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**ADSORPTION ISOTHERMAL CO₂ ON ACTIVATED CARBON
 FROM LOW RANK COAL OF INDONESIA**

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ABSTRACT

Adsorption Isothermal data carbon dioxide on activated carbon from low rank coal Indonesia were obtained at 300 , 308, 318 and 338 K at pressure up to 3.5 MPa by volumetric apparatus. The experimental data were analyzed using the Toth and Dubinin-Astakhov models and the isosteric enthalpies of adsorption were calculated for CO₂ on activated carbon by the Clausius-Clapeyron equation.

INTRODUCTION

Fossil fuels supply more than 98% of the world's energy needs. However, the combustion of fossil fuels is one of the major sources of the greenhouse gas CO₂. It is necessary to develop technologies that will allow us to utilize the fossil fuels while reducing the emissions of greenhouse gases. Commercial CO₂ capture technology that exists today is very expensive and energy intensive. Improved technologies for CO₂ capture are necessary to achieve low energy penalties [1].

Separation process can play a key role in alleviating this problem, and the adsorption of gases and vapors by microporous solids has attracted much attention because of its great practical importance in the fields of gas separation, gas purification, and environmental problems. Therefore, adsorption is one of the most effective methods for the separation of emitted CO₂ [2].

The development system of adsorption-based processes requires basic adsorption equilibrium data across a wide range of pressure and temperature [3]. These data are decisive for selection of type, size and number of adsorption reactors at given gas feed, product specifications and environmental conditions. As gas adsorption equilibria data up to now cannot be calculated accurately by theoretical or analytical simulation based models, it is necessary to measure them, i. e. to determine them by reliably and accurately performed experiments [4].

In this research, an adsorption apparatus based on a static volumetric method was constructed in our laboratory. Results are reported for a systematic study of the adsorption of two activated carbons, ones of the activated carbon is from Indonesia low rank coal. Experiments were performed at

temperatures ranging from (300 to 338) K and pressures up to 3.5 MPa. Experimental data were correlated by the Toth model and the Dubinin-Astakhov (D-A) model. The isosteric enthalpies of adsorption were calculated for CO₂ on activated carbon by the Clausius-Clapeyron equation.

NOMENCLATURE

| | | |
|-----------|---|--|
| A | [kJ·kg ⁻¹] | adsorption potential |
| C | [kg·kg ⁻¹] | adsorption capacity per unit mass of adsorbent at equilibrium |
| C_o | [kg·kg ⁻¹] | maximum uptake |
| E | [kJ·kg ⁻¹] | characteristic energy of the assorted adsorbent/adsorbate pair |
| h_{st} | Kj.kg ⁻¹ | isosteric heat of adsorption |
| K_o | [kPa ⁻¹] | equilibrium constant |
| P | [kPa] | pressure |
| P_s | [kPa] | saturated pressure |
| R | [kJ.kg ⁻¹ .K ⁻¹] | gas constant |
| T | [K] | temperature |
| T_{ads} | [K] | adsorption temperature |
| T_c | [K] | critical temperature |
| t | | parameter that indicates the heterogeneity of the adsorbent |
| V | [m ³] | Volume |
| W | [m ³ ·kg ⁻¹] | adsorbed volume |
| n | | exponential parameter describes isotherm |

EXPERIMENTAL SECTION

Materials

Two activated carbon, commercial and activated carbon from Indonesia coal (KT) were studied. Table 1 gives their structural characteristics (micropore volume, total pore volume, and surface area). The micropore volume and surface area was determined using the t-plot method from N₂ adsorption data at 77 K. The total pore volume is determined from the N₂ mass uptake at 77 K and for a relative pressure equal to 0.98.

Table 1. Structural Characteristics of the Adsorbents

| Activated Carbon | Micropore Volume m ³ ·kg ⁻¹ | Surface Area m ² ·kg ⁻¹ |
|------------------|---|---|
| Commercial | 0.514 x 10 ⁻⁴ | 0.885 x 10 ⁶ |
| KT | 0.470 x 10 ⁻⁴ | 0.668 x 10 ⁶ |

High purity of CO₂ was supplied by Samatur gas with purities equal to 99.99 % is used in this research.

Apparatus and Procedure

The experimental apparatus used a static volumetric method. A schematic diagram of it is shown in Figure 1, the experimental apparatus consists mainly of a stainless steel (SS 304) Measuring cell and a charging cell with internal volumes of 80.8 ml and 1118 ml, respectively.

