



# Natural gas storage in activated carbon pellets without a binder

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## Abstract

Activated carbon pellets without a binder from cellulose microcrystals as a raw material were investigated. After compression of the raw materials, the thus obtained raw material pellets were slowly carbonized to 1073 K under nitrogen. To activate them, the carbon pellets were heated to 1173 K under carbon dioxide. The activated carbon pellet shape, after heat treatment, was columnar by using the previous employed compression of the raw material. The total surface area, pore volume, and average pore diameter for all the samples were evaluated from the analysis of  $N_2$  adsorption isotherm data. The total surface area and the pore volume were decreased with an increase in compression pressure under the same heat treatment conditions. On the contrary, the bulk densities of the activated carbon pellets were increased. However, these properties can be easily controlled by changing the sintering temperature and time. The bulk density of sample pellet was  $0.56 \text{ g/cm}^3$ . It is 2.3 times higher than activated carbon powder, which was made without the compression process. The total methane storage capacity at 298 K reached  $164 \text{ cm}^3$  in  $1 \text{ cm}^3$  volume of activated carbon pellets at 3.5 MPa. © 2002 Elsevier Science Ltd. All rights reserved.

**Keywords:** A. Activated carbon; B. Activation; C. Adsorption; D. Gas storage

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## 1. Introduction

Natural gas storage is of great interest to many industries, such as natural gas vehicle, because of its inherent clean burning characteristics [1–6]. The most popular type of storage method is compressed natural gas (CNG) at 20 MPa (3000 p.s.i.g). However, CNG requires a high pressure-resistance cylindrical vessel that is generally difficult to integrate within a limited space. Moreover, CNG suffers from a major drawback, it is difficult to store with sufficient energy density comparable with liquid fuels.

An alternative to this storage method is an adsorbed natural gas (ANG) storage system. The possibility of an ANG storage system has been actively researched in recent years [7,8]. Among the adsorbents explored, microporous carbon adsorbents are the most attractive for the storage of natural gas. The majority of carbon adsorbents are granular, powder, or fibers [9]. These carbon adsorbents have several merits, such as high surface area and high

pore volume on a mass basis. For a storage system, however, the adsorption must be evaluated on volume basis because voids, where adsorption does not occur, are formed between the particles as a result of packing. Thus, the important parameter of adsorbents is their bulk density.

Many efforts have been made to minimize the useless voids and increase the bulk density. Typically, carbon adsorbent particles can be achieved by being bound together by using binders such as resin. However, the use of resin to increase bulk density has disadvantages; though the binder will increase bulk density, it can also block the micropores of the adsorbent. As a result, it is necessary to activate the reconstruction of the pores [10]. In view of the above shortcoming of the use of binders, it is desirable to find some other type of method that does not have this problem.

This study was an attempt to produce activated carbon pellets without any binder. The compressed cellulose microcrystal pellets were carbonized and activated to prepare activated carbon pellets. Characterization of pore structure was examined using  $N_2$  adsorption isotherm. Methane adsorption isotherms for all samples were mea-

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sured up to 0.86 MPa by a gravimetric method. The methane storage performances for pressure up to 10.0 MPa were evaluated by a volumetric method.

## 2. Experimental

### 2.1. Preparation of activated carbon pellets

Fig. 1 shows a schematic diagram of the apparatus used for the compression of the raw material. Anhydrous cellulose microcrystal powder (Merk Co. Ltd., NJ, USA) was used as the raw material. The size of the crystals was about 15  $\mu\text{m}$ . About 1.5 g of the raw material were placed between the pistons in the dice and a mechanical pressure,  $P$ , was loaded on them for 1 min by an oil hydraulic machine. The pressure range was from 0 to 98.1 MPa. After the compression, the raw material ejected from the dice was columnar pellet. The pellets were then carbonized by an electric furnace at the rate of 10 K/min up to 1073 K under nitrogen. The nitrogen flow rate and the carbonization period were 500  $\text{cm}^3/\text{min}$  and 6 h, respectively. When the carbonization process finished, the nitrogen was replaced with carbon dioxide. To activate, the carbon pellets were heated at the rate of 10 K/min from 1073 to 1173 K under carbon dioxide. The carbon dioxide flow rate was 500  $\text{cm}^3/\text{min}$ . The activation periods ranged from 6 to 19 h. The samples were gradually cooled to room temperature under carbon dioxide after the activation period.

