

## Methane Adsorption Characteristics of Activated Carbon†

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Methane adsorption on activated carbons was investigated in the present works up to 70 bars at 298 K. Coconut-shell was activated by potassium hydroxide, resulting in activated carbons with different porosities. Methane adsorption isotherms show type 1 shape. The complete reversibility and fast kinetics of methane adsorption show that most of the adsorbed quantity is due to physical adsorption. Methane adsorption capacities are linear function of microporosities such as specific surface area, micropore surface area, total pore volume and micropore volume. The maximum methane adsorption capacity of 22 wt. % at 70 bars, 298 K is obtained in these materials.

**Key Words:** Methane, Adsorption, Activated carbon, High pressure.

### INTRODUCTION

Methane can play a major role in future energy system. Methane is abundant as a natural gas in earth. The main composition of natural gas is methane. The interest in methane as a automobile fuel has grown since the beginning of the 1980s. There are several reasons for this growing interest. The first one is that methane is renewable and sustainable material made from biomass. The second one is that methane is much cheaper than petroleum fuels such as gasoline and diesel fuel. The third one is that the ratio of hydrogen to carbon of methane is much higher than any other fossil fuel, which means lower emission of global warming carbon dioxide after combustion<sup>1,2</sup>. The individual parts of methane energy system such as production, delivery and storage are closely interrelated. Among them, methane storage is one of the bottlenecks for the applications in automobile<sup>3</sup>. Methane storage by high pressure methane compression, low temperature liquefaction has severe disadvantages.

Methane cannot be liquefied at room temperature due to its low critical temperature, 191 K. Liquefied methane is usually stored in a cryogenic tank as a boiling liquid around 112 K at atmospheric pressure. The special tank design and refueling system required makes the low temperature liquefaction storage undesirable for automobile fuel application. High pressure methane compression, in other word compressed natural gas (CNG), is used now worldwide in CNG automobiles<sup>4</sup>. In the case of CNG, methane is usually stored as a supercritical fluid at room temperature in cylindrical tank

around 250 bar, very high and dangerous pressure. The CNG storage tank should be constrained in geometry to endure high pressure, such as cylindrical or spherical shape and also heavy in weight. And it is needed high costly multi-stage compression system to reach 250 bar. The explosion accidents of CNG system are frequently happened due to its high pressure.

Many researches are focusing on improving present technologies and searching advanced materials such as adsorbent<sup>5</sup>. Methane gas can be stored as a liquid phase in adsorbent above its critical temperature (adsorbed natural gas, ANG in abbreviation). This ANG can be a promising alternative method to solve the problems of CNG. Microporous activated carbons seem to be a good candidate for methane storage due to their high porosity and low cost<sup>6</sup>. The methane adsorption process in carbon porous materials at moderate temperature is due to physical adsorption based on van der Waals forces between adsorbent and adsorbate. This interaction force is so weak at room temperature that only low adsorption capacity can be obtained and becomes stronger at low temperature, which is proportional to the temperature.

In this work, activated carbons with different porosities have been prepared and investigated as a methane adsorbent up to 70 bars at 298 K to determine further direction to present research on methane storage materials. These activated carbons possess diverse porosities according to their preparation conditions. The methane adsorption capacity is correlated to the porosities of the activated carbons to understand the phenomena of methane adsorption process.

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## EXPERIMENTAL

**Preparation of activated carbon:** Various activated carbons are prepared by chemical activation. Coconut-shell was used as a raw material. The activating agent was potassium hydroxide. Coconut-shell is crushed up in a particle size smaller than 0.5 mm in diameter. Powder raw material was mixed with potassium hydroxide in vibration ball mill. The mixing ratio of raw material and potassium hydroxide ranges from 1:1 to 1:5 in weight. The mixture in the sample holder was heated in a tubular furnace using a heating rate of 5 K min<sup>-1</sup> up to activation temperature in argon inert atmosphere. The activation was performed for 2 h. The preparation condition is described in previous work<sup>7</sup>. The product was washed with distilled water to remove remaining potassium hydroxide and dried at 423 K for 3 h resulting in activated carbon.

**Pore characterization:** The pore structure of activated carbons was characterized by physical adsorption of nitrogen at 77 K in a Micromeritics 2010 apparatus. All the samples were degassed at 623 K for 15 h prior to the measurement. Nitrogen adsorption isotherms were used for calculating surface area and pore volume through BET equation, t-plot and Gurvitsch rule.

