1 Simple fabrication of molecular sieving carbon for biogas upgrading via a
2 temperature controlled carbonization of *Phyllostachys pubescens*

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1 **Abstract**

2 In this study, molecular sieving carbons (MSCs) for biogas upgrading were successfully
3 fabricated by a simple temperature controlled carbonization of moso bamboo (*Phyllostachys*
4 *pubescens*) without energy consuming steps (i.e. char activation and pore modification). As
5 the carbonization temperature increased from 600 to 900 °C, the specific surface area of
6 bamboo charcoals increased and the pore size distribution of bamboo charcoal became
7 narrower and closer to the dimensions of CH₄ (0.38 nm). Bamboo charcoals had a more
8 disordered carbon stacking structure than commercial MSC and contained more surface
9 oxides, which contribute to greater surface reactivity than commercial activated carbon.
10 Bamboo charcoal carbonized at 900 °C had the highest CO₂ adsorption capacity (121.6 g
11 kg⁻¹), even higher than commercial MSC (102.88 g kg⁻¹). Despite the poor kinetic CO₂
12 adsorption properties of bamboo charcoals compared to commercial MSC, synthetic biogas
13 (60% CH₄ + 40% CO₂) was successfully upgraded to concentrated CH₄ (>90%) by small-scale
14 pressure swing adsorption using bamboo charcoal. It is expected that bamboo charcoals can
15 contribute to sustainable small-scale biogas upgrading.

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17 Keywords: *Phyllostachys pubescens*, biogas upgrading, molecular sieving carbon,
18 carbonization

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1. Introduction

Biogas has received great attention as a source of renewable natural gas (RNG) for many sectors (e.g. power generation and vehicle fuel). Many countries are actively promoting “Biogas” not only as a secure energy source but also for its environmental benefits: the indirect reduction of CO₂ emissions from fossil fuel burning and prevention of direct CH₄ emission by biogas burning. Biogas is produced by anaerobic digestion of organic wastes such as municipal solid waste (MSW), wastewater sludge, animal waste (manure), and food waste. The facilities for digestion, purification (upgrading) and storage are often installed *in situ* at large scale waste treatment facilities (located away from residential areas). However, biogas, as a traditional energy source, is still a familiar and essential part of daily life in many developing countries.

Although the composition of biogas varies according to its feedstock [1], it can be roughly estimated that biogas contains about 45–75% v/v methane [2]. The main reason of the biogas upgrading is to allow biogas to be compressed for storage since carbon dioxide prevents biogas being compressed easily. The energy content of biogas (as a lower heating value) ranges from 15.2–21.8 MJ Nm³ [3], which is not as good as that of liquid natural gas (31.2–49.9 MJ Nm³; [3]), and therefore the upgrading of raw biogas is also essential to use as a transport fuel. In farm houses across many developing countries, direct burning without any treatment (sometimes after a simple desulfurization) is still common, since upgrading biogas in the farm house is still an economic burden. Therefore, development of a simple and affordable biogas upgrading system targeting household biogas digesters used in developing countries is the motivation of this study.

Biogas upgrading technologies can be divided into four categories [1, 2]: i) absorption (scrubbing), ii) adsorption, iii) membrane and iv) cryogenic separation. Although each

1 technique has advantages and disadvantages, the adsorption method is more favorable for
2 scale-down and process simplification.

3 Among the adsorptive processes, pressure swing adsorption (PSA) using specific activated
4 carbons which have a molecular sieving ability, so-called molecular sieving carbons (MSCs),
5 is often adopted for gas separation including biogas upgrading [1, 2]. MSCs are generally
6 fabricated in three steps: i) carbonization of biomass, ii) char activation and iii) pore
7 modification [4]. As previously reported, char activation and pore modification are energy
8 consuming processes, and pore modification requires very sophisticated techniques such as
9 chemical vapor deposition [5], which makes conventional MSCs unsustainable for household
10 biogas upgrading systems. There is a clear need for sustainable MSC fabrication methods and
11 in this study, a new strategy is proposed: MSC fabrication by carbonization of biomass
12 without activation and pore modification.

