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Development of a New Effective Biogas Adsorption Storage Technology

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Abstract. In this study, we report a new effective sludge-digestion gas (biogas) adsorption storage technology. The experimental data of the pure and binary adsorption equilibrium of methane and carbon dioxide, which are the main components of the biogas, on five types of activated carbons at a temperature range of 273–333 K and pressures up to 6 MPa, were measured. Pure isotherms were fitted with the Toth and extended Toth models. Binary equilibrium was predicted using the Ideal Adsorbed Solution Theory (IAST) based on the extended Toth model with the experimental data being predicted as well. The differential enthalpy of the pure and binary adsorption was calculated, and storage densities of the binary gases, methane and carbon dioxide, considering the increased activated carbon temperature, were estimated using the adiabat and isobar of mixed gases in the biogas composition.

Keywords: adsorption storage, activated carbon, biogas

1. Introduction

The unit treatment process of anaerobic digestion is used worldwide for the treatment of industrial, agricultural, and municipal wastewaters and sludges. The biogas (sludge digestion gas) typically consists of 55–65 vol% CH_4, 30–40 vol% CO_2, and trace components (water, hydrogen sulfide, organic acid, etc.). In Japan, the biogas generated in a sewage treatment plant is stored in a gas holder at pressures up to 0.7 MPa after desulfurization and is used as fuel for the boiler and for power generation in plants. However, the biogas utilization rate is approximately 60–70% with the remaining gas being incinerated. Effective biogas utilization can contribute toward promoting greenhouse gas reduction and creating a recycling society. However, delayed gas storage technology development prevents the effective utilization of biogas. In this study, we have focused on the development of an adsorption storage technology. This technology involves activated carbon being packed in a vessel in order to increase its storage density. Hence, this concept can potentially reduce the maximum storage pressure at similar capacities.

On the other hand, several researches have been conducted on adsorbed natural gas, fundamentals of mechanics, experimental measurement, molecular simulation, and material development and characterization. However, as we are aware, a limited amount of research has been conducted on the adsorbed storage of multicomponent gases. Moreover, since adsorption is an exothermic process, the heat of adsorption has a predetermined effect on performance during both the charge and discharge cycles (Chang and Talu, 1996).

In this study, the high-pressure adsorption equilibria of CH_4 and CO_2 were measured at temperatures of 273, 298, and 323 K and pressures up to 6 MPa on five activated carbons used for gas adsorption. Further, we calculated the differential enthalpies of adsorption on their adsorbents. The adsorption equilibria of a binary mixture of CH_4 and CO_2 at temperatures of 273, 298, and 323 K and pressures up to 1 MPa were also measured using a volumetric-flow desorption method and were predicted using the Ideal Adsorbed Solution Theory (IAST). The storage densities of the binary gases, methane and carbon dioxide, considering the increased

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Table 1. Physical properties of activated carbons.

Sample (fab.)	Shape	Raw material	S_{BET} (m^2/g)	V (cm^3/g)	d (g/cm^3)
Norit R0.8 Extra (Norit)	Cylinder	Peat	1450	0.47	0.43
BPL (Calgon Carbon)	Granular	Coal	1150	0.43	0.51
AID (AD'ALL)	Fiber	Petroleum pitch	1200	0.53	0.2
Maxsorb (Kansai Netsu Kagaku)	Powder	Chark	3250	1.79	0.29
Activated Carbon A (Osaka Gas)	Irregular granules	Coconut shell	1121	0.47	0.605

S_{BET}: BET surface area, V: Total pore volume, d: packed density.

activated carbon temperature, were estimated using the adiabat of mixed gases.

2. Experimental

2.1. Materials

In this study, we investigated four commercially-available activated carbons and one engineering sample (activated carbon A) for gas adsorption. Their characteristics are presented in Table 1. The predominantly microporous activated carbon A was made from a coconut shell.

2.2. Apparatus and Procedure

The experiment for the single component employed a static volumetric method. The equilibrium experiments for all activated carbons were performed at temperatures ranging between 273 and 333 K and pressures up to 6 MPa. All binary equilibrium data were measured by the volumetric-flow desorption method that was developed in our laboratory.