**Methane adsorption:** The methane adsorption has been performed by manually controlled high pressure balance, which consists of Rubotherm's magnetic suspension balance and methane boosting system. The resolution of this balance is 0.01 mg and working pressure is 150 bars. As it is gravimetric measurement, the apparatus can be used without any severe interference due to temperature deviation. The schematic diagram of methane adsorption apparatus is shown in Fig. 1. A typical methane adsorption experiment using high pressure manual system involved pressurizing a gas reservoir to *ca.* 100 bars by gas booster. The samples are degassed to eliminate adsorbed gases and water at 373 K for 15 h until pressure and mass did not change for 0.5 h. Then the desired pressure of methane is introduced into the sample space by opening the valve between the reservoir and the sample space. The pressure, temperature and weight monitored as a function of time. The measured value of balance display is caused by the methane uptake on activated carbon and buoyancy force. The influence of buoyancy can be corrected as follows:

$$M = W * [1/(1-D_H/D_{MA})]$$

where  $M$  = total mass of measurement load, activated carbon and adsorbed methane;  $W$  = value of the balance display;  $D_H$  = density of the methane under measuring room atmosphere;  $D_{MA}$  = density of measuring load including activated carbon;  $D_{MA}$  can be calculated as follows:

$$D_{MA} = (W_{ML} + W_{AC}) / (W_{ML}/D_{ML} + W_{AC}/D_{AC})$$

where  $W_{ML}$  = weight of measuring load;  $W_{AC}$  = weight of activated carbon;  $D_{ML}$  = density of measuring load, 8.354 g/cc;  $D_{AC}$  = density of activated carbon which is measured by pycnometer.

The increase in  $M$  is the amount of methane adsorbed.

After no more weight change is detected for 15 min, we get adsorption data. The adsorption temperature, 298 K was kept constant by room temperature control. Buoyancy effect was corrected. Each adsorption test is repeated at different

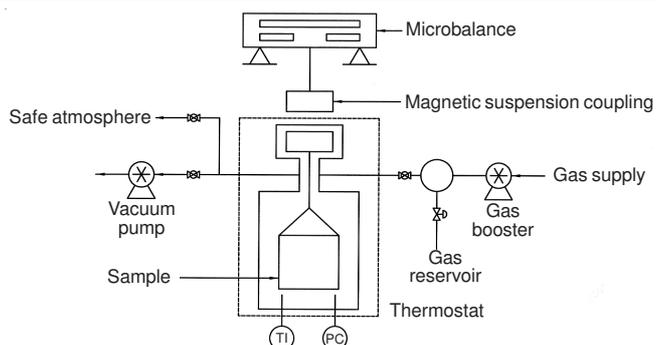


Fig. 1. Schematic diagram of methane adsorption apparatus

methane pressure from 10 bars to 70 bars. The mass of the activated carbon samples used for methane adsorption was 500-1,000 mg typically.

## RESULTS AND DISCUSSION

Fig. 2 shows representative methane adsorption isotherms of prepared activated carbons at 298 K over the methane pressure range 10-70 bars. We have obtained similar shapes of methane adsorption isotherms in spite of their different porosities for all prepared activated carbons. Methane adsorption isotherms show typical type 1 shape. Methane adsorption capacity reaches in saturation around 70 bars. The methane adsorption capacity of the different activated carbons is correlated to their porosities as follows.

