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Competitive Adsorption of Methane and Carbon Dioxide on Different Activated Carbons

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Adsorbed natural gas (ANG) is one of natural gas storage technologies, in which natural gas is adsorbed by a high porosity adsorbent material at relatively low pressure and room temperature with high methane capacity and low cost. Carbon-based materials, like activated carbons, are promising as an ANG storage adsorbent because of high surface area, high porosity, and high volumetric storage capacity. In this research, the adsorption capacity of single and binary component of CH_4 and CO_2 was investigated by using activated carbons including coconut shell activated carbon (CSAC), palm shell activated carbon (PSAC), and coal-based activated carbon (CBAC) in a packed bed column at room temperature. The composition ratio of single component of CH_4 and CO_2 was fixed at 20 vol% of the total feed gas, and the composition ratios of binary component of CH_4 and CO_2 were fixed at 14.6 : 5.4, 10.0 : 10.0, and 5.0 : 15.0 vol% of the total feed gases, respectively. The result of single component adsorption showed that all activated carbons exhibited preferential adsorption for CO_2 in relation to CH_4. It can be seen from binary component adsorption that the adsorbed amount increased with increased CO_2 composition, while the amount of CH_4 adsorbed decreased, indicating competition for adsorption sites and preferential adsorption of CO_2 over CH_4. In terms of the adsorption capacity of binary component, the methane selectivity was CSAC > PSAC > CBAC for the whole composition ratios of CH_4 and CO_2.

1. Introduction

One alternative to gasoline is natural gas as the advantages of natural gas include its abundance and environmental compatibility. Specifically, natural gas burns cleaner than gasoline as well as emitting fewer hydrocarbons and 90 % less carbon monoxide. Furthermore, another reason for this growing interest is because natural gas is much cheaper than that of conventional petroleum-based gasoline and diesel fuel (Zhang et al., 2010). In spite of the advantages of natural gas in comparison to liquid fuels, there is an inherent disadvantage: its low-energy density (heat of combustion/volume), which constitutes a limitation for some applications. Consequently, the storage of this fuel, whether in quantity or density, plays an important role for its use in diverse kinds of transport (Solar et al., 2010).

Several alternative methods have been considered in order to increase the energy density of natural gas and facilitate its use as a vehicle fuel (Lozano-Castello et al., 2002). Nevertheless, for large scale use to be feasible, it is necessary to store natural gas in a safe and economical way. Adsorbed natural gas (ANG) technology can provide adequate energy density at a moderate pressure of the order of 3.5 MPa (much lower than in CNG) and at room temperature (much higher than LNG) (Wang et al., 2010). Several studies about the use of ANG focused on the development of new materials, especially carbon-based ones, which should provide high adsorption capacity and delivery.

Activated carbons are the adsorbents with the most favourable characteristics for ANG storage, because they have a large microporous volume, are efficiently compacted into a packed bed, and can be cheaply

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manufactured in large quantities (Esteves et al., 2008). In addition, it has been shown that activated carbons are very good adsorbents, presenting the highest ANG energy densities, and thus the highest storage capacity (Lozano-Castello et al., 2002). It is well known that carbon dioxide also presents in natural gas, and it has higher adsorption capacity than methane on activated carbons. It can compete to adsorb with methane and decrease the amount of adsorbed methane on the adsorbents that can affect the adsorption capacity, energy density, and selectivity of methane (Yi et al., 2013). In this research, coconut shell activated carbon (CSAC), palm shell activated carbon (PSAC), and coal-based activated carbon (CBAC) were used as natural gas storage adsorbents. The dynamic adsorption of pure methane and carbon dioxide was used to study their adsorption capacity, and competitive adsorption of methane and carbon dioxide was also scrutinized on the activated carbons.

2. Experimental

2.1 Preparation of Adsorbents

The adsorbents were ground and sieved to obtain a particle size of 20-40 mesh. Then, they were dried at 120 °C in the oven for 24 h to remove moisture and kept in a desiccator.

2.2 Characterization of Adsorbents

The surface area, total pore volume, and micropore volume of the adsorbents were measured by a Quantachrom/Autosorb1-MP instrument. The adsorbents were firstly out gassed to remove the humidity on their surface under vacuum at 300 °C for 16 h prior to the analysis. After that, nitrogen was purged to adsorb on their surface. The volume-pressure data was used to calculate the BET surface area, total pore volume, micropore volume, average pore diameter, and pore size distribution. For morphology of the adsorbents, they were investigated by using the SEM, Hitachi S 4800, with an accelerating voltage of 5 kV and varying magnifications of 500 and 1,000. The adsorbents were coated with platinum under vacuum condition before characterization.