3. Result and Discussion

3.1. Single Component Equilibria

A reliable prediction of the multicomponent adsorption equilibria requires a precise representation of the single component data, and a simple model for calculating the amount adsorbed as a function of pressure p and temperature T is an essential requisite for this prediction. In this study, the Toth and extended Toth models were used for regression of the single component equilibria data (Sievers and Mersmann, 1994). The Toth and extended Toth models have the following form:

$$n = \frac{m \cdot p}{(b + p^t)^{1/t}} \tag{1}$$

$$n = \frac{n_{\max}(T)p}{\left(\frac{1}{K(T)} + p^{t(T)}\right)^{1/t(T)}} \tag{2}$$

$$n_{\max}(T) = n^*[1 - \alpha(T - T_{nbp})] \tag{3}$$

$$K(T) = \frac{1}{K_B} \exp\left[\frac{U_0}{RT}\right] \tag{4}$$

$$K_B(T) = 2.346\sqrt{MT} \cdot 10^8 \tag{5}$$

$$t(T) = t_1 - \frac{t_2}{T} \tag{6}$$

Figure 1 shows the single component adsorption isotherms of CH_4 and CO_2 on all the activated carbons studied. The experimental data are represented as symbols, and the isotherms that were fitted with Toth and extended Toth models are represented by solid and dashed lines, respectively. The isotherm parameters for the extended Toth model are tabulated in Table 2. Both these models are in close agreement with the experimental data for all temperatures and activated carbons. The results obtained from the Toth model are slightly more accurate than those obtained from the extended Toth model. However, since the parameters of the extended Toth model are independent of temperature, the prediction of the adsorption isotherm at all temperature ranges for the same gas-solid system is possible. Therefore, in this study, the extended Toth model was selected to predict the binary adsorption equilibrium, at a differential temperature, using the IAST.

3.2. Binary Adsorption Equilibrium

The binary mixtures of CH_4 and CO_2 on Norit R0.8 Extra and activated carbon A were experimentally determined. The mixture equilibria data were measured at temperatures of 273, 298, and 323 K with total pressures of 0.25, 0.5, 0.75, and 1.0 MPa and gas phase mole

Table 2. Parameters of the extended Toth model for activated carbons.

		Norit R0.8 Extra		BPL		A10		Maxsorb		Activated carbon A	
		CH_4	CO_2	CH_4	CO_2	CH_4	CO_2	CH_4	CO_2	CO_2	CO_2
n^*	(mmol/g)	24.0	27.7	11.1	18.2	11.2	16.1	40.5	78.5	11.9	15.0
a	(K^{-1})	0.00283	0.00346	0.00203	0.00358	0.00191	0.00300	0.00260	0.00295	0.00190	0.00254
U_0	(J/mol)	31400	32900	30700	32200	29800	31000	26000	28400	30400	33300
t_1	(–)	1.80	1.80	1.79	1.87	1.66	1.82	1.73	1.55	1.78	1.87
t_2	(K)	359	355	340	354	273	307	272	240	320	353