13 Activation and pore modification are very important steps for making tailored micropores.
14 Activation opens the pore by decomposition of tarry substances produced during
15 carbonization and pore modification controls the size of the pore entrance ($\text{\AA}$, 10^{-1} nm scale)
16 to enable molecular sieving [4]. Nevertheless, if those steps are omitted, the starting material
17 for carbonization may become an important factor to control the formation of micropores.

18 Characterization of bamboo charcoals has previously suggested that ultra-micropores may
19 be controlled by controlling of carbonization temperature [6, 7]. Bamboos are a sustainable
20 starting material for developing Asian countries since bamboos are one of the fastest-growing
21 plants [8, 9] and more than 60% of the world's bamboo resources are located in Asia [10].
22 Recently, bamboo charcoal has been used to prepare not only activated carbon for the
23 removal of water vapor [9] and pollutants (organic/ inorganic) [11–14] but also functional
24 composites [15, 16], fabrics [17], and photocatalysts [18] because of its high reactivity

1 derived from its porous properties. However, there has been no report on the utilization of
2 bamboo charcoal as an MSC for gas separation as far as the authors know.

3 To demonstrate bamboo charcoal's effectiveness as an MSC for biogas separation, the
4 authors chose *Phyllostachys pubescens* (known as moso bamboo) as a starting material and
5 characterized the bamboo charcoals carbonized at various temperatures. The applicability of
6 bamboo charcoal to small-scale biogas upgrading systems was also assessed by PSA testing.

7

8 **2. Materials and Methods**

9 **2.1 Preparation of bamboo charcoals**

10 Japanese moso bamboo (*Phyllostachys pubescens*) that was 3–4 years old was obtained
11 from Kanazawa, Ishikawa prefecture, Japan. After harvesting, the bamboo was air-dried in a
12 dry space until further use. It was coarsely cut into irregularly sized pieces and dried for 2
13 days in an oven at 110 °C before carbonization and then manually chopped into 10 cm long
14 chips. 10 g of bamboo chips laid on the quartz crucible boat was placed in the middle of a
15 tubular electric furnace equipped with a temperature controller. The bamboo chips in the
16 furnace were carbonized at different temperatures (300–1000 °C) under a N₂ stream of 300
17 mL min⁻¹. The heating rate was 15 °C min⁻¹ the carbonization temperature was maintained for
18 1 h. After carbonization, the bamboo charcoal was cooled down to room temperature in the
19 furnace with the N₂ stream. The bamboo charcoal samples were termed BC with their
20 carbonization temperatures, for example bamboo charcoal carbonized at 900 °C is BC 900.
21 The carbonization yield (*Y*) was calculated by the following equation:

$$22 \quad Y (\%) = \frac{W}{W_0} \times 100 \quad , (1)$$

23 where *W*₀ and *W* are the dry weight of sample before and after carbonization, respectively.

1 Before further experiments, bamboo charcoals were crushed to 600–840 µm sized particles
2 and stored in a desiccator.

3

4 **2.2 Specific surface area and effective pore size distribution of bamboo charcoals**

5 Specific surface area (SSA) was measured by methanol (MeOH) vapor adsorption. Gaseous
6 phase adsorption was performed with the gravimetric adsorption apparatus [19]. The
7 magnetic suspension balance of the gravimetric system was composed of quartz spring and
8 displacement sensor (weight resolution: 0.1 mg). Bamboo charcoal (0.1 g) was placed in the
9 sample basket and conditioned at 120 °C under vacuum before methanol adsorption. To
10 obtain the adsorption isotherm of methanol the time course of methanol vapor pressure and
11 the amount of methanol adsorbed onto bamboo charcoals at room temperature were
12 monitored simultaneously as the vapor pressure increased sequentially.
13 Methanol adsorption data in the range where the monolayer is saturated with adsorbate (P/P_0
14 =0.05–0.35 corresponding to $q/q_m=0.1–1.5$) were interpreted by the following BET
15 (Brunauer-Emmett-Teller) equation [20]:

$$16 \quad q = \frac{b q_m P}{(P_0 - P)(1 + (b - 1) \frac{P}{P_0})}, \quad (2)$$

17 where, q , q_m , b , P and P_0 are the amount of methanol adsorbed onto the unit adsorbent (g g^{-1})
18 ¹), the monolayer saturation amounts of adsorbed methanol onto the unit adsorbent (g g^{-1}),
19 adsorption equilibrium constant (unit less), the equilibrium methanol vapor pressure (mmHg)
20 and the saturation methanol vapor pressure of pure methanol at a given temperature (mmHg),
21 respectively.

