

Improving methane storage on wet activated carbons at various amounts of water

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Abstract: Different mesoporous activated carbons were prepared by both chemical and physical activation processes and were examined for methane uptake in the presence of water. Methane isotherms were obtained at wet condition by wetting samples with water at mass ratio of water/carbon (R) close to 1.0. To compare, the amount of methane storage were also measured at dry situation. The maximum amount of methane stored was attained as 237 V/V at $R=1.0$ by hydrate formation at the methane critical pressure. In the next step, mass ratios of water/carbon were changed to investigate various amount of water for methane storage enhancement. Two other values of mass ratio of water/carbon ($R=0.8$ and 1.4) were selected and methane isotherms were obtained at the same conditions. Maximum values of 210 and 248 V/V were reached for methane storage, respectively. It was also observed that, in the pressure range lower than hydrate pressure, by increasing water ratio the hydrate formation pressure was decreased and methane uptake was much less than that of dry condition due to pore filling by water.

Key words: methane storage; hydrate; isotherm; water; wetting

In recent years, natural gas (with more than 80% methane) has noticed considerable regard as a clean fuel for vehicles and transportation because of various advantages such as abundant reserve, low price and clean fuel compared with the conventional fossil fuels^[1,2]. Utilization of methane gas as a fuel produced less carbon dioxide and more water vapor per energy unit than burning gasoline or diesel^[3]. Although methane is an appropriate fuel, it is difficult to store due to its low density, therefore suitable storage method is necessary to use NG as vehicular fuel^[4]. Four different techniques known for methane (or natural gas) storage namely liquefied natural gas (LNG), compressed natural gas (CNG), adsorbed natural gas (ANG) and natural gas hydrate (NGH), have been considered to improve the energy density^[5–9]. Among these methods, adsorbed natural gas on the porous materials have the advantage of operating at low pressure and room temperature, allowing methane consumption comparable to the other conventional petroleum based fuels^[3,10–12]. Maximum storage pressure utilized in the ANG is normally in the range of 3.5–4.0 MPa and activated carbons with deliverable capacities ranging from 70 to 150 V/V at room temperature and pressure of around 3.5 MPa are appropriate adsorbents for this purpose^[13–16]. The U.S. Department of Energy (DOE) has adjusted target of 180 V/V for methane storage at 3.5 MPa and ambient temperature^[17].

Recently, one of the latest methods that has been investigated for storing methane onto wet activated carbons is the combined utilization of ANG and NGH techniques. In this method, hydrate formation plays major role to enhance methane storage and for this purpose a mesoporous structure is required for adsorbent. Methane molecules are trapped in cages made of water units that linked with each other through hydrogen bonding. However, the formation condition of NGH is rigorous and its formation rate is low^[8,9]. Different research groups have conducted experiments with wet activated carbons to store methane. Perrin et al investigated the storage of methane proposed by two patents dealing with methane adsorption on wet activated carbons^[18]. They applied commercial carbons for storing methane in the presence of water and isotherms for all samples in both wet and dry conditions were obtained. Methane storage of 227 V/V was attained for their best sample at wet condition.

Zhou et al tried to achieve high gas adsorption by using moderate pressure and room temperature condition in microporous activated carbons produced from coconut shell. But, they found very little enhancement with wet activated carbons because pore size and pore size distribution of carbon samples used in their experiments were quite inappropriate and most of the micropores were filled by water^[19]. Zhou et al studied the influence of pore size distribution on the adsorption

in wet condition. They obtained methane uptakes on three different activated carbons at various water to carbon mass ratios (R) and maximum amount of storing was obtained as 30 mmol/g for a carbon sample named BY-1^[20]. Najibi et al examined natural gas storage in dry and wet conditions on three commercial activated carbons named NC120, Picazine and Sigma. In their investigations on these three different ACs, a maximum methane storage of 180 V/V was achieved^[21].

In most previous studies, methane storages were obtained with constant water/carbon ratio close to 1.0. There is not enough investigation on the various amount of water for methane storage at the wet condition. Only Celzard et al and Zhou et al examined various amounts of water to increase methane uptake and they reported various ratios as optimums for different adsorbents^[22]. Besides, they have not performed good comparison among the results due to applying various amounts of water for diverse activated carbons.

In the present work, we have investigated methane adsorption on wet activated carbons made from coconut shell and examined three different amounts of water/carbon ratio equals to 0.8, 1.0 and 1.4 for all samples to improve methane storage and to obtain the better amount of water. Activated carbons were also prepared by the combined chemical and physical activation techniques.

