

# Preparation of activated carbon with high surface area for high-capacity methane storage

Bingsi Liu<sup>a\*</sup>, Wenshuo Wang<sup>a</sup>, Na Wang<sup>a</sup>, (Peter) Chak Tong Au<sup>b</sup>

*a. Department of Chemistry, School of Science, Tianjin University, Tianjin 300072, China;*

*b. Department of Chemistry, Hong Kong Baptist University, Kowloon Tong, Hong Kong, China*

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## Abstract

Activated carbon (AC) was fabricated from corncob, which is cheap and abundant. Experimental parameters such as particle size of corncob, KOH/char weight ratio, and activation temperature and time were optimized to generate AC, which shows high methane sorption capacity. AC has high specific surface area (3227 m<sup>2</sup>/g), with pore volume and pore size distribution equal to 1.829 cm<sup>3</sup>/g and ca. 1.7–2.2 nm, respectively. Under the condition of 2 °C and less than 7.8 MPa, methane sorption in the presence of water ( $R_w = 1.4$ ) was as high as 43.7 wt% methane per unit mass of dry AC. The result is significantly higher than those of coconut-derived AC (32 wt%) and ordered mesoporous carbon (41.2 wt%,  $R_w = 4.07$ ) under the same condition. The physical properties and amorphous chaotic structure of AC were characterized by N<sub>2</sub> adsorption isotherms, XRD, SEM and HRTEM. Hence, the corncob-derived AC can be considered as a competitive methane-storage material for vehicles, which are run by natural gas.

## Key words

corncob; activated carbon; methane storage; hydrate; adsorption

## 1. Introduction

Because natural gas (with methane being the major component) as a vehicle fuel is cheap, abundant and clean, its storage, transportation and utilization have attracted global attention [1]. The natural resource of methane in the form of flammable ice is much more abundant than that in natural gas [2]. Technically, there is no barrier for methane to be used for natural gas vehicles (NGV), and methane as a fuel is as important as hydrogen. The improvement in methane storage technology will certainly reduce the fuel cost and is favorable for the development of NGV. Recently, compressed natural gas is the only mode in practice for NGV, however, the storage pressure of 20 MPa is too high for low-cost fuel and guaranteed safety. In addition, in terms of equal fuel-tank volume, the energy density of natural gas at pressure of 20 MPa is only 29% of that of gasoline. It is noted that 1 m<sup>3</sup> clathrate can release 164 m<sup>3</sup> natural gas and 0.8 m<sup>3</sup> water. Clathrate is a form of natural gas hydrates that consist of methane located inside water cages. In other words, the thermal value (per unit volume) of clathrate in combustion is remarkably higher

than those of coal, oil and natural gas. In NGV technology, to decrease storage pressure and to increase energy density of a suitable fuel remain a challenge.

AC is used in methane storage, referred to as adsorption of natural gas (ANG). However, to be commercially viable, the ANG technology requires a methane storage target of 180 v/v [3]. In the late 1990s, Menon and Komarneni [4] reviewed the characteristics and prospects of different types of porous materials, such as carbon materials, zeolites, silica gels, and mesoporous solids for methane storage. It was reported that specific surface area rather than chemistry of the porous materials has a direct relationship with the methane adsorption capacity. There are reports on the storage of methane in porous carbon materials in the form of clathrate [5,6]. Adsorption of methane into wet carbon materials leads to clathrate formation inside the pores of the materials. The need of using carbon materials of large surface area for high sorption capacity is obvious. Despite materials with metal-organic frameworks of high specific surface area [7] have made a significant impact on methane storage [8,9], they are commercially not viable because of high fabrication cost. On the other hand, it is less costly to produce AC that is high in specific surface area, pore

\* Corresponding author. Tel: +86-22-27892471; Fax: +86-22-27403475; E-mail: [bingsiliu@tju.edu.cn](mailto:bingsiliu@tju.edu.cn)

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volume and porosity [10]. It is well known that AC can be prepared from a variety of substances such as bituminous coal, pistachio shell, coconut shell [11,12], cassava peel [13], fir wood [14], oil-palm shell, and corncob [15], and AC with surface area ranging from 500 to 2800 m<sup>2</sup>/g has been reported. In terms of cost and abundance, corncob as a biomass and agricultural waste is an attractive candidate for AC production. Derived from corncob by means of chemical activation with potassium salts and/or physical activation with CO<sub>2</sub>, Tsai et al. [16] generated granular AC with surface area of ca. 1600 m<sup>2</sup>/g. The AC derived by Tseng [17] from corncob at different KOH/char weight ratios (denoted as KOH/char ratios hereinafter) ranging from 0.5 to 6 showed surface areas ranging from 841 to 2595 m<sup>2</sup>/g. With optimization of preparation parameters, AC with surface area as high as 2844 m<sup>2</sup>/g was obtained by the same research group [15].