Fig. 2 shows a typical process for producing binders-less activated carbon pellets compared with the traditional process for activated carbon pellets.

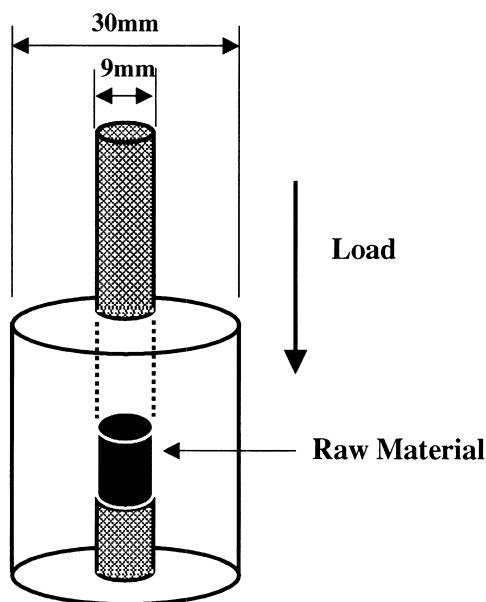


Fig. 1. Schematic illustration of the dice used for briquetting.

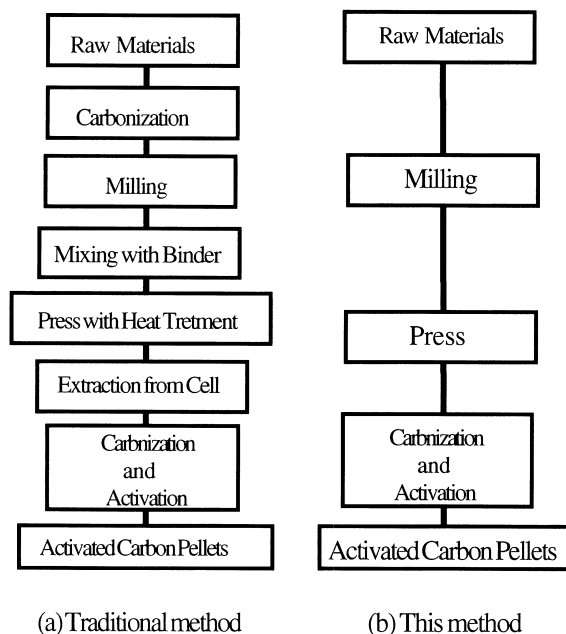


Fig. 2. The methods of preparing the activated carbon pellets.

### 2.2. Characterizations

The surface morphologies of activated carbon pellets and powder were examined by scanning electron microscope (Hitachi Co. Ltd., Ibaraki, Japan S-2380 N). The true density of all the samples were measured using a helium pycnometer (AccuPyc, Model 1330, Shimadzu Corporation, Tokyo, Japan) after degassing 473 K. The true density of a nonporous graphite used as reference was 2.3  $\text{g}/\text{cm}^3$ . The bulk densities of all the samples were determined by the weight of the dried activated carbon pellet and its geometrical volume. The destruction pressure was evaluated using the compressive fracture test. The load was applied to both end faces of the pellet. Nitrogen isotherms were determined at 77 K using a micromeritics ASAP 2400 instrument after degassing at 383 K. The nitrogen isotherms were fitted to both  $t$ -plot equations for the determination of the micropore volume and the BET equation for the relative surface area. The total pore volumes were determined from a point on the isotherm at a relative pressure above 0.98. The average pore diameter, ( $d$  in nm), was calculated by the following equation:  $d = (4000 \times V_{\text{total}})/S_{\text{BET}}$  where  $V_{\text{total}}$  and  $S_{\text{BET}}$  are the total pore volume and BET surface area, respectively.