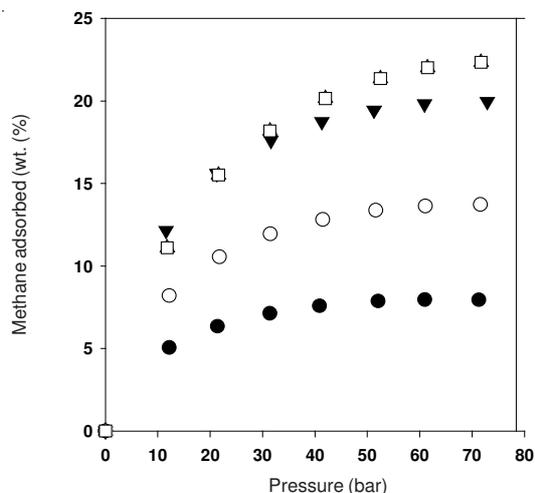


Fig. 2. Representative methane adsorption isotherm at 298 K

Fig. 3 shows the effect of specific surface area on the methane adsorption capacity of the different activated carbons at 70 bars and 298 K. The methane adsorption capacity increases almost linearly according to their specific surface area. As the specific surface area was calculated from nitrogen adsorption isotherm at 77 K and methane adsorption capacity was calculated from methane adsorption isotherm at 70 bars and 298 K, there were differences in adsorptive, adsorption temperature and adsorption pressure. It could be thought that the activated diffusion of methane molecules may be possible through very narrow constrictions into cavity, which nitrogen molecules can't diffuse through. The Y-axis intercept may be explained due to the activated diffusion.

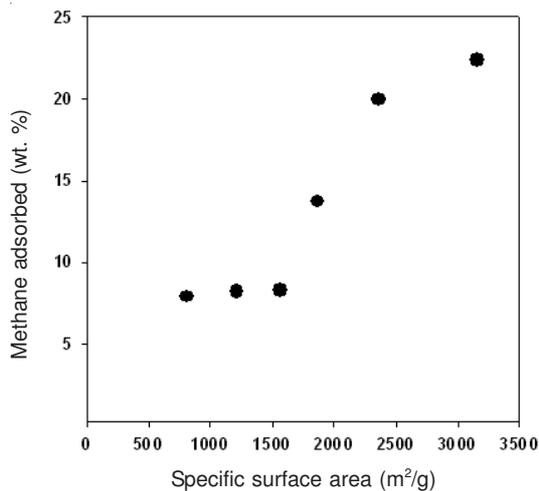


Fig. 3. Effect of specific surface area on the methane adsorption capacity at 70 bars, 298 K

Fig. 4 shows the effect of total pore volume on the methane adsorption capacity. Fig. 4 shows better linearity than Fig. 3 which means that pore volume has more effect on methane adsorption capacity than surface area.

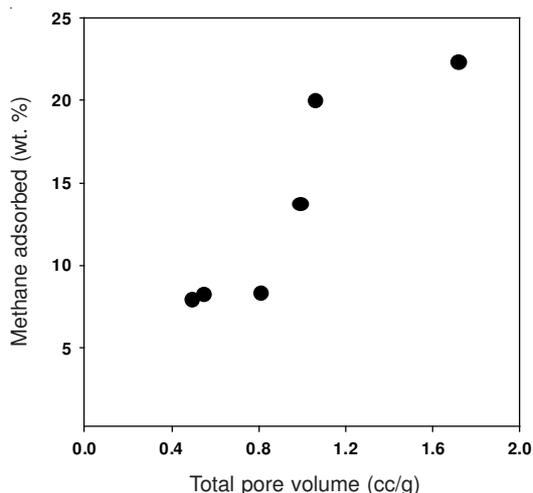


Fig. 4. Effect of total pore volume on the methane adsorption capacity at 70 bars, 298 K

Fig. 5 shows the effect of total micropore volume on the methane adsorption capacity. It shows good linearity. Among several pore volumes, micropore volume seems to exercise an important effect on methane adsorption capacity.

Fig. 6 shows the effect of mesopore volume on the methane adsorption capacity. It is impossible to see any relationships. The contribution of mesopore and macropore to methane adsorption seems to be negligible in activated carbon.

As shown in Figs. 3-5, the amount of methane adsorption on activated carbon was linearly related to their microporosity. All these results show that the higher the development of microporosity, the higher the methane adsorption capacity. It confirms the necessity of using a well-developed microporous carbon material. The broad range of activated carbons studied in this work and the high methane adsorption capacity shows the possibility in large methane storage by activated carbon at room temperature.