In previous report [18], we studied adsorption kinetics of H<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> on AC in the range of 77–301 K and proposed a pseudo-second-order Freundlich kinetic model. The adsorption capacity was significantly higher than the results reported. Here, we prepared AC of high specific surface area and pore volume from corncob by proper adjustment of experimental parameters such as particle size of ground corncob, KOH/char ratio, and activation temperature and time. The methane storage capacity of the AC samples was evaluated in the presence as well as absence of water for commercial application in NGV technology. The AC samples were characterized by means of N<sub>2</sub> adsorption-desorption method as well as X-ray diffraction (XRD), scanning and high-resolution transmission electron microscopic (SEM, HRTEM) techniques.

## 2. Experimental

### 2.1. Preparation of AC from corncob

Corn cob from northeast China was collected and rinsed with water and dried at 50 °C. Then the corncob was ground using a roller crusher and sieved into different particle sizes (40–60, 20–40, 6.4–8.5, and 4.2–5.1 mesh). The as-sieved particles were placed in a stainless steel tube (50 cm length and 3.5 cm inner diameter) positioned inside a pipe furnace. After proper sealing of the stainless steel tube, the corncob particles were purged with N<sub>2</sub> at a rate of 25 mL/min while the tube was heated from room temperature (RT) to 450 °C at a rate of 30 °C/min and kept at this temperature for 0.5 h. Under such an oxygen-deficient condition, the corncob particles were thermally decomposed into porous carbonaceous materials and hydrocarbon. The whole carbonization process was completed after cooling the entire assembly to RT. The obtained chars were well mixed with a solution of KOH at a particular KOH/char ratio and the mixture was stirred continuously for 0.5 h. Then water was evaporated in an oven at 110 °C for 12 h. The dry mixture consisted of chars and KOH was then placed in a stainless-steel-tube oven under the purging of N<sub>2</sub> (25 mL/min), heated to 850 °C at a rate of 30 °C/min, and kept at this temperature for 1 h. After cool-

ing to RT, the as-obtained material was rinsed repeatedly with aqueous HCl and hot water until the water effluent reached a pH of 6–7. The material was then dried at 110 °C.

### 2.2. Characterization of AC derived from corncobs

The specific surface area ( $S_{\text{BET}}$ ), total pore volume ( $V_{\text{T}}$ ), and average pore diameter of AC were derived from the N<sub>2</sub> adsorption isotherms obtained at 77 K using a self-assembled BET apparatus [19]. The samples were first dried overnight at 120 °C, and then placed quickly into the sample tube. Prior to measurement, the samples were degassed again in vacuum at 200 °C for 1 h. The volumes of micropores ( $V_{\text{mi}}$ ) and mesopores ( $V_{\text{me}}$ ) were obtained by the volume of N<sub>2</sub> adsorbed ( $V_{\text{m}}$ ) at  $p/p_0 = 0.10$  and 0.95, respectively. The pore size distribution of AC was evaluated by a simplified local density (SLD) approach, which is a thermodynamic model that can be used with any equation of state and offers some predictive capability with adjustable parameter for modeling of slit-shape pore.

The powder XRD investigation of AC fabricated under different conditions was conducted on a Rigaku automatic diffractometer (Rigaku D-MAX) with monochromatized Cu  $K_{\alpha}$  radiation ( $\lambda = 0.15406$  nm, 40 kV and 50 mA). The patterns acquired were referred to the powder diffraction files-1998 ICDD PDF Database for phase identification. The morphology and selected area electron diffraction (SAED) pattern of AC were examined using a scanning electron microscopy (SEM) with a field emission gun (FEI, nanosem 430) and a HRTEM instrument (Tecnai G2 F20) that was equipped for energy dispersive X-ray (EDX) analysis [20]. The procedure for sample preparation and the operation conditions for HRTEM analysis are similar to those reported in literature [21].

### 2.3. Methane adsorption performance

The methane sorption isotherms were acquired using a typical volumetric setup [22], as shown in Figure 1. Reference and adsorption cells were connected by a tube via valve C. The temperature ( $T_{\text{r}}$ ) of the reference cell (volume  $V_{\text{r}}$ , including the tube volume between the reference cell and valve C) was kept close to RT (i.e., 25±0.1 °C) using a thermostat. The adsorption cell charged with adsorbent was maintained at a particular temperature ( $T_{\text{a}}$ ) for methane adsorption. Prior to measurement, the AC sample which was previously dried at 120 °C for 12 h and cooled down to RT (in a vacuum desiccator) was degassed in situ in vacuum in the adsorption cell at 120 °C for 2 h. After having valve C switched off (Figure 1), the adsorption cell was moved to a water bath of 2 °C. At first, the amount of methane in the reference cell was measured using the  $p$ - $V$ - $T$  readings. Then valve C was opened and there was decline of pressure due to CH<sub>4</sub> adsorption. The system reached equilibrium for approximate 40 min. The amount of methane adsorbed was calculated from the  $p$ - $V$ - $T$  readings. In addition, a given amount of distillation water was mixed with dry AC, and the wet AC sample with water/carbon weight ra-

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