Methane adsorption isotherms at 303 K for all samples were measured up to 0.86 MPa by a gravimetric method (Bel Japan, Inc., Osaka, Japan). The methane storage performances for pressures up to 10.0 MPa were evaluated volumetrically at 298 K by the underwater collection method. The experimental set-up is shown schematically in Fig. 3. The cell volume was 10.0  $\text{cm}^3$ . All samples were

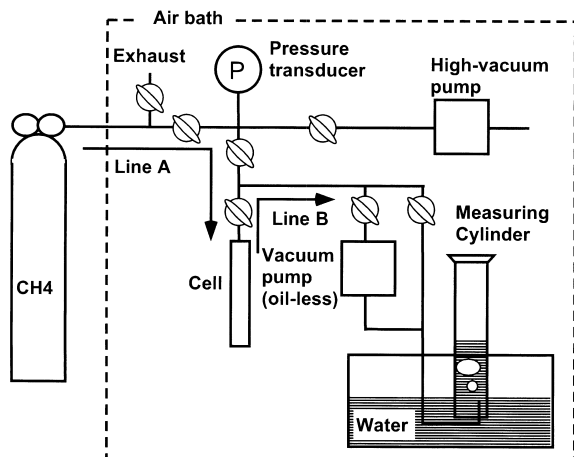


Fig. 3. Experimental set-up for the measurements of  $\text{CH}_4$  adsorptions up to pressures of 10.0 MPa.

previously degassed at 423 K for 5 h with a high vacuum pump. In the case of charging methane, the line A was used. The equilibrium pressure was measured when a constant charge pressure of methane was maintained for 20 min. The collections of storage gas were taken after the gas line has been evacuated by the high vacuum pump except cell. The line B was used for collection of storage methane. The oil-less vacuum pump was employed for the collection of storage methane gas under atmospheric pressure. The total volume was evaluated with a measuring cylinder. The cell was heated by an electric heater at 353 K. The collected gas was checked by gas chromatography and was solely methane without any other gas. The efficiency of methane storage,  $V/V_0$ , was calculated by following the equation:

$$V/V_0 = [V_a - (V_{\text{cell}} - V_{\text{pellet}}) \times \text{Pa}/Z]/V_{\text{pellet}}$$

where  $V_a$ ,  $V_{\text{cell}}$ ,  $V_{\text{pellet}}$ , Pa and Z are the total volume of collected gas at 298 K, cell volume, activated carbon volume, the equilibrium pressure and Z factor at 298 K, respectively. The number of measurements was four at each equilibrium pressure.

### 3. Results and discussion

#### 3.1. Activated carbon pellets

The photograph of activated carbon pellets and raw material pellet is shown in Fig. 4. The raw material pellets prepared at a pressure  $P=98.1$  MPa was 0.9 cm in diameter and 1.5 cm in thickness. After 6 h of activation, pellet size decreased to 0.6 cm in diameter and 0.7 cm in thickness. The bulk density also decreased from 1.30 to

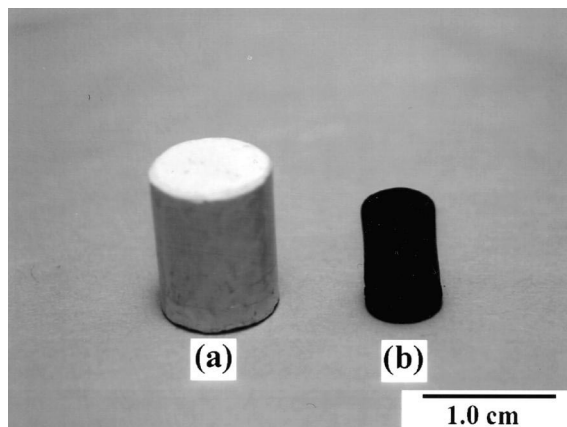


Fig. 4. Photo image of the raw material (a) and activated carbon pellet (b).

0.99  $\text{g}/\text{cm}^3$ . The shape of the activated carbon pellets was maintained as columnar.