2.3 Experimental Apparatus

Thermo-volumetric apparatus was constructed to study the gas-solid interaction between methane/carbon dioxide and potential solid adsorbents. The schematic of the experimental set-up for the dynamic adsorption of methane and carbon dioxide is shown in Figure 1.

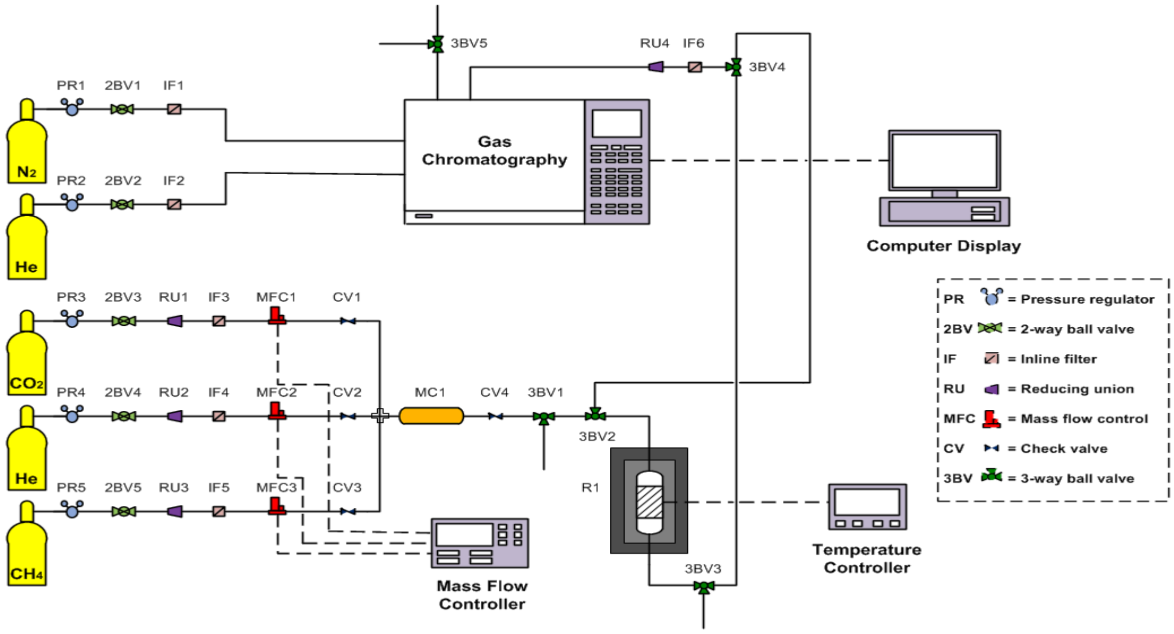

Figure 1: Schematic of the experimental set-up for the dynamic adsorption of CH_4 and CO_2.

2.4 Dynamic Adsorption of Methane and Carbon Dioxide

Methane and carbon dioxide adsorption experiment was carried out at atmospheric pressure and room temperature. Fill 5 g of an activated carbon in the middle of packed column. The feed stream consisted of 5.0 ml/min CH_4 and 0 mL/min CO_2, 3.65 mL/min CH_4 and 1.35 mL/min CO_2, 2.5 mL/min CH_4 and 2.5 mL/min CO_2, 1.25 mL/min CH_4 and 3.75 mL/min CO_2, and 0 mL/min CH_4 and 5.0 mL/min CO_2 with 20 ml/min He.
The stream was controlled and monitored by a mass flow controller. The outlet gases (CH_4 and CO_2) from the column were analysed by a Hewlett Packard 5890 series II gas chromatograph.

3. Results and Discussion

3.1 Adsorbent Characterizations

Table 1 shows the summary of the BET surface area, total pore volume, micropore volume, and average pore diameter of the adsorbents. The surface areas of CSAC, PSAC, and CBAC are 941, 750, and 744 m^2/g, respectively. The total pore volume of CSAC, PSAC, and CBAC are 0.52, 0.42, and 0.43 cm^3/g and micropore volume of CSAC, PSAC, and CBAC are 0.50, 0.40, and 0.42 cm^3/g, respectively.
The micropore volume of adsorbents is almost similar with total pore volume confirming that the pore size distribution is in the range of micropore.

