neural Network.

The input vector is 90 set of experimental data containing input pressure, temperature and surface area of the adsorbent. The output data is the amount of adsorption at the related conditions. The input and output layers contain three and one neurons, respectively. In the beginning, data are randomized and then the first 65% of the data is considered for training, the next 15% for cross validation and the last 25% for testing. The ANNs contain one hidden layer and feed forward back propagation is used for training the input data. A batch mode using a Levenberg-Marquardt's algorithm strategy sensitive to the number of neurons in the hidden layer is used to train the neural network [16].

The numbers of neurons in the hidden layer obtained by GA is eleven. Also, GA is used to obtain the optimal network size and the learning rate and the momentum rate in the ANN adsorption amount of methane estimation model. The weights in the network are to be adjusted by the learning rate. Properties of the ANN and GA are shown in Table 1. Then the heat of adsorption is estimated by using adsorption amount of experimental data and that predicted by ANN-GA.

The ANN-GA is tested with experimental data set of AC2 and AC1 at 280, 290 and 300 K. The parameters were used to the network and a comparison between the simulation results and experimental data are shown in Tables 2 and 3.

These tables show good agreement of experimental data and simulation results. For quantification of this comparison, an error analysis is done on these data and the results are reported in Table 4.

Table 1. Properties of ANN and GA used in the simulation

Learning rule	Levenberg-Marquardt
Maximum epoch	1000
Population size	50
Maximum Generation	20
Mutation	Uniform
Cross over	Uniform
Operator	Best

Table 2. Comparison of experimental results for AC2 and simulation results of ANN-GA

P_0 (KPa)	T (K)	Experimental N (mol/Kg)	Simulated N (mol/Kg)
1500	300	1.6	1.71
2000	280	2.13	2.17
2500	300	2.1	2.05
3500	280	2.68	2.73
7000	290	2.9	2.95
5500	300	2.65	2.65
5000	290	2.73	2.73
6000	300	2.72	2.72
2000	300	1.9	1.86
6500	290	2.9	2.91
4000	290	2.56	2.59
2500	280	2.38	2.43

Table 3. Comparison of experimental results for AC1 and simulation results of ANN-GA

P_0 (KPa)	T (K)	Experimental N (mol/Kg)	Simulated N (mol/Kg)
4000	290	4.1	4.07
7000	300	4.4	4.35
3500	280	4.24	4.21
3000	300	3.6	3.49
2500	300	3.3	3.27
5500	280	4.7	4.77
3000	290	3.7	3.73
2000	290	3.1	3.16
8500	290	4.8	4.91
6000	280	4.84	4.85
7500	300	4.5	4.42
2000	300	2.9	2.94
2000	280	3.5	3.42

Table 4. Performance of GA-ANN simulation for test data set for network

Parameter	Define	Amount
MSE	Mean standard error	0.003053916
NMSE	Normal mean standard error	0.0034723
MAE	Mean absolute error	0.045994678
AE_{min}	Minimum absolute error	0.000319302
AE_{max}	Maximum absolute error	0.108126162
R^2	Regression fitting parameter	0.998313855

The ANN-GA simulator is used to predict adsorption isotherm. The results for adsorption of methane on AC1 and AC2 at temperatures 310 K and 320 K are presented in Fig. 5.

3. Isosteric Heat of Adsorption

The experimental and simulated isotherm data are used to predict isosteric adsorption heat based on Eq. (2). The logarithmic form of the equilibrium pressures was plotted against the inverse temperature at the constant adsorbed amount (N) and shown in Figs. 6 and 7 for AC1 and AC2, respectively. The slopes of these lines were calculated as the isosteric heat of adsorption. This isosteric energy is a measure of the interaction between adsorbate molecules and

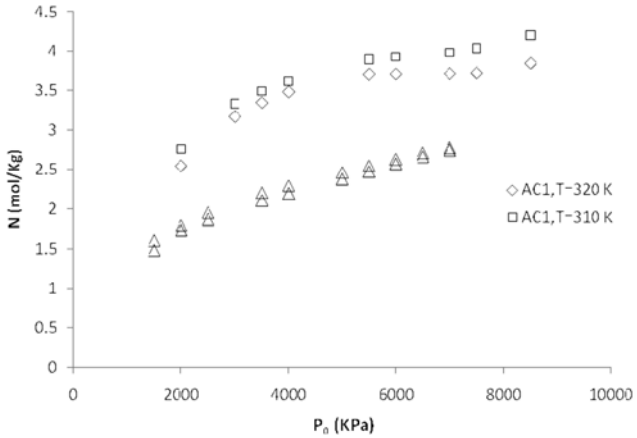

Fig. 5. Prediction of methane adsorption amount with ANN-GA on AC1 and AC2 at temperatures 310 K and 320 K.