Table 1 shows the property of activated carbon pellets. The yield and bulk density of the activated carbon pellets were increased with higher compression pressures of the raw material under the same heat-treatment conditions. Inversely, if the activation period was increased under the same treatment temperature, the yield and bulk density decreased. However, the bulk density of sample 6, which has lower yield compared with the activated carbon powder (sample 1), was 0.56  $\text{g}/\text{cm}^3$ . It has a 2.3 times higher bulk density than that of activated carbon powder. The true density of the carbon pellet does not depend on the compression pressure of the raw material and heat-treatment period. The destructive pressure was only measured for sample 4 and was 4.3 MPa, which was averaged over ten samples.

This new preparation of binder-less activated carbon pellets is useful for easily reducing the length of the process as shown in Fig. 2, and also it controls the bulk density by changing the compression pressure of the raw material.

Fig. 5a and b shows SEM images of surface morphology of activated carbon powder (sample 1) and activated carbon pellets (sample 4), respectively. The cellulose domains did not bind together and maintain the morphology after activation in both samples. The carbonized cellulose microcrystals are highly packed in sample 4.

Natural materials such as coconut shell, peach stone, and coffee beans were used as the raw materials in order to evaluate the possibility of this method. Each material was crushed to 300  $\mu\text{m}$  and washed with boiling water for the extraction of soluble matter. The preparation conditions were the same as for sample 3. Activated carbon pellets can be made from all these raw materials. The activated carbon pellet bulk densities of coconut shells, peach stones, and coffee beans were 0.60, 0.79, and 0.88  $\text{g}/\text{cm}^3$ ,

Table 1  
Property of activated carbon pellets from cellulose microcrystals<sup>a</sup>

Sample number	Compression pressure (t/cm <sup>2</sup> )	Yield (%)	Bulk density (g/cm <sup>3</sup> )	True density (g/cm <sup>3</sup> )	Destructive pressure (MPa)	Activation time (h)
1	0	10.0	0.24	1.9	–	6.0
2	0.25	11.2	0.61	1.9	–	6.0
3	0.50	13.0	0.72	1.9	–	6.0
4	1.00	13.7	0.99	1.9	4.3	6.0
5	1.00	10.2	0.60	1.9	–	9.5
6	1.00	8.0	0.56	1.9	–	19.0

<sup>a</sup> Carbonization temperature and time were 800°C and 6 h, respectively. Activation temperature was 900°C.

respectively. The porous texture characterizations for these samples are under investigation.

### 3.2. Porous texture

Fig. 6 presents the nitrogen adsorption isotherms. It can be observed that all samples have Type I isotherms characteristic of microporous materials. The degree of

activation for these carbonaceous materials is high and the micropore volumes obtained are large. Table 2 shows the property of activated carbon pellets. The pore volume and BET surface area decreased with an increase in the compression pressure of the raw materials under the same heat-treatment conditions. The relationship between the compression pressure and the pore volume is nonlinear and the change of porous texture is saturated at  $P=49.0$  MPa. Thus, the higher the compression pressure of the raw material, the more difficult it is to increase the activation efficiency under the same heat-treatment conditions. In fact, the total pore volume, the micropore volume, and the relative surface area increased at longer activation periods as shown in Table 2. In contrast to the consequence of pore

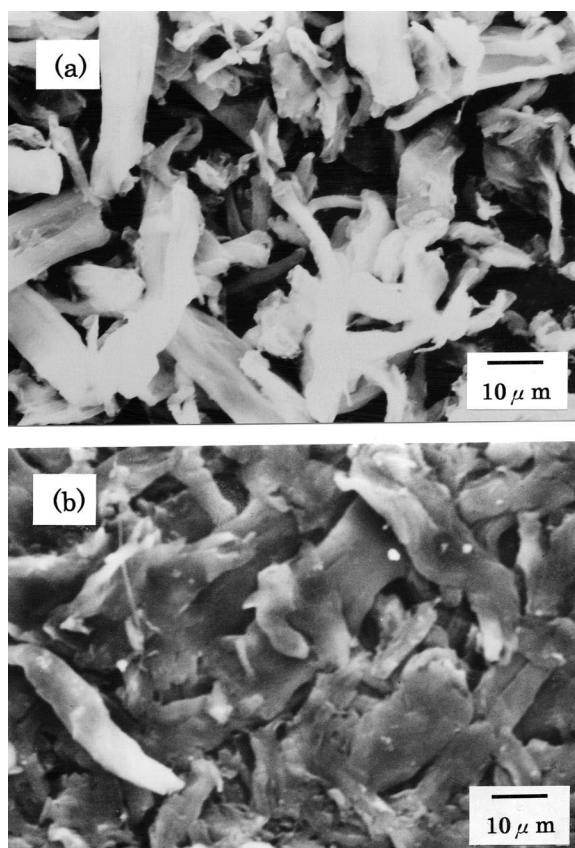


Fig. 5. Scanning electron micrographs of activated carbon. (a) Activated carbon powder and (b) activated carbon pellet.