1 Experimental

1.1 Preparation and characterization of activated carbons

Four activated carbons were prepared from coconut shell by the application of both chemical and physical activation processes. In brief, raw material was sieved to uniform size in the range of 1.0–2.0 mm and was activated by $ZnCl_2$ as a chemical agent with various mass ratios of $ZnCl_2$ /raw material. The sample was placed in a boat inside a rotary furnace and kept under nitrogen flow of 300 mL/min until the temperature was reached 800°C. After that, N_2 gas was switched to CO_2 as a physical agent for a certain time. After finishing the experiments and cooling samples to the ambient temperature, they washed several times with hydrochloric acid and distilled water to remove all the remained chemicals. Samples were then dried for 24 h at 110°C in an oven.

By using an automatic adsorption instrument (Micromeritics, Autosorb-1C), N_2 adsorption isotherms of samples were measured at 77 K to determine BET, mesoporous surface areas, total pore volumes, micropore volumes and mean pore diameters. Table 1 shows different conditions used in the preparation of ACs and major characteristics for each sample.

1.2 Density measurement

The density of activated carbon is a very important parameter in ANG applications, as higher packing density leads to higher methane uptake in the limited vessels. Packing densities of samples were measured in a small stainless steel cylinder by applying the pressure of about 335 kg/cm². It had been shown that pressure up to 550 kg/cm² did not affect methane uptake of the samples at dry condition^[23].

1.3 Methane storage instruments

Each activated carbon sample was weighted and placed into a high pressure stainless steel vessel and degassed at 220°C for 10 h to remove any impurity and then cooled to room temperature. In the next step, water was added to the carbon powder. For uniform distribution of water, the sorbent bed stayed untouched for 1 h and then sample was degassed again under vacuum condition at 243–247 K (by the help of dry ice bath) for 2 h to remove any air or gases which trapped inside the AC porous structure. Two pressure sensors and a thermocouple were used to measure pressure and temperature of the bed. A thermostatic device could adjust the temperature to be constant at about 2°C (bath with N,N Dimethyl Aniline at its melting point) and also all the apparatus was isolated in that constant temperature. For each adsorbent sample, the methane uptake was measured by loading methane into the vessel up to 8.0 MPa. The quantity of loaded methane was determined by the pressure decrease using pressure transducer and the charging rate was controlled by a needle valve. Finally, the number of moles of methane really stored in the sample holder was obtained by the application of Van der Waals equation of state^[18,22]. The experimental charging process onto wet activated carbons was carried out in a set-up shown in Fig. 1.

Table 1 Different preparation conditions and characteristic of samples

Sample	(R) (water/ carbon)	CO_2 flow (mL·min ⁻¹)	Temp. t /°C	Carbonization time t /h	Soaking time t /h	$A_{BET}/$ (m ² ·g ⁻¹)	Average pore diameter d /nm	Total pore volume v / (cm ³ ·g ⁻¹)	Packing density ρ / (cm ³ ·g ⁻¹)
L7	3	300	730	2	2	1548	3.423	1.324	0.437
L8	3	200	800	2	2	2100	3.336	1.752	0.402
L11	3.5	105	730	3	2	1585	2.985	1.183	0.414
L15	4	150	730	2	3	1640	3.131	1.248	0.604

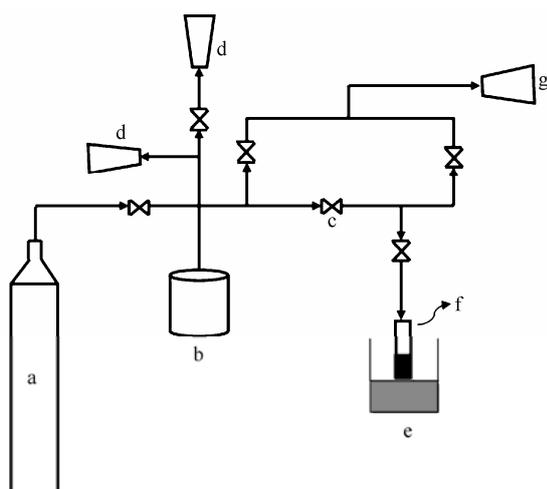


Fig. 1 Methane adsorption set-up

a: methane gas cylinder; b: gas loading cell; c: valves;
d: pressure transducers; e: N,N dimethyl aniline bath;
f: sample holder; g: high vacuum pump

2 Results and discussion

2.1 Methane storage at wet and dry conditions

Methane isotherms were collected at 2°C and up to the pressure of 8.0 MPa for both dry and wet conditions. Methane uptakes were first measured for all AC samples at dry condition and the isotherms are shown in Fig. 2.