Figure 1 shows the schematic diagram of the experimental apparatus, where the dosing and charging cells are connected through a capillary tube. The cells are immersed in a constant-temperature water bath (HÜBER) and are controlled to pre-selected temperatures of 27 to 200°C with an accuracy of $\pm 0.2^\circ\text{C}$. The pressure was measured by an absolute pressure transmitters (DRUCK, PTX 1400), the pressure range are 0–40 bar abs. and its reading uncertainty is $\pm 0.15\%$ of full scale in measurement. Class-A thermocouple type K is used for temperature measurement. At the measuring cell, the thermocouple was in contact with the activated carbon to enable direct temperature measurement. All temperature and pressure readings are monitored by National Instrument data logger.

The entire assembly was evacuated for 8 hours using a ARUKI single stage vacuum pump to a vacuum level of 0.01 mbar. During the evacuation, the adsorption cell was maintained at 130–140°C to desorb any residue gas in the cell. Helium gas is injected into the system during desorption to improve the evacuation. After degassing process, the measuring cell and charging cell is cooled down to the required sorption temperature.

After evacuation, the charging cell is pressurized with CO₂ from its source, the initial pressure and temperature are then recorded. The CO₂ vapor is released into the measuring cell and left to reach an equilibrium state. Subsequently, the temperature of the bath is changed and the next data point along an isochore is obtained. Measurements are made over four temperature ranges, namely 300, 308, 318, and 338 K. The temperature of the charging cell and measuring cell were adjusted to the required sorption temperature using Huber circulating thermal bath. The same procedures are repeated with a different initial quantity of gas being charged into the charging cell. For a low initial charge, it is possible to reach a system pressure within the cell to below 1 bar. The upper pressure was limited to 3.5 MPa in the experiment.

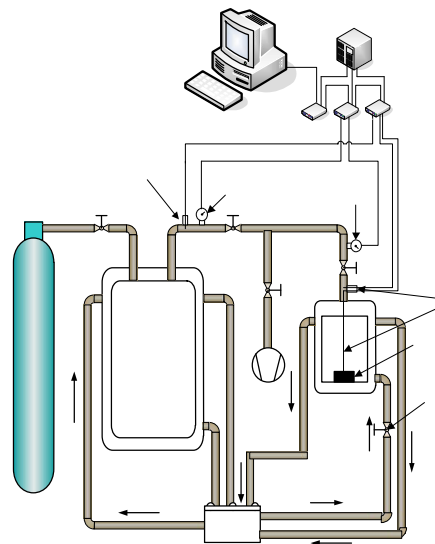


Figure 1 Schematic diagram of the experimental apparatus

RESULTS AND DISCUSSION

Adsorption Isotherm

Data of the adsorption of carbon dioxide onto two activated carbons were obtained for temperatures ranging from 300 to 338 K and pressures up to 3.5 MPa. The experimental data are graphically presented in Figures 2 to 6. The isotherms obtained for carbon dioxide adsorption on all activated carbons were found to belong to type 1 of the IUPAC classification. The CO₂ adsorption increased rapidly when the pressure was increased up to 1500 kPa. The increase in CO₂ adsorption after 1500 kPa appears to be gradual.

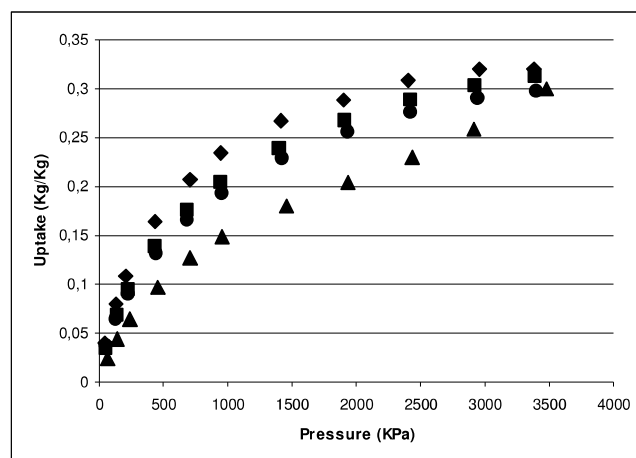


Figure 2 Adsorption Isotherm of CO₂ on KT Activated Carbon; ♦ 27°C; ■ 35°C; ● 45°C; ▲ 65°C