22 The specific surface areas (A_s) of bamboo charcoals were calculated by the following
23 equation:

$$24 \quad A_s = \frac{q_m N a_m}{M}, \quad (3)$$

where N , a_m and M are *Avogadro's* number (mol^{-1}), the occupied surface area of one molecule of methanol ($0.219 \times 10^{-18} \text{ m}^2$), and the molecular weight of methanol (g mol^{-1}), respectively.

A molecular probe method was used to indirectly measure the pore size distribution. Probe molecules and their dimensions were: H_2O (0.28 nm), C_6H_6 (0.32 nm), CH_3OH (0.38 nm), $\text{C}_2\text{H}_5\text{OH}$ (0.4 nm), CHCl_3 (0.46 nm), $(\text{CH}_2)_6$ (0.51 nm) and CCl_4 (0.56 nm). The probe molecules are adsorbed onto adsorbents at its saturated vapor pressure. Gas phase adsorption experiments using the above probe molecules on bamboo charcoals were performed with the gravimetric adsorption apparatus mentioned above. For comparison, pore size distributions of MSC used for biogas separation in Yamada biomass town in Chiba prefecture, Japan, here termed “MSC-B” and MSC 4A/5A (Takeda), were also determined in the same way.

2.3 Structural analyses of bamboo charcoals

X-ray diffraction (XRD) was performed with an RINT- 2000 diffractometer from Rigaku Corporation (λ : 0.15418 nm ($\text{CuK}\alpha$), 40 kV and 40 mA) at a scanning rate of $1.2^\circ (2\theta) \text{ min}^{-1}$ over the range of $5\text{--}65^\circ (2\theta)$ to examine the changes in the carbon structure of bamboo charcoals according to carbonization temperature. X-ray photoelectron spectroscopy (XPS) of bamboo charcoals was performed with a Quantera SXM from ULVAC-PHI INC. ($\text{AlK}\alpha$ radiation) with Smartsoft-XPS data handling software. The amount of surface oxides on bamboo charcoals were analyzed by temperature programmed desorption (TPD) to estimate the surface reactivity of bamboo charcoals. The experimental procedure has been previously described [21].

2.4 CH_4 and CO_2 adsorption

To demonstrate the effectiveness of bamboo charcoal as an MSC for biogas separation, the adsorption properties of CH₄ and CO₂ (major components of biogas) onto bamboo charcoals were examined. Single component adsorption isotherms were obtained by the gravimetric adsorption method mentioned above (section 2.2). Before the adsorption experiment, bamboo charcoals were conditioned at 120 °C under vacuum. High purity CH₄ and CO₂ were used. Adsorption equilibrium data were interpreted by the Langmuir equation:

$$q = \frac{q_{sat}K\left(\frac{P}{P_{atm}}\right)}{1+K\left(\frac{P}{P_{atm}}\right)}, \quad (4)$$

where q , q_{sat} , K and $\frac{P}{P_{atm}}$ are the amount of adsorbed adsorbate (CH₄ or CO₂) per unit adsorbent (g kg⁻¹), the monolayer saturation amounts of adsorbed adsorbate per unit adsorbent (g kg⁻¹), the Langmuir equilibrium constant (-) and the equilibrium CH₄ or CO₂ pressure relative to atmospheric pressure.

Single component breakthrough curves were examined by the adsorption column test. Bamboo charcoals were packed in a cylindrical adsorption column (ø 11 mm × 176 mm) with an adsorbent density of 0.24–0.265 kg L⁻¹. Before the experiments, bamboo charcoals in the column were conditioned at 120 °C for 3–4 h in a He stream. After cooling down to room temperature in the He stream, 10% v/v CH₄ or CO₂ prepared by mixing with a carrier gas (He) was fed into the adsorption column with a flow rate of 15 mL min⁻¹. The flow rate and CH₄ or CO₂ concentration of the gas stream from the adsorption column were monitored with a digital flow meter and quadrupole mass spectrometer (PrismaTM, Pfeiffer Vacuum) simultaneously.