Table 1: BET surface area, total pore volume, micropore volume, and average pore diameter of investigated adsorbents

Adsorbents	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Micropore volume (cm^3/g)	Average pore diameter (Å)
CSAC	941	0.52	0.50	21.96
PSAC	750	0.42	0.40	22.12
CBAC	744	0.43	0.42	22.49

From Figure 2, the SEM micrographs show that all activated carbons exhibit dust or impurity in the pores, which may block pores, and the adsorbates cannot reach into the pore, resulted in the decrease in the adsorption capacity.
The SEM micrographs also show the different structures of the activated carbons. The CSAC and PSAC have smaller pore structure, while the CBAC has larger pore structure.

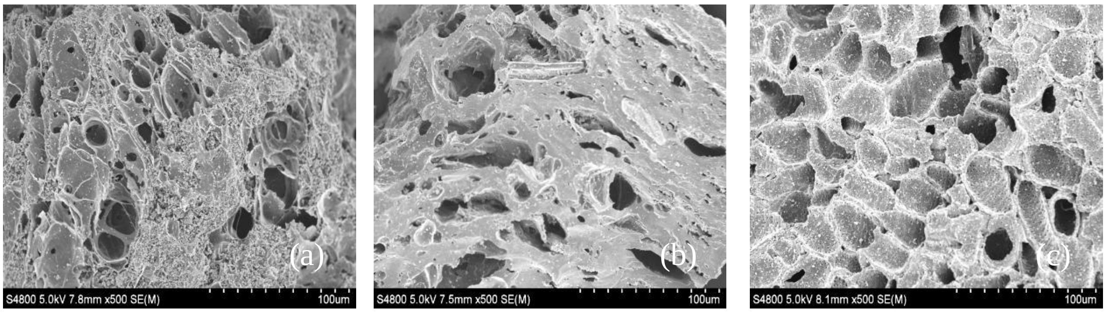

Figure 2: SEM micrographs for (a) CSAC, (b) PSAC, and (c) CBAC.

3.2 Dynamic Adsorption of Methane and Carbon Dioxide

Results of single component adsorption show that all activated carbons exhibit preferential adsorption for CO_2 in relation to CH_4. In terms of the adsorption capacity of single component, the CSAC shows the highest CH_4 adsorption capacity, 1.49 mmol/g (Figure 3), while the PSAC has the highest adsorption capacity of CO_2, 5.36 mmol/g (Figure 3).
In addition to the binary adsorption, all activated carbons adsorb CO_2 showed higher than CH_4, shown in Figure 3.