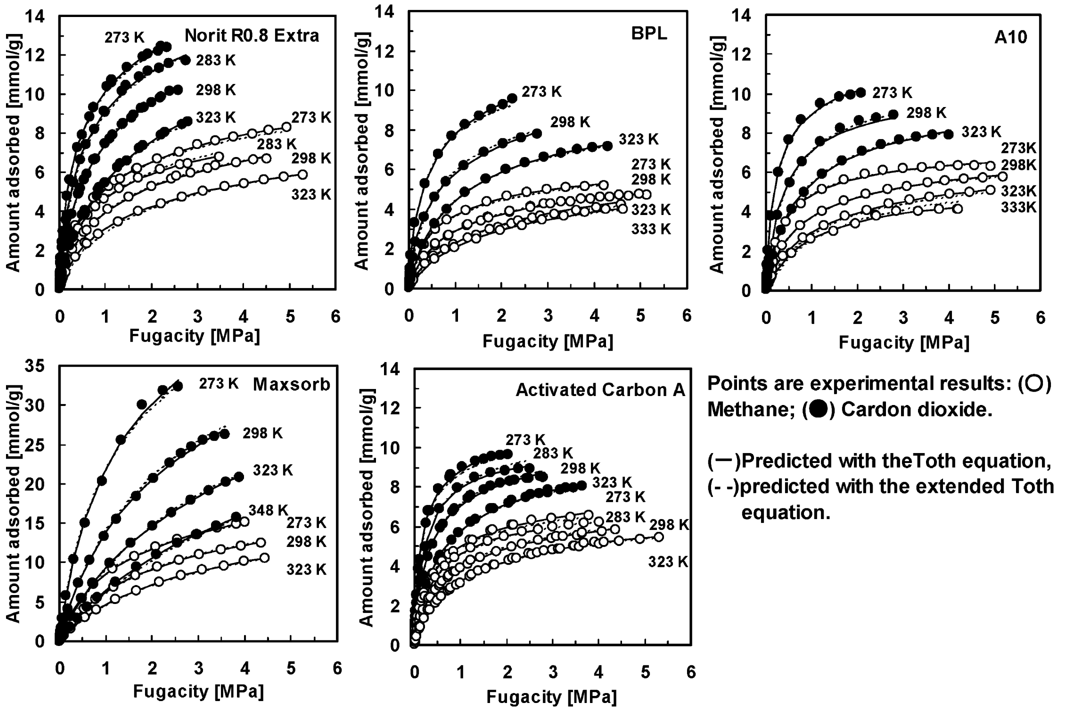

Figure 1. Adsorption isotherms of methane and carbon dioxide on activated carbon.

fractions of 0.25, 0.5, 0.65, and 0.75. Figure 2 shows the measured binary equilibria and prediction lines of IAST. Based on the extended Toth model, since these deviations were within a range of less than 7%, the IAST can accurately predict wide ranges of pressure, temperature, and gas phase mole fraction without any additional parameters.

3.3. *Differential Enthalpy of Adsorption of Pure and Binary Gases*

The heat of adsorption affects the adsorption performance of the gas storage process. The differential enthalpy of adsorption is generally applied to characterize the influence of the heat of adsorption on an adsorbent. The differential enthalpy of adsorption was calculated using the Clausius-Clapeyron equation. In Fig. 3, the differential enthalpies of adsorption for the two adsorbates are plotted as a function of loading. In order to predict the differential enthalpy of binary gas adsorption by IAST, the regression of the differential enthalpy of adsorption for the pure component, using a simple function of the amount adsorbed, is necessary (Siperstein and Myers, 2001). The differential enthalpies of adsorption shown in Fig. 3 were able to fit by a Maclaurin series. For obtaining an ideal solution of binary gases, the differential enthalpy of adsorption of the 1th component is shown in Eq. (7) (Siperstein and Myers,