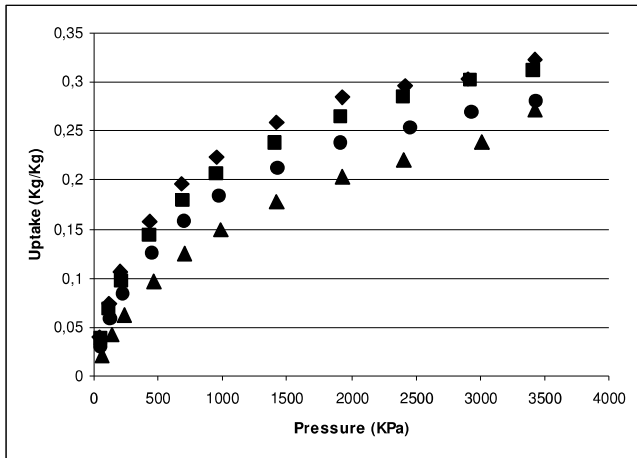


Figure 3 Adsorption Isothermal of CO₂ on Commercial Activated Carbon; ♦ 27°C; ■ 35° C; ● 45°C; ▲ 65°C

The adsorption isotherms for repeated cycles were very similar as shown in figure 4. This indicated that the adsorption is fully reversible and complete regeneration can be obtained by evacuation of the material after adsorption.

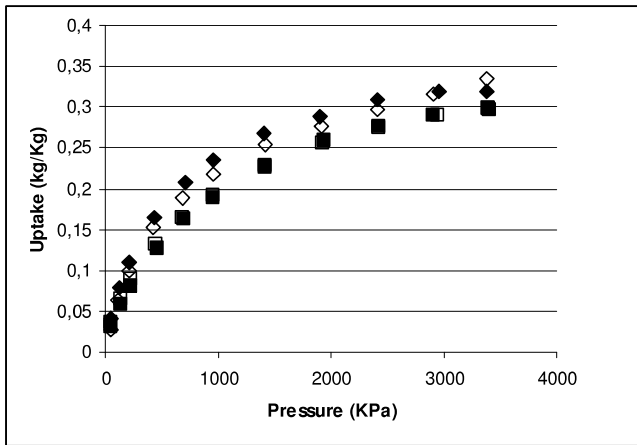


Figure 4 Repeatability of Adsorption Isothermal of CO₂ on KT Activated Carbon; ♦ 27°C and ■ 45°C

The adsorption isotherm carbon dioxide on all activated carbon was compared as shown in figure 5 and 6. That figure describes that KT activated carbon has a higher adsorption capacity than commercial activated carbon, may caused by the micropore volume of KT activated carbon more bigger than commercial activated carbon.

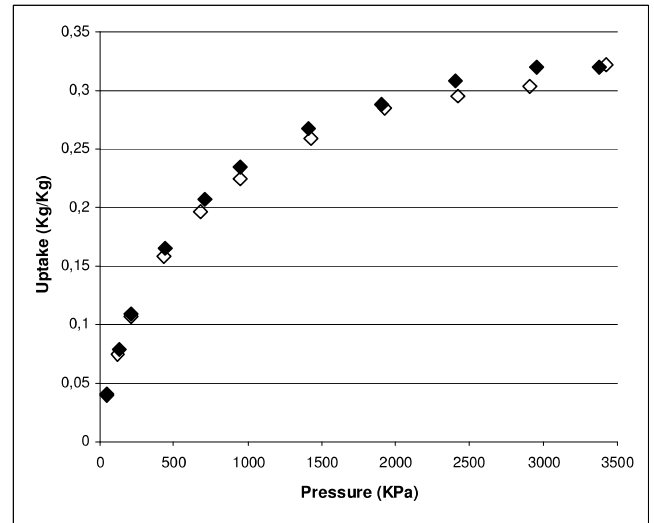


Figure 5 Comparison Adsorption Isothermal CO₂ on KT Activated Carbon (♦) and Commercial Activated Carbon (◇) at 27°C

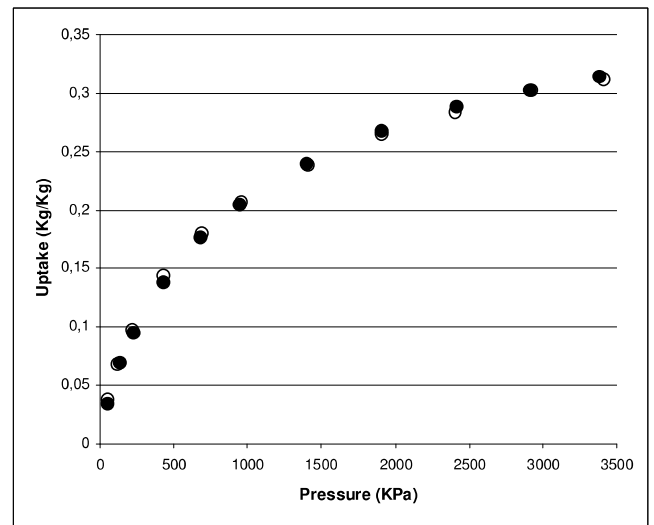


Figure 6 Comparison Adsorption Isothermal CO₂ on KT Activated Carbon (●) and Commercial Activated Carbon (○) at 35°C