21

2.5 Pressure swing adsorption

Figure 1 shows the two-bed vacuum PSA apparatus (3L for a single bed) and its periodic cycle. All gas lines and joints were made by *Swagelok*. The purge step was carried out with a

1 vacuum pump (DTU-20, ULVAC KIKO, Inc., Japan). The valve sequence was controlled by
 2 a programmable logic controller (KV-3000, Keyence) with KV Studio operation program
 3 (Ver. 5.5). Synthetic biogas (60% v/v CH₄ and 40% v/v CO₂) was used as a feed for PSA.
 4 The feed gas flow rate was controlled by a digital gas flow controller (3200 series, KOFLOC).
 5 The flow rates and concentrations of CH₄ and CO₂ in the product gas were monitored
 6 simultaneously and in the same way as the single component breakthrough curve mentioned
 7 above. The performance of PSA for 10 cycles was examined by purity and recovery defined
 8 as:

9
$$\text{Purity (\%)} = \frac{\int_0^t Q_T C_T dt}{\int_0^t Q_T dt} \times 100 \quad (5)$$

10
$$\text{Recovery (\%)} = \frac{\int_0^t Q_T C_T dt}{\int_0^t Q_F C_F dt} \times 100 \quad (6)$$

11 where Q_T and Q_F are the flow rates (L min⁻¹) of the top product gas and feed gas, respectively.
 12 C_T and C_F stand for the CH₄ mole fraction (i.e. volume fraction) of top product gas and feed
 13 gas, respectively.

Figure 1 Two-bed vacuum PSA apparatus and its periodic cycle with valve sequence.

3. Results and discussion

3.1 SSA and pore size distribution of bamboo charcoals depending on carbonization

temperature

Carbonization of biomass is the thermal conversion of organic matter to carbon (char), which is affected by many factors such as heating rate, inert gas (N₂) flow rate, reaction time, temperature and starting materials [4, 22, 23]. Although the heating rate is an important factor for the distribution of product phases (char, oils and gases), the heating rate was fixed to 15 °C min⁻¹ in this study because relatively slow heating rates (5 – 25 °C min⁻¹) have previously been adopted for char production [4]. Likewise, the carbonization times (30 min – 2 h) and inert gas flow rates (100 – 500 mL min⁻¹) were chosen based on previous studies [23]. The carbonization temperature and starting materials are the most important factors in determining the structure and yield of char [24]. This is because cleavage and rearrangement of starting materials during carbonization is strongly affected by the amount of energy in the system [23]. Therefore, the authors focused on the carbonization temperature as the crucial factor in determining the porous structure of bamboo charcoals.

Figure 2(a) shows the methanol adsorption isotherms of bamboo charcoals carbonized at different temperatures. The specific surface areas (SSA) of bamboo charcoals shown in Fig. 2 (b) were calculated by eq. (2) and (3) and the parameters estimated are listed in Table 1. The SSA increased with the carbonization temperature until 900 °C, and then decreased beyond 900 °C. A similar trend for the same type of bamboo charcoal (though the inflection temperature was different) was found previously [11]. Previous studies with various starting materials showed that the surface area and micropore volume reached a maximum value between 700 and 800 °C (or 900°C) but declined beyond those temperatures [25, 26]. Although the SSA was strongly affected by temperature changes, carbonization yields (Y, %), shown in the inner panel of Fig. 2(b), were insensitive to carbonization temperature. This is

1 because 50–80% of the volatiles (i.e. holocellulose) in the materials were given off when the
 2 carbonization temperature reached 500 °C but only an additional 4–10% of volatiles were
 3 given off by increasing the temperature to 900 °C [23, 27]. Considering the significant
 4 changes in SSA with temperature without large variations in yield, it can be expected that the
 5 main processes that strongly affect the micropore structure of charcoal during carbonization
 6 were molecular rearrangement, thermal polymerization and aromatic condensation. This will
 7 be investigated further with the pore size distributions of bamboo charcoals shown in Fig. 3.