The applicable unit for gas storage purposes is usually defined as the STP volume of methane stored per unit volume of the storage vessel (V/V), therefore the amount of methane adsorbed in moles per gram of adsorbent have been converted to V/V unit after applying ACs bulk densities. As in Fig. 2 shown the data points are typically type I isotherms at this particular temperature and pressure range. In the low pressure range, the methane storages increase rapidly illustrating adsorption of methane molecules inside the micropores. By increasing pressure, the rates of gas uptake decrease and slowly reach the plateau at the high pressures.

The above AC samples were then wetted by the deionized water with a water/carbon mass ratio (R) of 1.0 and new isotherms were measured at the same conditions. Fig. 3 shows methane uptakes for wet activated carbons with $R=1.0$. The first part of isotherms shows classical physisorption related to adsorption inside the pores before critical pressure and hydrate formation occurring. In comparison with the dry situation, before the hydrate formation pressure, the isotherms indicate much lower methane uptake in the wet condition than that of dry due to the presence of water inside the pores.

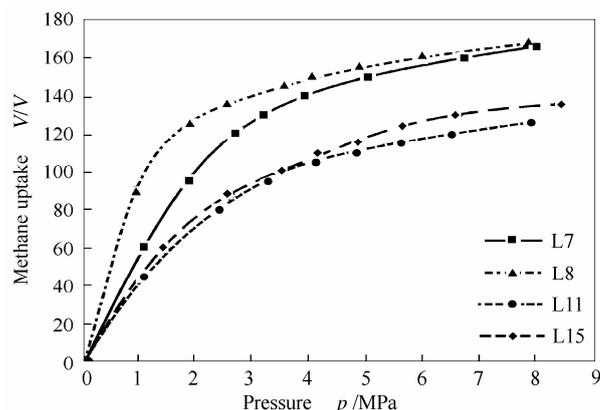


Fig. 2 Methane isotherms for activated carbons at dry condition at 2°C

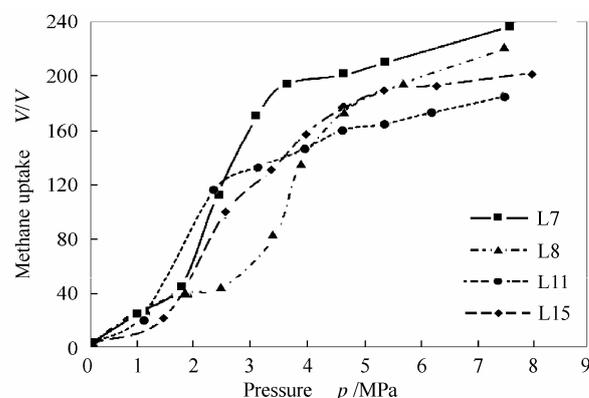


Fig. 3 Methane uptakes of activated carbons listed in Table 1 at 2°C and wetted with a constant water/carbon mass ratio =1.0

Table 2 Methane storage values with different amounts of water

Sample	$R=0.8$ (V/V)	$R=1.0$ (V/V)	$R=1.4$ (V/V)	Dry condition (V/V)
L7	210	237	248	166
L8	185	220	226	168
L11	161	184	197	133
L15	158	202	198	138

Secondly, with increasing pressure, at the critical pressure, hydrate is formed inside the mesopores and the methane uptake increases rapidly (creating stepwise at isotherms) and becomes much higher than that measured at dry condition. This jump corresponds to the formation of the hydrate within the large pores. On the other hand, with the increasing of pressure to higher values, the methane adsorptions in some pores which do not contain enough water to form hydrate, provide positive slopes at the end of the isotherms.