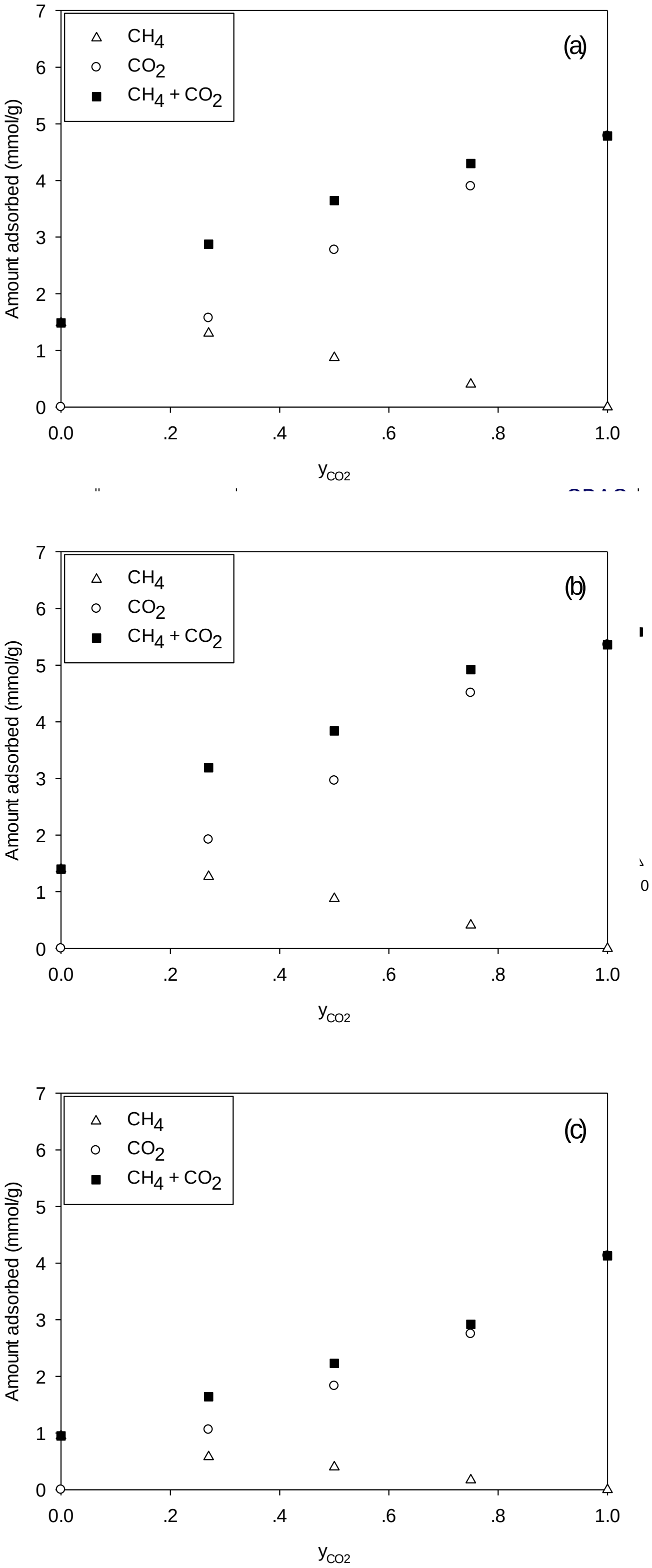

Figure 3: Binary adsorption isotherms of CO_2-CH_4 mixtures on a) CSAC, b) PSAC, and c) CBAC at room temperature and atmospheric pressure

Moreover, the adsorption of CH4 selectivity is ordered as follows: CSAC > PSAC > CBAC for the whole composition ratios of CH4 and CO2 because of the physical properties of CASC including BET surface area, total pore volume, and micropore volume, as shown on Table 1.

For all activated carbons studied in this work, the total adsorbed amount increases with increased CO_2 composition, while the amount of CH_4 adsorbed decreases, indicating competition for adsorption sites and, again, preferential adsorption of CO_2 over CH_4. The main reason for this behaviour is significantly higher critical temperature (T_c) of CO_2 in comparison with CH_4 (Table 2). So, CO_2 is more likely to behave as a condensable steam than as a supercritical gas, becoming less volatile and increasing its adsorption.

Furthermore, CO_2 has higher polarizability, which may enhance attractive forces with the surface, while the permanent quadrupole of CO_2 leads to stronger interactions with the solid surface. In case of energetically heterogeneous adsorbents, there is an initial and preferential filling of high-energy sites, for which the more strongly adsorbed component (CO_2) is even more preferred in the competition for the sites than when competing for energetically weaker adsorption sites (Rios et al., 2012).

Table 2: Physical-chemical properties of CO_2 and CH_4 (Rios et al., 2012)

Molecule	Kinetic diameter (Å)	Polarizability (Å3)	Quadrupole moment (D. Å)	Critical temperature (K)
CO_2	3.30	2.51	4.30	304
CH_4	3.80	2.45	0.02	190

4. Conclusions

In this study, the dynamic adsorption of single and binary component of CH_4 and CO_2 on various types of activated carbons were obtained by thermo-volumetric apparatus experiment. All investigated activated carbons can be classified as a microporous adsorbent.

The CSAC showed the highest CH_4 adsorption capacity, while the PSAC showed the highest adsorption capacity of CO_2 for single component adsorption. For the binary component adsorption, it was discovered that CO_2 showed the higher adsorbed amount with respect to CH_4 for all investigated activated carbons.

Moreover, the total adsorbed amount increased with increased CO_2 composition, while the amount of CH_4 adsorbed decreased, indicating competition for adsorption sites and, again, preferential adsorption of CO_2 over CH_4 because of physical-chemical properties of CO_2 and CH_4. The adsorption of CH_4 selectivity is as follows: CSAC > PSAC > CBAC for the whole composition ratios of CH_4 and CO_2 because of the physical properties of activated carbons.

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