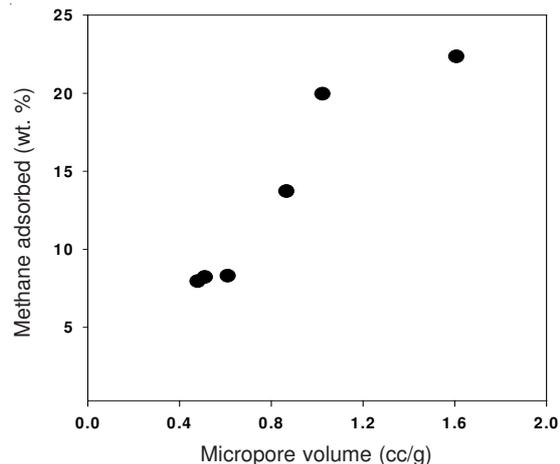


Fig. 5. Effect of micropore volume on the methane adsorption capacity at 70 bars, 298 K

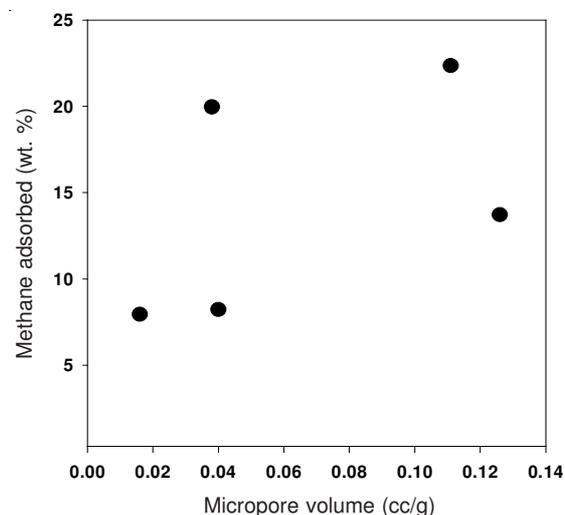


Fig. 6. Effect of mesopore volume on the methane adsorption capacity at 70 bars, 298 K

Methane adsorption measurement seems to be simple, but there are numerous traps to be avoided. The first one is the force of buoyancy at high pressure is so strong that most of weight change is due to buoyancy force rather than methane adsorption in gravimetric adsorption apparatus. Therefore, the effect of buoyancy was carefully excluded to calculate correct methane adsorption quantities. The second source of error is that pressure change arising from system temperature variations can incorrectly interpreted as adsorption in volumetric adsorption apparatus. This error effect increases with pressure and may result in several wt. (%)/°C at 100 bars. The third is that it is difficult to distinguish leaks from methane adsorption in volumetric adsorption apparatus. If methane gas leaks from a sample space, it could incorrectly attribute the pressure decrease to methane adsorption. As we used a gravimetric adsorption apparatus, we could avoid the second and the third errors. We think that leaks prevention and constant temperature maintenance is important in volumetric adsorption apparatus and buoyancy effect is carefully calculated in gravimetric adsorption apparatus to get correct methane adsorption quantity.

## Conclusion

This article reports on the methane adsorption characteristics of chemically activated carbons up to 70 bars at 298 K. We have prepared microporous activated carbons with different porosities. The methane adsorption capacities depend almost linearly on microporous structure parameters such as specific surface area, micropore surface area, total pore volume and micropore volume. It seems that the promising candidate for methane storage is a well-developed microporous material.

Due to the fast adsorption and desorption kinetics and almost complete reversibility, physical adsorption by activated carbon is a promising method for methane storage at moderate temperature, however, the highest measured methane adsorption capacity is less than 18 wt. % at 35 bars, 298 K, in spite of their highly developed porosities reaching up to 3,200 m<sup>2</sup>/g in specific surface area. New materials with ultra-high

microporosity porosity and high apparent density should be investigated to achieve sufficient methane storage capacities at room temperature.

## REFERENCES

1. D.C. Carlsaw and N. Fricker, *Chemistry & Industry*, 7 August, p. 601 (1995).
2. N.H. Ravindranath, H.L. Dattaprasad and H.I. Somashekar, *Curr. Sci.*, **59**, 557 (1990).
3. T.D. Burchell and F.S. Baker, The Development and Characterization of Novel Adsorbent Carbons, CRADA Final Report For CRADA C/ORNL-97-0483 (2001).
4. T.L. Cook, C. Komodromos, D.F. Quinn and S. Ragan, *Carbon Materials for Advanced Technologies*, Pergamon, pp. 269-302 (1999).
5. S. Yun, J. Wan, H. Jin, Y. Kim and T. Lee, *Solid State Phenomena*, **135**, 73 (2008).
6. F.S. Baker, Low Pressure Methane Storage with Highly Microporous Carbon, U.S. Patent 5,62,6637 (1997).
7. H. Jin, I. Hong and Y. Lee, *Catal. Today*, **120**, 399 (2006).