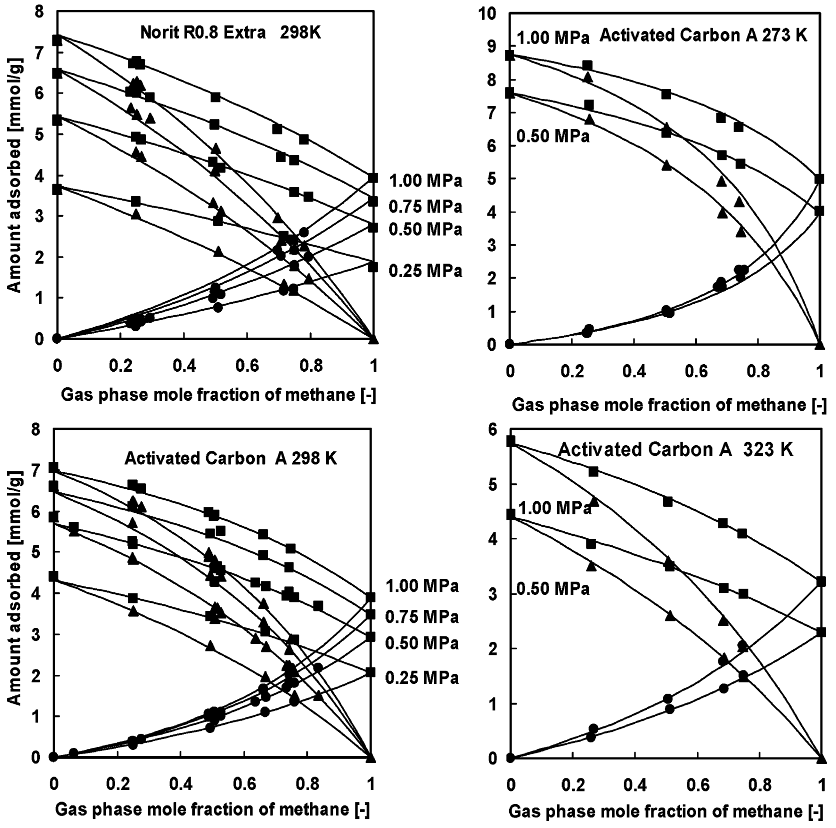

Figure 2. Mixed-gas adsorption isotherms of methane and carbon dioxide on Norit R0.8 Extra at 298 K. Points are experimental results: (■) total adsorption; (●) partial adsorded Methane; (▲) partial adsorbed Cardon dioxide. (–) Predicted with IAS theory.

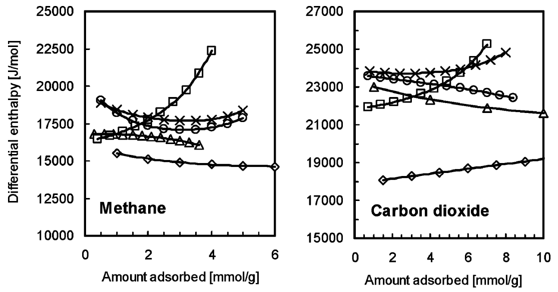

Figure 3. Differential enthalpies of methane and carbon dioxide on activated carbons: (○) Norit R0.8 Extra, (△) BPL, (□) A10, (◇) Maxsorb, (×) Activated carbon A. Lines are fitted by Maclaurin series.

2001).

$$\Delta\bar{h}_1 = \Delta h_1^0 + \frac{1}{n_1^0} \times \left[\frac{x_1 G_1^0 n_1^0\left(\Delta\bar{h}_1^0 - \Delta h_1^0\right) + x_2 G_2^0 n_2^0\left(\Delta\bar{h}_2^0 - \Delta h_2^0\right)}{x_1 G_1^0 - x_2 G_2^0}\right] \tag{7}$$

$$G_i^0 \equiv \frac{1}{\left(n_i^o\right)}\left(\frac{\partial \ln n_i^0}{\partial \ln f_i^0}\right) \tag{8}$$

where $\Delta\bar{h}_i$ is the differential enthalpy of the ith component, $\Delta\bar{h}_i^0$ is the pure differential enthalpy of the ith component, Δh_i^0 is the pure integral enthalpy of the ith component, and x is the mole fraction in the adsorbed phase. The differential enthalpy of binary gases was calculated by Eq. (7) and mole fraction in the adsorbed phase.

3.4. Adiabatic and Isothermal Filling

For a quick, adiabatic filling, the undissipated heat of adsorption raises the temperature of the carbon; then, its capacity is lower than that of the isothermal filling. Due to the undissipated heat of adsorption, the activated carbons occupying the center of the container were considered to be in an adiabatic state. The adiabatic area in the container increased with the increase