2.2 Effect of water amounts on methane storage

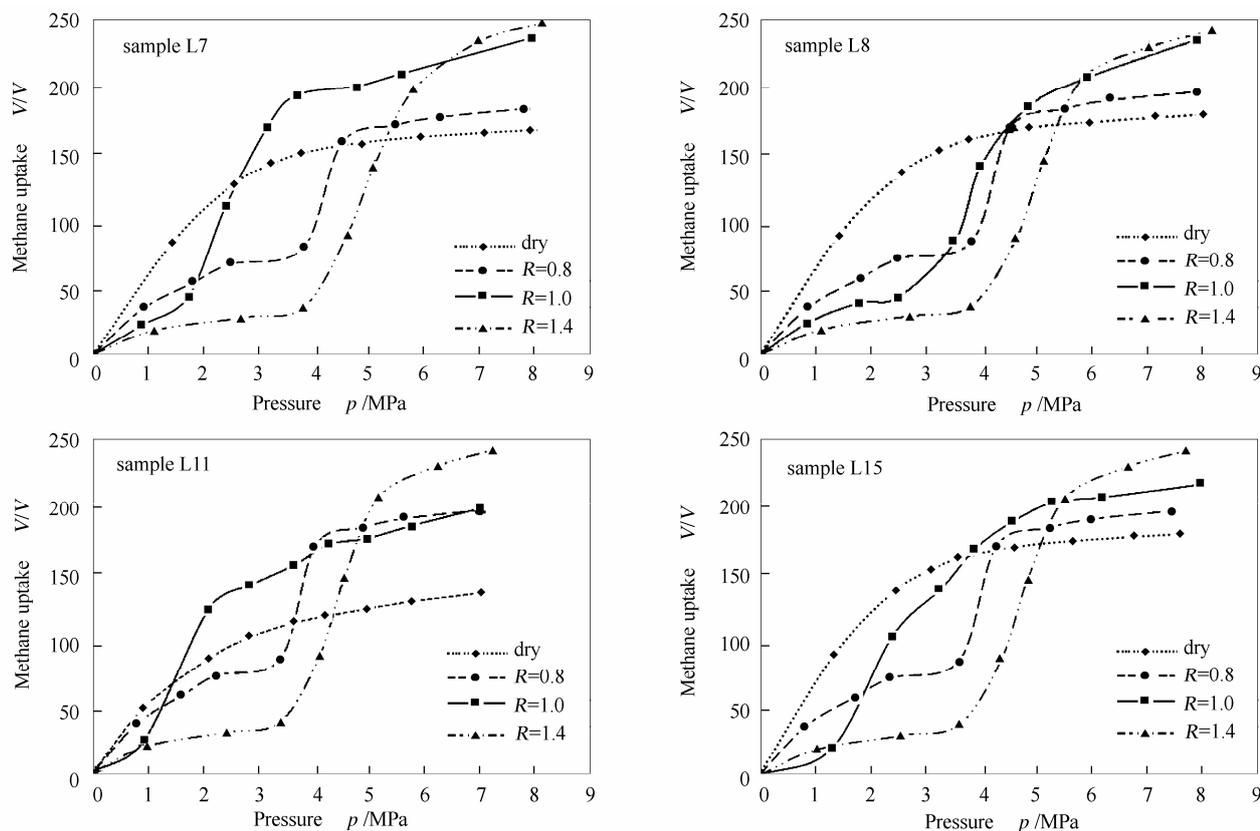


Fig. 4 Methane uptakes of AC samples with different amounts of water

In the previous section, methane uptakes were studied at the ratio of water/carbon equal to 1.0. To achieve maximum amount of methane storage, two different water/carbon mass ratios of 0.8 and 1.4 were examined for the above mentioned activated carbon samples.

Figure 4 shows isotherms for these samples with different wetting ratios. Meanwhile, for comparison the dry isotherms were also illustrated. All isotherms present the similar shape to those in Fig. 3. The hydrate formation pressure is seen to be different depending on the activated carbon sample. Based on the above results, a large amount of methane is observed to be stored in activated carbons containing higher amounts of water. Table 2 shows the amounts of methane uptake at wet and dry conditions. Researches by other groups indicated that wetting more than the saturation value ($R > R_{sat}$) leads to very low methane storage, because most of the pores would be filled by water and resulted in low hydrate formation^[23].

3 Conclusions

The present study shows that hydrate formation inside the pores of activated carbons plays major role in enhancement of methane storage. The results indicate that before the hydrate formation pressure, the methane uptakes are much less than that of dry condition due to the presence of water which fills and blocks the majority of the porosity. After the hydrate

formation, isotherms show stepwise increase indicating the high methane storage. With the increasing water/carbon mass ratio studied, the uptakes of methane increase. The condition with water/carbon mass ratio of 1.4 illustrates the best performance in terms of methane uptakes among other values of R . According to the results, for L7 sample (with higher average pore diameters), the amounts of methane storage are 210, 237 and 248 V/V for water/carbon ratio equals to 0.8, 1.0, and 1.4, respectively.

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