9 Figure 2 (a) Methanol adsorption isotherms and (b) specific surface area of bamboo charcoals
 10 carbonized at different temperatures (inner panel: carbonization yield).

13 Table 1. The adsorption parameters for bamboo charcoals and MSC

Samples	Methanol (BET)		CO ₂		CH ₄	
	q_m	b	q_{sat}	K	q_{sat}	K
BC 600	0.09	77.323	99.6 (2.26) ^a	5.38 (0.13) ^b	-	-
BC 800	0.102	33.194	118.9 (2.7) ^a	3.90 (0.1) ^b	10.18	1.35
BC 900	0.12	78.339	121.6 (2.76) ^a	5.26 (0.13) ^b	4.97	2.92
BC 1000	0.07	14.475	71.05 (1.61) ^a	2.19 (0.05) ^b	4.88	1.41
MSC-B	-	-	102.88 (2.34) ^a	3.73 (0.09) ^b	4.57	27.52

14 a: mol kg⁻¹, b: m³ mol⁻¹

1

2 In contrast to activated carbons which have a “Trimodal shape” of pore size distribution
 3 over a wide range, MSCs have a very narrow pore distribution in the ultra-micropore range
 4 (0.3–0.7 nm) [28]. To examine the potential of bamboo charcoals as MSCs, ultra-micropores
 5 should be evaluated in a reliable way. Although N₂ adsorption at 77 K is the most common
 6 method to determine the pore size distribution of various adsorbents, it is inadequate when
 7 the pore size is close to the molecular size of adsorbates [20]. Therefore, the ultra-micropores
 8 of bamboo charcoals were assessed by the molecular probe method since it is the best
 9 approach to measure the ultra-micropores in MSCs [28].

10 **Figure 3(a)** shows the pore volumes of bamboo charcoals measured by probe molecules
 11 with different dimensions. The data were interpreted by a reverse cumulative distribution
 12 function of the log-normal distribution as below:

$$13 \quad V = \left\{ 1 - \frac{1}{2} \left[1 + \operatorname{erf} \left(\frac{\ln x - \mu}{\sqrt{2}\sigma} \right) \right] \right\} \times V_0, \quad (7)$$

14 where V_0 , V , μ and σ are the total accumulated pore volume per unit adsorbent (mL g⁻¹), the
 15 accumulated pore volume per unit adsorbent (mL g⁻¹) at pore size x (Å, 10⁻¹ nm), μ is the
 16 natural logarithm of the median (i.e. e^μ = median) and σ is the standard deviation.

17 The differential changes in pore volume according to pore size (i.e. pore size distribution
 18 curve) based on **Fig. 3(a)** are shown in **Fig. 3(b)**. The same analyses were carried out with
 19 commercial MSCs (4A and 5A) and MSC-B, which has been used for biogas separation. For
 20 BC 1000, reasonable adsorption data with various probe molecules could not be obtained
 21 because the size and shape of the ultra-micropores' mouth was probably no longer valid for
 22 the molecular probe method, assuming that MSC usually contains slit-like pores of the order
 23 of 0.1 nm [29].

1 As shown in Fig. 3(a), the total volume of ultra-micropores of the bamboo charcoals were
 2 not much different from those of the commercial MSCs. The carbonization temperature does
 3 not seem to have much effect on the total volume of ultra-micropores of bamboo charcoals
 4 but does affect the pore size distributions significantly. This phenomenon was also found
 5 with commercial bamboo charcoals in the authors' previous study [7]. As shown in Fig. 3(b),
 6 the pore size distribution of bamboo charcoal became narrower and closer to the dimensions
 7 of CH₄ (0.38 nm) as the carbonization temperature increased to 900 °C. This implies that
 8 kinetic separation of CH₄ by molecular sieving is possible by controlling the carbonization
 9 temperature. Considering the difficulties in conventional pore modification processes, pore
 10 size control by merely controlling the carbonization temperature with bamboo as a “starting
 11 material” is advantageous and innovative.