Correlation of Isotherms

Two different models those of Toth and Dubinin-Astakhov have been used to correlate our experimental equilibrium data.

The Toth model is commonly used for heterogeneous adsorbents such as activated carbon because of its correct behavior at both low and high pressures [3]. The Toth equation is written as [7]:

$$\frac{C}{C_0} = \frac{K_0 \cdot \exp(h_{st} / RT) P}{\left[(1 + k_0 \exp(h_{st} / RT) P)^y \right]^{1/y}} \quad (1)$$

The Dubinin-Astakhov (DA) equation is found to provide the best representation of the adsorption data [6]. The D-A equation is written as:

$$W = W_0 \exp \left[- \left(\frac{A}{E} \right)^n \right] \quad (2)$$

$$\ln W = \ln W_0 \left[- \left(\frac{A}{E} \right)^n \right] \quad (3)$$

Where A is the adsorption potential and W is the adsorbed volume. W₀ is the limiting volume of adsorption space of the adsorbent, E is the characteristic energy of the adsorption system, and n is the structural heterogeneity parameter.

The adsorption potential A is given by,

$$A = RT \ln \left(\frac{P_s}{P} \right) \quad (4)$$

where R is the gas constant, T is the equilibrium temperature, and P_s is the saturated pressure.

The fundamental adsorption equation involves the vapor pressure P_s at the adsorption temperature T. This implies that the equation is applicable only to sub critical adsorbates. However, experiments of gas adsorption on microporous solids have shown that there is no abrupt change in the adsorption during the transition from sub critical to super critical condition. These suggest that the D-A isotherm equation can be empirically applied to super critical gases as well [5].

Vapour Pressure P_s for super critical gases sometimes called pseudo vapour pressure and to evaluate the pseudo vapour pressure at any temperature above Temperature Critic T_c by using the following Dubinin equation [5].

$$P_s = P_c \cdot \left(\frac{T}{T_c} \right)^2 \quad (5)$$

In this experiment for KT activated carbon the limiting of uptake is 0.34678 kg/kg, the characteristic energy of the adsorption system is 7924.178 kJ/kg and the structural heterogeneity parameter 1.724. The regression results fit the experimental data of Dubinin-Astakhov model within ±3.696%

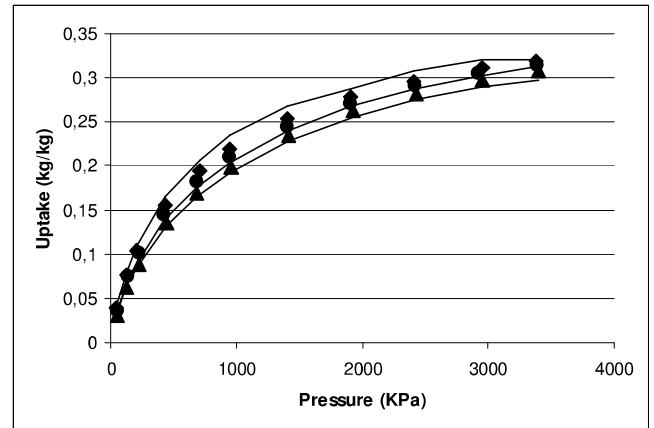


Figure 6 Adsorption Isothermal of CO₂ on KT Activated Carbon; ♦, 27°C; ●, 35°C; ▲, 45°C; Solid lines are from the D-A equation fit

In this experiment for Commercial activated carbon the limiting of uptake is 0.34 kg/kg, the characteristic energy of the adsorption system is 7903.44 kJ/kg and the structural heterogeneity parameter 1.654. The regression results fit the experimental data of Dubinin-Astakhov model within ±5.05%. The Dubinin-Astakhov model for commercial activated carbon is not accurately, may caused this commercial activated carbon is not good for gas used.