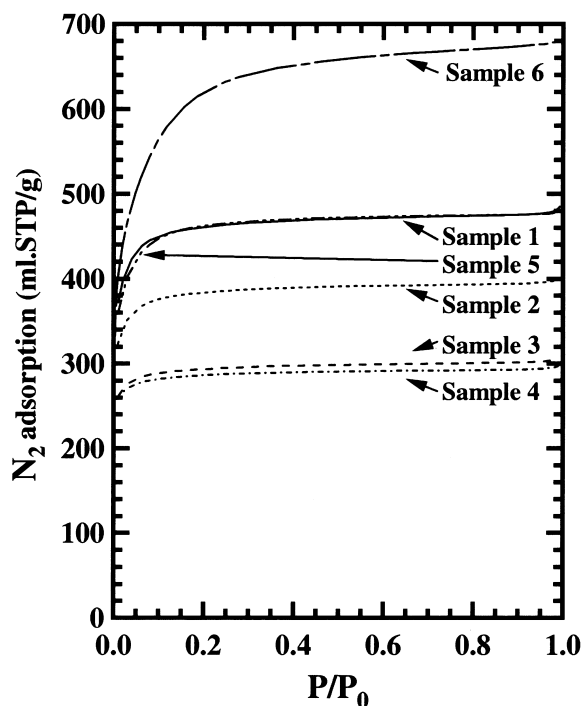


Fig. 6. The adsorption isotherms of N<sub>2</sub> on activated carbon samples at 77 K.

Table 2  
Pore structures of activated carbon pellets from cellulose microcrystals

Sample number	BET surface area (m <sup>2</sup> /g)	Total pore volume (cm <sup>3</sup> /g)	Micro pore volume (cm <sup>3</sup> /g)	Micro pore volume (cm <sup>3</sup> /g)	Average pore diameter (nm)
1	1790	0.74	0.70	0.17	1.6
2	1480	0.62	0.58	0.35	1.6
3	1130	0.47	0.45	0.32	1.6
4	1100	0.46	0.44	0.44	1.6
5	1780	0.74	0.71	0.44	1.6
6	2340	1.05	0.98	0.55	1.7

volume and BET surface area, the average pore diameter was independent of the compression pressure. In this paper, the average pore diameter was calculated under cylindrical assumption because all the samples had an amorphous structure. However, as for the average pore diameter a close examination has to be made.

The micropore volume (cm<sup>3</sup>/g) is a very important parameter to methane adsorption on a mass basis. For the storage system, however, the adsorption must be evaluated on a volume basis because voids were formed between the particles of activation carbon as a result of the packing. Thus, the micropore volume (cm<sup>3</sup>/cm<sup>3</sup>) that was calculated from micropore volume (cm<sup>3</sup>/g) times bulk density (g/cm<sup>3</sup>) is shown in Table 2.

The micropore volume (cm<sup>3</sup>/cm<sup>3</sup>) almost increased with increased compression pressure of the raw material.

Fig. 7 illustrates the changes that occur in total pore volume and BET surface area with activation expressed as the percent of weight yield from the raw material. These show the same trend, that is, as activation increases, increases are observed in the total pore volume and BET surface area. In this figure, triangles and circles indicate the value of the powder and pellets, respectively. A linear