12
 13 Figure 3 (a) Pore volumes of bamboo charcoals and MSCs measured by probe molecules
 14 with different dimensions. (b) Pore size distribution curve of bamboo charcoals and MSCs.
 15 (Å, 10⁻¹ nm)
 16

1 3.2 Structural and chemical properties of bamboo charcoals

2 In addition to the SSA and pore size distribution, further analyses were performed to
3 estimate the structural and chemical properties of bamboo charcoals. Figure 4(a) shows the
4 X-ray diffraction patterns of bamboo charcoals and other carbonaceous samples (MSC 5A
5 and graphite) for comparison. XRD analysis is a fundamental method for evaluating the
6 carbon stacking structure such as the internal spacing (d_{002}) and the crystallite size (L_{100} and
7 L_{002}) [30]. The black-filled area (Fig. 4a) corresponds to the graphite XRD pattern measured
8 previously [31]. For BC 300, the carbon stacking structure was not developed probably due to
9 poor aromatic condensation and insufficient expulsion of volatiles at the low carbonization
10 temperature. Compared to graphite, BC 850 had a lower diffraction angle and higher full
11 width at half maximum (FWHM) of the (002) peak and a broader (100) peak which suggests
12 randomly oriented stacking of the graphene layers, so-called turbostratic carbon [31]. The
13 carbon stacking structure in bamboo charcoal could not be developed effectively during
14 carbonization even at high temperatures. Therefore, bamboo charcoals have more disordered
15 stacking structures than commercial MSC (MSC 5A).

16

Figure 4 (a) X-ray diffraction patterns of bamboo charcoals and other carbonaceous samples. (b) XPS measurements of the C1s and O1s peaks of bamboo charcoals and activated carbon.

The elemental properties (especially oxygen in the surface oxides) of bamboo charcoals that contribute to surface reactivity (e.g. wetting and adsorption behavior) were examined. XPS peak size can be used to estimate the relative surface concentration of the various species [32]. Fig. 4(b) shows the C1s and O1s peaks of bamboo charcoals. FILTRASORB 400 (F 400, Calgon Carbon), a granular activated carbon, was also measured for comparison. Considering that bamboo charcoals contained more surface oxides than F 400, it can be presumed that bamboo charcoals are a hydrophilic adsorbent compared to activated carbon. Moreover, oxygen atoms were hardly removed from bamboo charcoals even when the carbonization temperature reached 1000 °C.

Additionally, the variation in the amount of surface oxides on bamboo charcoals according to air contact time was examined by TPD (Fig. 5). The amounts of CO and CO₂ released were monitored since surface oxides decompose to CO and CO₂ on heating to high

1 temperature [32]. Pine wood charcoal carbonized at 900 °C (WC 900) in the same way as BC
 2 900 and F 400 was also used for comparison.

3
 4 Figure 5 The amount of surface oxides on bamboo charcoals according to air contact time
 5 (inner panel: amount of surface oxides on bamboo charcoals carbonized at different
 6 temperatures after 7 days of air contact).
 7

8 Charcoal samples (bamboo and wood) were removed from the furnace after cooling down
 9 in the N₂ stream and simply placed in the open air at room temperature. F 400 was also
 10 placed in the open air without any treatment.

11 As shown in Fig. 5, the amount of oxides on BC 900 was slightly higher than that of F 400
 12 in the initial state (shown as “Not contacted”); however, wood charcoal (WC 900) had more
 13 oxides than the others. As reported previously [32], highly reactive sites on the carbon
 14 surface remain among the decomposed surface oxides during thermal treatment (i.e.
 15 carbonization) in a free-radical state. New surface oxides can be formed from the free-radical
 16 state by contact with oxygen in the air or water vapor after cooling down. Air contact resulted
 17 in a large increase in surface oxides on the carbon except for activated carbon (F 400). The
 18 amount of surface oxides is strongly related to the wettability of carbon, which leads to
 19 “deterioration” or “aging” [32]. Bamboo charcoal is much better than wood charcoal as an

adsorbent but it can deteriorate more easily than activated carbon. Furthermore, increasing the carbonization temperature reduced the surface oxides (Fig. 5 inner panel), although the effect was not particularly significant.

