



Biochar as a renewable source for high-performance CO₂ sorbent



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ABSTRACT

Natural gas wells evolve CO₂ along with the hydrocarbon stream. Because of the wide use of natural gas as an energy source, the emission of CO₂ from high pressure natural gas wells is of concern. While various sorbents have been developed to purify natural gas, studies are lacking on the use of renewable biosources, especially biochar, to prepare porous carbon sorbents for CO₂ capture at high pressure. Here we report the use of low-cost biochar as the feedstock for a one-step KOH activation towards high surface area solid state CO₂ sorbents. Under the optimal activation conditions, a surface area of 3167 m² g⁻¹ is reached with a CO₂ uptake of 26.0 mmol g⁻¹ (1.15 g g⁻¹) at 30 bar and 25 °C. The cycling stability and CO₂/CH₄ selectivity of the synthesized biochar-derived porous carbon have been evaluated, and activity screenings show that wood wastes pyrolyzed at a mid-range temperature, 450 °C, are the preferred type of biochar for use as high performance CO₂ sorbents in high pressure applications.

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1. Introduction

Natural gas is a major source of fuel that serves to meet the world's rapidly growing demand for electrical power. However, natural gas wells contain significant amounts of carbon dioxide (CO₂), a component generally vented to the atmosphere after gas purification, which contributes to global climate change [1,2]. Thus, it is important to efficiently separate CO₂ from high pressure natural gas in order to reduce the concentration of atmospheric CO₂, and to pursue the "green carbon" approach [3–5]. Various technologies and materials have been developed to separate CO₂ from natural gas in a sorption process [6–10]. Although aqueous amine-based solutions are commonly used for CO₂ capture, they are corrosive, there is the loss of sorbent with amine degradation, high energy is required for sorbent regeneration, and there is a large space requirement that cannot be used offshore [8,10]. The less developed solid-state sorbents such as porous carbons [11–18], zeolites [19], metal organic frameworks (MOFs) [20–22], and functionalized porous silica [23–26] have also shown potential as alternative materials for CO₂ sorption, having advantages such as

low energy regeneration requirements, high capacity and selectivity, non-corrosive nature, and easier handling. The use of solid state sorbents in pressure swing processes could make them more efficient in CO₂ capture due to their high thermal and chemical stability, low heat capacities and fast sorption-desorption kinetics [27,28].

Among the family of solid state CO₂ sorbents, meso- and microporous carbon materials have superior features such as high surface area, a metal-free framework, efficient CO₂ uptake at high pressure, and the wide variety of carbon sources available [6,7,9]. Compared to porous carbon sorbents made from synthetic polymer precursors [11,13,15], directly using natural products as the feedstock for activation could significantly simplify the manufacturing process, and thus make it cost-efficient at the industrial production level [12,14,16–18]. Recently, we reported that porous carbon materials synthesized from natural asphalt, designated **A-rNPC**, showed an absolute CO₂ uptake of 26 mmol g⁻¹ (1.14 g g⁻¹) at 30 bar and 23 °C; 30 bar is the estimated CO₂ partial pressure at natural gas well heads [14]. Unfortunately, specialty asphalt Versatrol-HT was the only feedstock that yielded porous carbons with such high CO₂ uptake performance after KOH activation. Thus, the use of an alternative raw material that gives high surface area porous carbon sorbent with similar performance, especially at high pressure, would be advantageous, especially if it were a renewable natural source.

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Biochar, an alternative natural carbon source, can be easily prepared from low-cost or negative-cost biomass through a pyrolysis process at 200 to 900 °C with limited oxygen exposure [29–31]. Biomass includes agricultural crops, crop residues, grass, wood, animal litter, dairy manure, and other solid biologic wastes. The biomass is abundant and the producers are sometimes forced to pay for their disposal, rendering it a negative-cost material. Thus, the use of biochar as the raw material for the synthesis of porous carbon as CO₂ sorbents would be both economically efficient and environmentally helpful. Although biosources have been used to prepare porous carbons for CO₂ capture [12,16–18], the CO₂ uptake performances were usually evaluated only at the low pressure of 1 bar. Moreover, the biosources were usually directly activated without pyrolysis into biochar, and studies on how different types of biochar could yield porous carbon sorbents with different properties are limited.

In this study, we demonstrate a one-step synthesis of biochar-derived porous carbon (**B-PC**) for high pressure CO₂ capture. A variety of activation conditions have been studied regarding physical properties and CO₂ uptake performances of **B-PC**. An absolute CO₂ uptake of 26.0 mmol g⁻¹ (1.15 g g⁻¹) at 30 bar and 25 °C was achieved from mesquite biochar (pyrolyzed at 450 °C) using the optimized KOH amount and activation temperature, with a BET surface area as high as 3167 m² g⁻¹. In addition, biochar made from various biosources activated at different pyrolysis temperatures was evaluated based on the CO₂ uptake values of the synthesized **B-PCs**. Wood wastes pyrolyzed at 450 °C are the most promising type of biochar for the synthesis of high performance **B-PC** sorbents for CO₂ capture at high pressure.