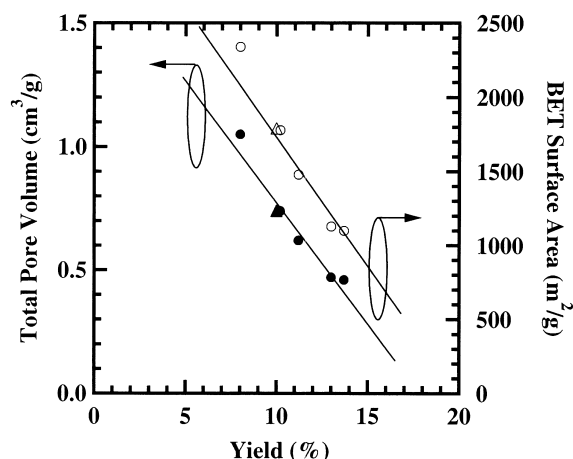


Fig. 7. Total pore volume and BET surface area with percent yield. Solid and open triangles: powder samples; solid and open circles: pellet samples.

relationship is observed between the yield and porous properties. Thus, the porous texture depends on the degree of activation efficiency.

The ratio of micropore volume to the total pore volume was over 93% in all samples. This is an advantage for their application in methane storage.

### 3.3. Methane storage

The methane isotherms, expressed in milligrams of methane per gram of carbon, at 303 K up to pressures of 0.85 MPa are shown in Fig. 8. All the adsorption isotherms are Langmuirian, indicating the presence of micropores in which supercritical methane can be filled. In this plot it can be observed that the methane capacities of the pellets were

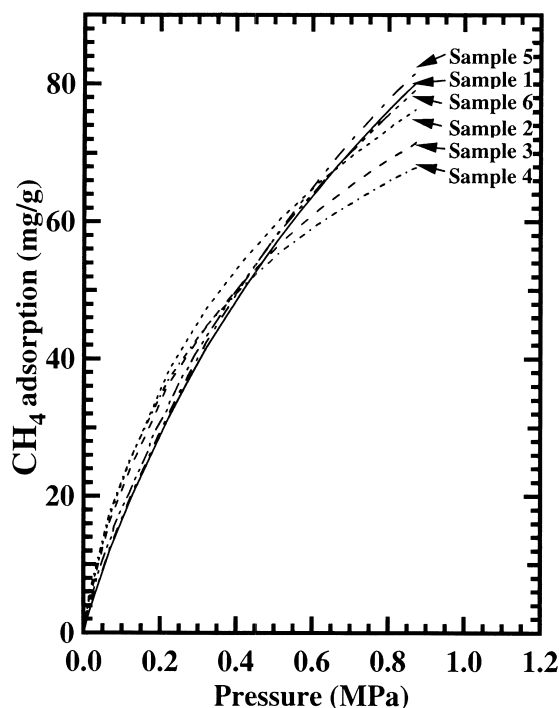


Fig. 8. The adsorption isotherms of CH<sub>4</sub> on activated carbon samples at 303 K.

greater than that of the powder at low pressures (<0.4 MPa), indicating different micropore size distributions.

The stored methane capacity of the activated carbon is shown in Fig. 9. The sensitivity of the underwater collection method is high, since the measurements of CNG agreed fairly with the calculation of CNG. The methane storage capacity increased with increasing of the pore ratio of sample volume. The pellet samples used in this study have large volumetric methane adsorption capacities because of their high micropore volume and high bulk density. The maximum values reached 164  $V/V_0$  at 3.5 MPa in the case of sample 6.

Fig. 10 illustrates the changes of  $V/V_0$  at 3.5 MPa with the micropore volume ( $\text{cm}^3/\text{cm}^3$ ). The open circles show that  $V$  was the amount of storage methane gas in the adsorbent volume, which included voids. In this case,  $V/V_0$  was not a liner relationship to micropore volume because of the compressed gas, which was stored in the voids, was involved with  $V$ . Closed circles represent that  $V$  was the amount of storage methane in the micropore region. The amount of storage methane in the micropore region ( $V_m$ ) was calculated by the following equation:

$$V_m = V_a - \{[(V_{\text{total}} - V_{\text{micro}}) + V_{\text{void}}] \times \text{Pa}/Z\}$$

where  $V_a$ ,  $V_{\text{total}}$ ,  $V_{\text{micro}}$ ,  $V_{\text{void}}$ ,  $\text{Pa}$  and  $Z$  are the total volume