3.3 Single component (CO₂/CH₄) adsorption properties of bamboo charcoals

Figure 6(a) shows the single component adsorption isotherms of bamboo charcoals and MSC-B. As shown in Fig. 6(a) and Table 1, the CO₂ adsorption capacity (q_{sat}) of bamboo charcoals, except for BC 1000, was quite comparable to that of MSC-B. Previous studies have reported similar values; 2.35–2.62 mol kg⁻¹ for MSC produced by pitch activated carbon [33] and about 2.25 mol kg⁻¹ at 0.1 MPa for activated carbon [34]. The CO₂ adsorption capacity increased with the carbonization temperature up to 900 °C, but decreased significantly at 1000 °C. Compared to the CO₂ adsorption capacity, the CH₄ adsorption capacity of all samples was quite small and decreased as the carbonization temperature increased, although there was little variation between samples (see Table 1). Bamboo charcoals seem to highly selective CO₂ adsorbents.

Figure 6(b) shows the single component breakthrough curve for bamboo charcoals and MSC-B. The adsorption equilibrium of CH₄ in the column was reached quickly for BC 900 and MSC-B, though a tailing of CH₄ was present for BC 800. CH₄ breaks through the column very fast compared to CO₂ because the narrow pore mouth of the MSC micropores prevents diffusion of CH₄ into the MSC [35]. Considering the pore size distribution of BC 800, BC 900 and MSC-B shown in Fig. 3 (b), it can be estimated that the driving force of CO₂/CH₄ separation is derived not only from adsorption equilibrium but also from adsorption kinetics.

Figure 6 (a) Adsorption isotherms and (b) breakthrough curves of CO₂ and CH₄ for bamboo charcoals and MSC-B

From the kinetic viewpoint of CO₂/CH₄ separation, CO₂ diffusivity is very important factor affecting the product purity and recovery of the periodical biogas separation processes (i.e. PSA). The CO₂ adsorption rate in the packed column (CO₂ breakthrough curve) was interpreted as follows:

$$\text{Material balance in the column: } u \left(\frac{\partial c}{\partial z} \right) + \varepsilon \left(\frac{\partial c}{\partial t} \right) + \gamma \left(\frac{\partial q}{\partial t} \right) = 0, \quad (8)$$

$$\text{Pore diffusion control for spherical particles: } \frac{\partial q}{\partial t} = D_s \left(\frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right), \quad (9)$$

$$\text{Adsorption isotherm: } q = \frac{q_{sat} K c}{1 + K c}, \quad (10)$$

$$\text{Interface transport: } \frac{\partial q}{\partial t} = -D_s a_v \rho_s \left(\frac{\partial q}{\partial r} \right)_{r=r_0}, \quad (11)$$

$$a_v = \frac{3}{r_0} \frac{\gamma}{\rho_s}, \quad (12)$$

Initial and boundary conditions:

$$c(0, t) = c_0 ,$$

$$c(z, 0) = 0 ,$$

$$\left(\frac{\partial q}{\partial r}\right)_{r=0} = 0 \text{ and}$$

$$q(r, z, 0) = 0 ,$$

where c , z , q , t , r and r_0 are the concentration of CO₂ (mol m⁻³), the distance measured from the column inlet (m), the amount of CO₂ adsorbed (mol kg⁻¹), the time (s), the distance from the adsorbent solid center (m) and the radius of adsorbent (m), respectively. D_s , q_{sat} , K , a_v and ρ_s are the effective intra particle diffusivity (m² s⁻¹), the monolayer saturated adsorption amount (mol kg⁻¹), the Langmuir equilibrium constant (m³ mol⁻¹), the surface area per unit volume of the adsorbent (m² m⁻³) and the density of the adsorbent (kg m⁻³), respectively. u , ε and γ are the linear velocity in the column (m s⁻¹), the voidage of the adsorbent bed and the packing density of adsorbent in the column (kg m⁻³), respectively.