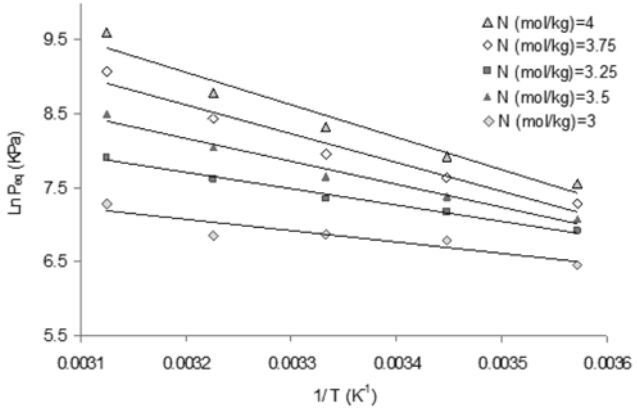

Fig. 6. Plot of Ln(P_{eq}) versus 1/T to calculate isosteric adsorption heat for AC1.

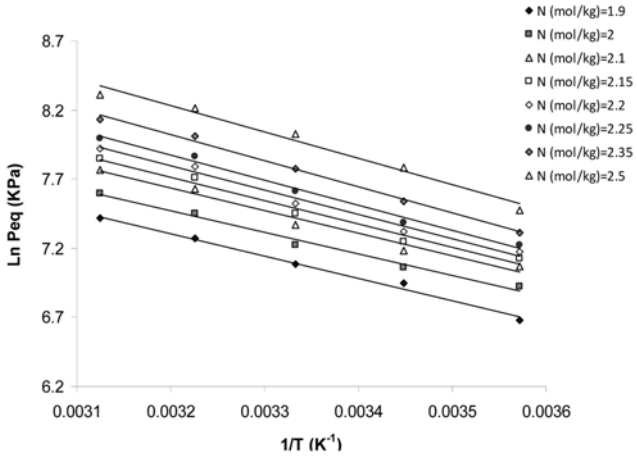

Fig. 7. Plot of Ln(P_{eq}) versus 1/T to calculate isosteric adsorption heat for AC2.

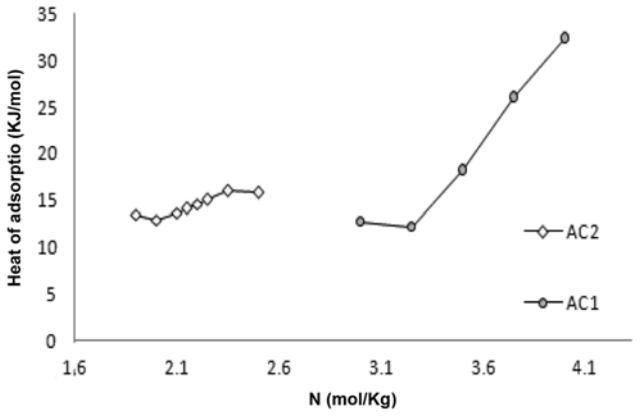

Fig. 8. Isosteric heat of adsorption determined as a function of adsorption amount for AC1 and AC2.

adsorbent lattice atoms, and it is a criterion of the energetic heterogeneity of a solid surface. It has been recognized that energetic heterogeneity may come from the surface, pore structure, and geometric heterogeneity. For the heterogeneous adsorption system, this isosteric energy curve varies with the adsorption amount. The isosteric heat of adsorption values are calculated and presented in Fig. 8 versus adsorption amount for AC1 and AC2.

This study showed that the isosteric enthalpies of adsorption varied with the surface loading in the range −12 to −33 kJ/mol. Comparison of two curves in Fig. 8 shows that the adsorbent AC1 has lower variation range in the adsorption enthalpy relative adsorbent AC2. This is because AC1 with higher surface area, and consequently with higher methane adsorption capacity, has more heterogeneity in the surface and pore structure than AC2.

CONCLUSION

Experimental data of methane adsorption on two types of activated carbons at temperatures of 280, 290 and 300 K and pressures from 1.5-8.5 MPa were obtained. The experimental results showed that the adsorbent AC1 with surface area 1,060 m^2/gr has utmost methane storage capacity equal 113.5 V/V at temperature 280 K and pressure 8.5 MPa. The ANN-GA model with one hidden layer was used to design the neural network. The network contains eight neurons in the hidden layer. These numbers of neurons for the hidden layers have been achieved by GAs. After training of the model, it was tested and its results were compared to experimental data and a good agreement was observed. In addition, the simulation was used to predict amount of adsorption at temperatures of 310 and 320 K and pressures of 1.5-8.5 MPa for AC1 and AC2.

The predicted results of the simulation with experimental data were used to calculate isosteric heat of adsorption by using the Clausius-Clapeyron equation. The isosteric heat of adsorption was plotted versus amount of adsorption. This determination showed variation of the isosteric enthalpies of adsorption with the surface coverage in the range −12 to −33 kJ/mol. In addition, comparison of the adsorption heat on the adsorbents showed more heterogeneity in AC1 than AC2. Consequently, simulation with the neural networks based on genetic algorithm could be applied to optimize the methane storage process.

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