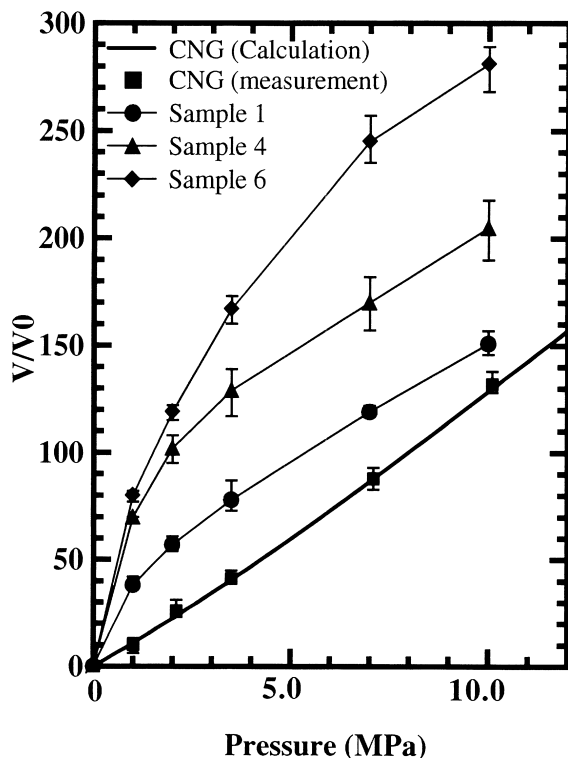


Fig. 9. Changes of  $\text{CH}_4$  storage efficiency ( $V/V_0$ ) in the same volume of activated carbon with compression pressure.

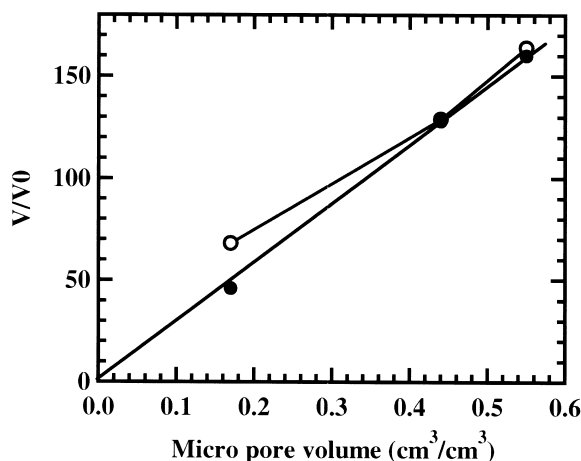


Fig. 10. Changes of  $\text{CH}_4$  storage efficiency ( $V/V_0$ ) at 3.5 MPa with micropore volume ( $\text{cm}^3/\text{cm}^3$ ). Open circles:  $V$  was the amount of storage methane gas in the adsorbent volume, which included the voids. Closed circles:  $V$  was the amount of storage methane in the micropore region.

of collected gas in the adsorbent volume at 3.5 MPa, total pore volume, micropore volume, void volume, the equilibrium pressure (3.5 MPa) and  $Z$  factor at 3.5 MPa, respectively. In this case, the relationship between  $V/V_0$  and the micropore volume was not linear. The  $V/V_0$  increased with an increase in the micropore volume.

As a result, it is important to increase the micropore volume ( $\text{cm}^3/\text{cm}^3$ ) and to decrease the voids to improve the efficiency of methane storage.

#### 4. Conclusion

A method was presented to prepare activated carbon pellets from cellulose microcrystals as the raw material without any binders. The bulk density of the carbon pellets was controlled easily in the range of 0.56–0.99  $\text{g}/\text{cm}^3$  by changing the compression pressure of the raw materials and the heat-treatment conditions. The bulk density of the pellet sample, which has maximum pore volume in this experiment, was 0.56  $\text{g}/\text{cm}^3$ . It is 2.3 times higher than that of activated carbon powder. The total methane storage capacity at 298 K reached 164  $\text{cm}^3$  in 1  $\text{cm}^3$  volume of activated carbon pellets at 3.5 MPa. This value clearly surpasses the 150  $V/V_0$  values, which is considered useful from a commercial point of view.

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