2. Experimental

2.1. Synthesis of biochar

Novus pallet scrap biochar was synthesized by Novus Wood Group using an industrial gasifier at 450–550 °C for ~8 min. Other biochar was synthesized using a published procedure [31]. Typically, the biosources were pyrolyzed at 450 °C for 4 h with restricted O₂ exposure.

2.2. Synthesis of **B-PC**

0.50 g of mesquite biochar (pyrolyzed at 450 °C) and 2.50 g of KOH were well-mixed using a mortar and pestle, and the solid was heated from room temperature to 800 °C at a rate of 25 °C min⁻¹ in a tube furnace under an Ar flow rate of 500 sccm at 1 atm; the intermediate was then activated by holding at 800 °C at 1 atm under 500 sccm Ar for 45 min before being allowed to cool to room temperature. The solid product was then washed with 200 mL of DI water (3×) and dried at 120 °C for 12 h to yield 0.20 g of **B-PC**. Biochar pyrolyzed from other sources at different temperatures were also used to synthesize **B-PC**.

2.3. Volumetric sorption

Volumetric sorption measurements of CO₂ or CH₄ were carried out in an automated Sievert instrument (Setaram PCTPro) [13,14]. Typically, ~120 mg of sorbent was placed in a stainless steel sample cell and pretreated at 150 °C for 2 h under vacuum (~20 mTorr). The sample volume was calibrated by He (absorption at ~3 bar, desorption at ~1 bar, 23 °C) before the sorption measurement. Excess gas uptake data was acquired from the sorption measurements.

2.4. Gravimetric sorption

Gravimetric sorption measurements of CO₂ were carried out in a Rubotherm magnetic suspension balance (Rubotherm, Germany) [14]. A blank test without sample was used to measure the weight and volume of the sample holder. For a typical CO₂ uptake measurement, ~120 mg of sorbent was placed in the sample holder and pretreated at 120 °C for 4 h under vacuum (~20 mTorr). A buoyancy test with He (absorption from 0 to 50 bar, 25 °C) was used to measure the sample weight and volume before the sorption measurement, and the density of the sample is calculated from the measured weight and volume from the buoyancy test. Excess gas uptake data was acquired from the sorption measurements.

2.5. Calculation of absolute gas uptake

Absolute gas uptakes were calculated as: absolute gas uptake = excess gas uptake + total pore volume × gas density [13,14,32]. Detailed explanations are shown in Fig. S1.

2.6. Characterization

The XPS spectra were obtained on a PHI Quantera SXM scanning X-ray microprobe system using a 100 μm X-ray beam of which the take-off angle was 45° and the pass energy was 140 eV for the survey and 26 eV for the high resolution elemental analysis. The N₂ adsorption-desorption isotherms (at 77 K) were obtained using an automated BET surface analyzer (Quantachrome Autosorb-3b), and the samples were heated at 150 °C for 15 h under vacuum (~20 mTorr) before each measurement. SEM images were taken in a FEI Quanta 400 high resolution field emission scanning electron microscope. TEM images were obtained in a 2100F field emission gun transmission electron microscope.

3. Results and discussion

3.1. Characterization and textural properties

The synthesis of **B-PC** is shown in Fig. 1a. Biochar was synthesized by the pyrolysis of biomass using a published procedure [31]. The biochar was then activated with KOH in a tube furnace at elevated temperature under an inert atmosphere [13,14]. This activation process was performed with different biochar/KOH weight ratios and at various temperatures. The **B-PC** prepared with 0.5 g mesquite biochar (pyrolyzed at 450 °C) and 2.5 g KOH by activating at 800 °C was used as the optimized sample for detailed characterizations. Fig. 1b,c shows the scanning electron microscope (SEM) images of **B-PC** at different scales. A wood-like macrostructure could be identified, and the combination of larger channels (>10 μm) and smaller pores (<100 nm) could be beneficial for fast CO₂ adsorption-desorption kinetics. The amorphous nature of **B-PC** is shown by the transmission electron micrograph (TEM) in Fig. 1d, where no ordered domains could be observed, similar to other porous carbon materials with high surface areas [13–15].

To analyze the physical properties of the **B-PC** prepared with different activation conditions, Brunauer–Emmett–Teller (BET) measurements have been conducted with the N₂ adsorption-desorption isotherms at 77 K shown in Fig. 2a. With mesquite biochar (450 °C) as the starting material, all **B-PC** samples exhibit a typical type I isotherm, with a narrow knee indicated rapid N₂ uptake at low pressure range (P/P₀ < 0.3), a plateau that indicates limited adsorption at higher pressure range, and an absence of hysteresis between the adsorption and desorption cycles. These characteristics show that the **B-PC** samples prepared are mainly microporous (<2 nm) with limited mesopore (2–50 nm)

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