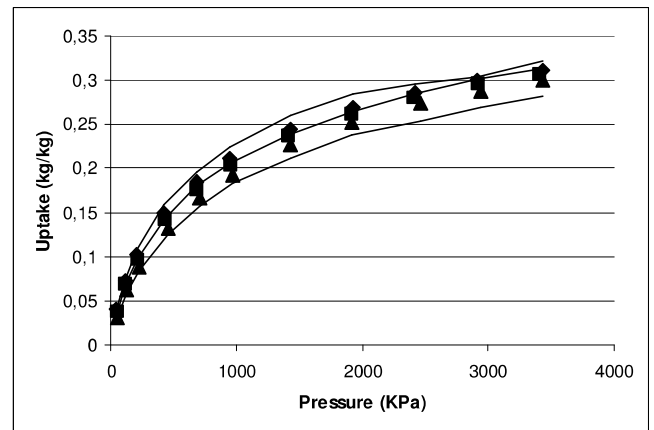


Figure 7 Adsorption Isothermal of CO₂ on Commercial Activated Carbon; ♦, 27°C; ■, 35°C; ●, 45°C; Solid lines are from the D-A equation fit

In this experiment for KT activated carbon the maximum uptake is 0.4497 kg/kg, equilibrium of constant is 1.54.10⁻⁶ kPa⁻¹, isosteric heat of adsorption h_{st}/R is 2177.02 K, and parameter that indicates the heterogeneity of the adsorbent is 0.6972. The regression results fit the experimental data of Toth model within ±2.239%

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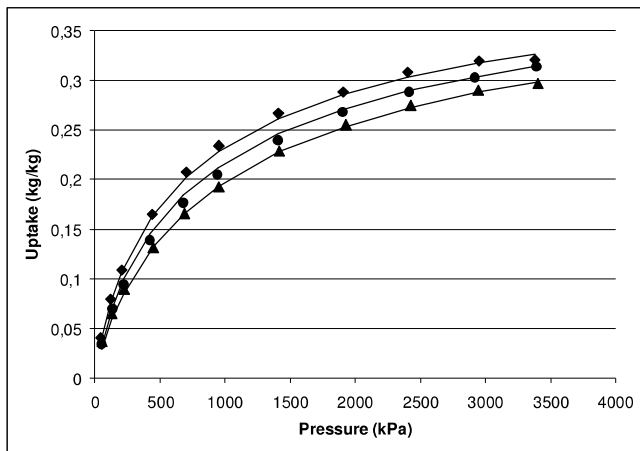


Figure 8 Adsorption Isothermal of CO₂ on KT Activated Carbon; ♦ 27°C; ● 35°C; ▲ 45°C; Solid lines are from the Toth equation fit

The Toth model the regression results fit the experimental data within $\pm 2.239\%$. The Toth equation provided more accurate correlation than the D-A equation. However, because the parameters of the D-A equation are independent of temperature, it is possible to predict the adsorption isotherm at all temperatures for the same gas-solid system, and the D-A equation is effective in evaluating the influence on temperature.

For commercial activated carbon carbon the maximum uptake is 0.6032 kg/kg, equilibrium of constant is $2.2 \cdot 10^{-6} \text{ kPa}^{-1}$, isosteric heat of adsorption h_{st}/R is 2112.81 K, and parameter that indicates the heterogeneity of the adsorbent is 0.488. The regression results fit the experimental data of Toth model within $\pm 2.8586\%$.

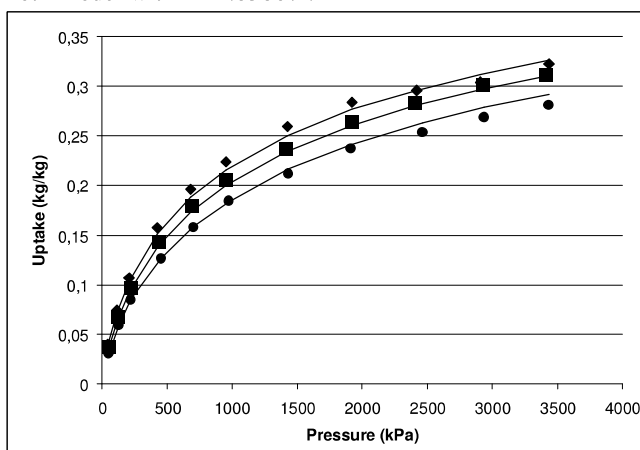


Figure 9 Adsorption Isothermal of CO₂ on Commercial Activated Carbon; ♦ 27°C ■, 35°C; ● 45°C; Solid lines are from the Toth equation fit

Heat of Adsorption

Heat of adsorption is an important thermodynamic function that can be used to characterize the surface of solid [8]. The isosteric enthalpy of adsorption is calculated by the Clausius-Clapeyron equation applied to adsorption [8]:

$$\left(\frac{\partial \ln P}{\partial T} \right)_N = \frac{\Delta H}{RT^2} \quad (6)$$

As shown in figure 10, heat of adsorption decreases with increasing vapor uptake.