The linear velocity, u , in the column was assumed to be constant. Moreover, it was assumed that material transfer from the bulk state into particles was controlled by pore diffusion and that gas-solid film transfer resistance was negligible. Adsorption isotherms were obtained from Fig. 6(a). Calculations using the above equations were performed with Scilab software. Since “ r ”, the radius of diffusion, cannot be specified, the diffusion rate was described as “ $D_s r^{-2}$ ” in the calculations. Calculated data are shown as a solid line in Fig. 7. CO₂ breakthrough curves were well described by the above calculation, except for BC 900 probably because the ultra-micropores were very close to the dimensions of CO₂ (see Fig. 3b) which introduces a spectrum of CO₂ diffusion resistance, so that the breakthrough curve cannot be described by a single diffusion rate. Although this will not be discussed here in detail, the rate of CO₂ diffusion in bamboo charcoals, which is central to determining

1 separation performance, is sensitive to the precise formation of ultra-micropores depending
 2 on carbonization temperature.

3

4

5 Figure 7 CO₂ breakthrough curve analyses for bamboo charcoals and MSC-B. ($z=0.176\text{m}$,
 6 $u=0.00399\text{ m s}^{-1}$, $\square=0.4-0.5$, $c_0=4.07\text{ mol m}^{-3}$, $\gamma=244.9-264.7$)

7

8 3.4 Application of bamboo charcoal to PSA for biogas upgrading

9 The possibility of utilizing bamboo charcoals as molecular sieving carbon for biogas
 10 upgrading was outlined by the analysis above. To test this, bamboo charcoal was used in the
 11 pressure swing adsorption process. The operational scheme of a two-bed PSA is described in
 12 **Fig. 1**. The periodic cycle is composed of 4 steps; feed, blowdown, purge and
 13 repressurization. During the repressurization step, the low pressure bed was pressurized by
 14 the top product gas for 5 s.

1 **Figure 8(a)** shows the performance over 10 cycles with BC 900 according to different half
2 cycle times (i.e. time span of feed or purge step). As the half cycle time increased, the
3 recovery also increased but the purity decreased. Half cycle time, along with feed gas flow
4 rate, is one of the most important operational factors for the performance of PSA because it
5 affects the diffusivity of components (i.e. breakthrough time). At the given flow rate, 600 s
6 seems to be a sufficient half cycle time to obtain high purity as well as good recovery.
7 Increasing the feed gas flow rate up to nearly 5 L min⁻¹ at the fixed half cycle time (600 s)
8 enhanced the recovery while still maintaining over 90% CH₄ in the top product gas (**Fig. 8b**).
9 The PSA performance with MSC-B is also shown in **Fig. 8(b)**. Compared to bamboo charcoal,
10 PSA with MSC-B provided high purity and recovery that was stable at various conditions (i.e.
11 feed gas flow rate and half cycle time). Although bamboo charcoal was not effective for
12 biogas upgrading as much as MSC-B was, bamboo charcoals seem suitable for low capacity
13 biogas upgrading.

14 Of course, recovery should be as high as possible in terms of process efficiency, but purity
15 is the highest priority in the biogas upgrading process. For PSA operation with bamboo
16 charcoals, recovery may be decreased to maximize the CH₄ concentration in the top product
17 gas as shown in **Fig. 8**. However, PSA operation combined with other biogas utilization
18 processes such as co-generation can overcome the low recovery of CH₄ since the bottom
19 product gas contains unrecovered CH₄, which can be mixed with a biogas stream for
20 generation.

Figure 8 (a) Performance (purity and yield) of PSA with BC 900 according to half-cycle time (feed gas rate: 2.45 L min⁻¹). (b) Performance comparisons of PSA with BC 900 (half-cycle time: 600 s) and MSC-B (half-cycle time: 200 s for 10 L min⁻¹; 280 s for 7 L min⁻¹; 450 s for 4 L min⁻¹).

4. Conclusions

A simple fabrication method of MSC using bamboo for biogas upgrading was proposed. Although char activation and pore modification were omitted, pores with a narrow size distribution and similar dimensions to CH₄ were successfully obtained by temperature controlled carbonization. Bamboo charcoals had high CO₂ adsorption selectivity, which was comparable to that of commercial MSCs used in biogas upgrading, but the kinetic separation of CO₂/CH₄ fell a little short of commercial MSCs. The feasibility of bamboo charcoals as an MSC for biogas upgrading was determined by PSA testing. It is expected that bamboo charcoals can contribute to sustainable small-scale biogas upgrading.

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