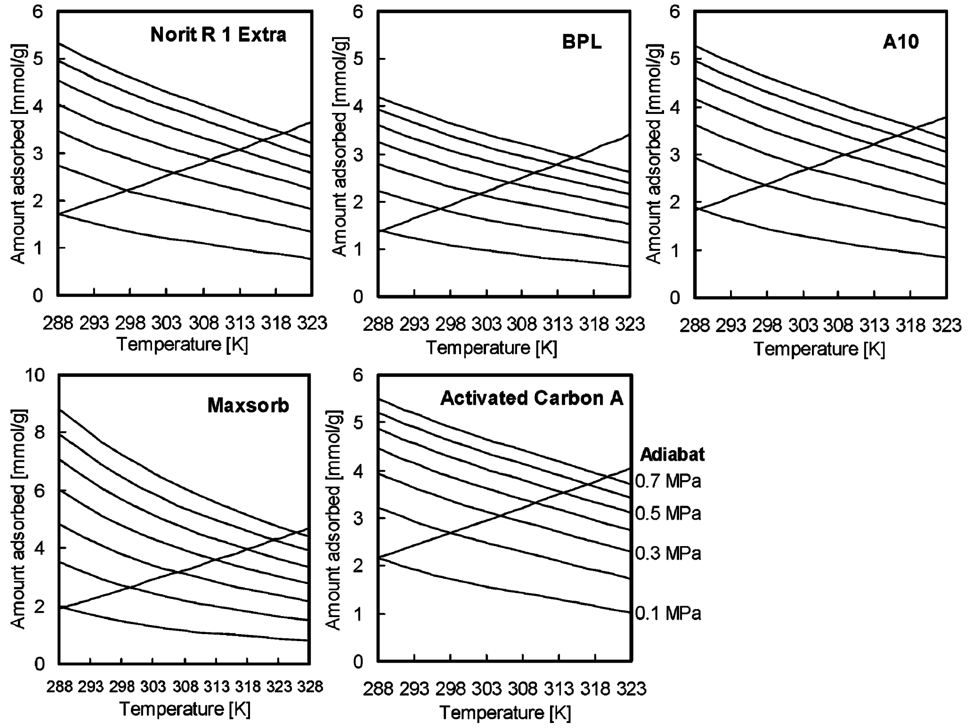

Figure 4. Adiabat and adsorption isobar of mixed gas in the biogas composition.

in the container size. The storage densities of the binary gases of biogas composition were estimated using the adiabat and isobar of the binary gases in consideration of the increased activated carbon temperature during the adiabatic filling.

The isobars of the binary gases were calculated using the IAST based on the extended Toth model, and the adiabat was calculated by numerically integrating Eq. (9) using the heat capacity and differential enthalpy of the mixed gases (Matranga et al., 1992).

$$\frac{dn}{dT} = \frac{C_p}{\Delta \bar{h}} \tag{9}$$

where C_p is the specific heat of carbon plus that of the total amount of methane and carbon dioxide in the container. The adiabatic fill operating lines in Fig. 4 have slope equal Eq. (9). The intersection of the adiabat with the isobar for the set-up pressure (loading pressure) represents the final state of adiabatic filling. Figure 4 shows the adiabat and isobar on each activated carbon at the starting point with a temperature of 288 K and pressure of 0.1 MPa. In the case of storage at pressures up to 0.7 MPa, the temperature increase for BPL was the lowest (+27 K), while that of Maxsorb was the highest (+38 K). The amount of adsorbed for Maxsorb was larger than that of other activated carbons at same pressures, a large temperature rise was observed in comparison with others. In this study, in order to evaluate the storage capacity of digestion gases, the dimensionless density (Matranga et al., 1992) of the binary gases, methane and carbon dioxide, was calculated, and the standard conditions of temperature and pressure were found to be 288 K and 0.1 MPa. Figure 5 shows the storage capacity of

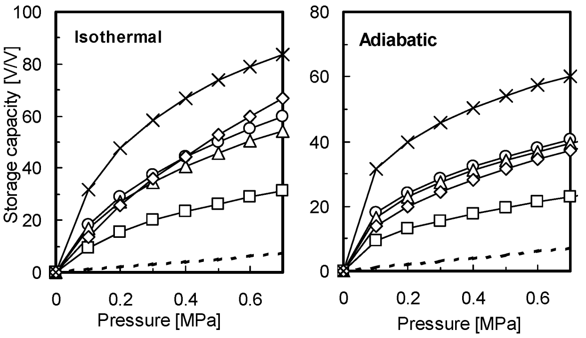

Figure 5. Storage capacities of isothermal filling and adiabatic filling on activated carbons: (○) Norit R0.8 Extra, (△) BPL, (□) A10, (◇) Maxsorb, (×) Activated carbon A, and the dashed lines are compressed storage capacities.

isothermal and adiabatic filling on activated carbons, respectively. Due to the high-packed density, activated carbon A has the greatest capacity of isothermal and adiabatic filling. In adiabatic filling, the heats of adsorption have reduced storage capacities of 26–44% compared to isothermal filling at pressures up to 0.7 MPa. However, the storage capacity using activated carbon A is not less than 7 (0.7 MPa) to 10 (0.5 MPa) times higher than the compressed storage capacity.

4. Conclusion

In this study, a new effective adsorption storage technology for digestion gas was introduced, and the storage capacity in consideration of the adsorption heat was evaluated. We concluded that the adsorbed storage capacity was 5 to 7 times higher than the compression storage capacity at storage pressures up to 0.7 MPa.

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