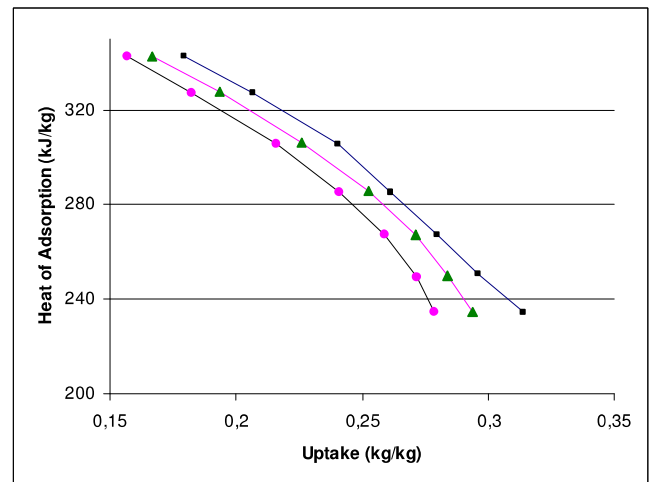


Figure 10 Heat of Adsorption KT Activated Carbon; ♦, 27°C, ▲ 35°C, ● 45°C

CONCLUSION

In this paper adsorption equilibria of pure gases carbon dioxide (CO₂) on activated carbon has been measured in the pressure up to 3.5 MPa at range of temperature 300 to 338 K using the volumetric method. Activated carbon from East of Kalimantan Coal has a lower adsorption capacity than the commercial activated carbon. It is caused by the micropore volume of commercial activated carbon higher than KT activated carbon.

The experimental equilibrium data of carbon dioxide were correlated with the Toth equations and the Dubinin-Astakhov equations and the regression results fit the experimental data are $\pm 2.239\%$ and $\pm 3.696\%$ (KT activated carbon) and 2.8586% and 5.05% (Commercial activated carbon).

For this experiment the Toth equation provided more accurate correlation than the D-A equation.

The heat of adsorption was calculated using the Clausius-Clapeyron equation, resulting in the heat of adsorption decreasing by increasing adsorption of gas.

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REFERENCE

- [1] Siriwardane Ranjani V., Ming-Shing Shen, Edward P. Fisher, and James A. Poston, Adsorption of CO₂ on Molecular Sieves and Activated Carbon, *Energy & Fuels* 2001, 15, 279-284
- [2] Jong-Seok Lee, Jong-Hwa Kim, Jin-Tae Kim, Jeong-Kwon Suh, Jung-Min Lee, and Chang-Ha Lee, Adsorption Equilibria of CO₂ on Zeolite 13X and Zeolite X/Activated Carbon Composite, *J. Chem. Eng. Data* 2002, 47, 1237-1242
- [3] Shuji Himeno, Toshiya Komatsu, and Shoichi Fujita, 2005, High-Pressure Adsorption Equilibria of Methane and Carbon Dioxide on Several Activated Carbons, *J. Chem. Eng. Data* 2005, 50, 369-376
- [4] Keller, Jürgen U, Reiner Staudt, Gas adsorption equilibria: Experimental methods and Adsorptive isotherms, *Springer Science + Business Media, Inc.*, Boston, United States of America, 2005
- [5] Do, Duong D., Adsorption Analysis: Equilibria and Kinetics, *World Scientific Publishing Co. Pte. Ltd.*, Singapore, 2008
- [6] Dubinin M. M., 1975, *Progress in Membrane and Surface Science*, Cadenhead, D. A., Ed.: Academic Press: New York, vol.9, pp. 1-70, 1975.
- [7] Kazi Afzalur Rahman, Wai Soong Loh, Anutosh Chakraborty, Bidyut Baran Saha and Kim Choon Ng, 2009, Adsorption Thermodynamics of Natural Gas Storage onto Pitch-Based Activated Carbons, Proceedings of the 2nd Annual Gas Processing Symposium, Elsevier
- [8] Bansal, Roop Chand & Meenakshi Goyal, *Activated Carbon Adsorption*, Taylor & Francis Group, USA, 2005