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Coconut shell-based carbon adsorbents for ventilation air methane enrichment

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HIGHLIGHTS

- The pyrolysis behaviors of coconut shells up to 700 °C were systemically investigated.
- The effect of pyrolysis temperature on the grindability of coconut shell chars was revealed.
- The separation factor of CH_4/N_2 of the coconut shell-based carbon adsorbent is 6.18.
- The VAM consisted of 0.42% CH_4 was enriched to 1.09% by VPSA with the carbon adsorbent.

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ABSTRACT

Coconut shell-based carbon adsorbents were prepared and applied to vacuum pressure swing adsorption (VPSA) process for ventilation air methane (VAM) enrichment. The preparation procedure consists simply of pulverization of the coconut shell chars, pelletization with phenolic resin as binder, and carbonization of the pellets under N_2 flow. The pyrolysis characteristics of coconut shells, including the composition of gas products at different pyrolysis temperature interval, the porous characteristics, the proximate and ultimate analyses, the surface functional groups, and the grindability of the chars from varied pyrolysis temperature, were systematically investigated. So that the reasonable pyrolysis temperature for coconut shell chars production was determined. The ratio of phenolic resin to char powder was optimized in regarding of the compressive strength, packing density, textural characteristics, and CH_4/N_2 separation factor of the carbon adsorbents. The performance of the carbon adsorbent prepared under optimum condition for VAM enrichment by VPSA was examined, and it merits the need for flow-reversal reactor or lean-burn combustion turbine to generate power.

1. Introduction

Methane desorbed from deep coal seams brings a serious safety problem for underground coal miners because it can cause explosion when its concentration falls into 5–15% in air. To maintain safe working condition, i.e. to keep in-mine methane concentrations below the lower explosive limit, large-scale ventilation systems are employed for gassy underground coal mines to dilute methane with air and expel the methane with the ventilation air (VA) out into the atmosphere. The concentration of VA methane (VAM) ranges from 0.1 to over 1.0 vol.% [1–3], typically between 0.3 and 0.5 vol.%. In China, the upper limit for VAM is 0.75 vol.%. Each year, underground coal mines throughout the world emit more than 14 billion m^3 of methane from their ventilation systems [4]. It is a great waste of energy and creates an environmental problem as well because methane is a powerful greenhouse gas (GHG) with a global warming potential 25 times that of carbon dioxide (CO_2) over a 100-year period. Due to the low methane concentration, the beneficial use of VAM presents significant challenges [5].

There are several technologies for destroying or beneficially using VAM. They fall in two categories: as ancillary fuel and as principal fuel [6]. As ancillary fuel, VAM is served as combustion air to replace a small fraction of the primary fuel in combustion processes, such as conventional boilers, turbines and engines. Such technologies rely on site needs and the VAM usage is limited to stoichiometric levels of combustion air. One of the principal fuel uses of VAM is flow-reversal reactor, including the thermal flow-reversal reactor (TFRR) developed by MEGTEC Systems (De Pere, Wisconsin, United States) and the catalytic flow-reversal reactor (CFRR) developed by Canadian Mineral and Energy Technologies (CANMET-Varennes, Quebec, Canada). The technologies employ similar principles to oxidize methane contained in VA. To sustain the TFRR and the CFRR operation, the minimum methane in VA should be above 0.2% and 0.1%, respectively. In order to recover surplus heat for power generation while retaining stable operation,

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the minimum methane concentration in the feed gas should be kept at about 0.9% [7,8]. Higher concentration VAM (between 0.8% and 1.6%) can also be utilized in lean-burn combustion turbines technologies to generate power, such as the carbureted gas turbine (CGT) by Energy Developments Limited (EDL) of Australia, the catalytic combustion gas turbine (CCGT) by CSIRO, the lean-fueled catalytic microturbine by FlexEnergy and recuperated microturbine by Ingersoll Rand.

To increase the methane concentration in the feed gas, it is necessary to add natural gas into VA [8–10]. Alternatively, the use of a concentrator is a better option. Concentrator acts as a buffer to cope with the fluctuation in methane concentration and VA flow rate, in which VAM can be enriched to a level that meets the requirement of oxidizer and combustion technologies. Environmental C&C, Inc. (ECC) manufactured a fluidized bed concentrator with activated carbons as optimized adsorbent for the enrichment of VAM with 0.5% CH_4 [8]. The trials have stopped because of the disappointing experiments results [11]. Liu et al. have tried to enrich VAM by vacuum pressure swing adsorption (VPSA) with activated carbons as adsorbents. The concentration of the VAM has been enriched from 0.3% to 0.75%, but the methane retains still 0.2% in off-gas [12–14]. Thiruvenkatachari et al. have developed a honeycomb monolithic carbon fiber composite (HMCFC) adsorbent for VAM capture. The adsorption capacity of the HMCFC adsorbent was twice that of commercial activated carbon. Methane concentration of 0.56% in the inlet VAM gas stream is reduced to about 0.011% after it passes through the HMCFC adsorbent at ambient temperature and atmospheric pressure. This amounts to a maximum capture efficiency of 98% [15].

To develop a satisfactory adsorbent, which is the key for enhancing the performance of the concentrator, specific coconut shell-based carbon adsorbents have been prepared in this work after a systematic study of the pyrolysis of coconut shells. The VPSA performance of the carbon adsorbents for the enrichment of methane from a model VAM has been evaluated.

2. Experimental

2.1. Preparation of coconut shell chars

The proximate and ultimate analyses of the coconut shells are shown in Table 1. The proximate analysis was carried out according to GB/T 17664-1999 and the ultimate analysis was conducted using Vario EL, Elementar. TG/DTG anaylsis of the coconut shells of about 10 mg was made with a DTU-2B thermal balance at a heating rate of 10 °C/min under N_2 gas flow.

Coconut shells crushed to 0.25–1.7 mm were pyrolyzed in an electrically heated rotary kiln. Prior to pyrolysis, the coconut shells were dried at 110 °C for 2 h. About 500 g of the dried coconut shells was loaded into the rotary kiln. The sample was heated up to the pyrolysis temperature with a heating rate of 10 °C/min and held for 30 min at this temperature under a N_2 gas flow of 270 cm^3/min. Then the rotary kiln was cooled down under flowing N_2 to room temperature to get the coconut shell chars. The chars prepared at 300, 400, 450, 500, 600 and 700 °C are denoted as C300, C400, C450, C500, C600 and C700, respectively.

The volatiles during the pyrolysis were cooled in three sequential ice-cooled condensers to be separated into liquids and gas. The liquids were collected in three liquid traps. The gas passed through a filter filled with glass wool to capture the remaining aerosol before it was collected in a gasbag. The gas was off-line analyzed by a GC-9790 gas chromatograph quipped with a NC-2000 chromatograph data workstation.

The surface property of the coconut shell chars was characterized by the EQUINOX55 FT-IR spectrometer (Germany Bruker Optics). The grindability of the chars was measured according to GB/T 12496.6-1999. The proximate and ultimate analyses of the chars are determined by the methods mentioned above.

Table 1
Proximate and ultimate analyses of the coconut shells.

Proximate analysis (ad, wt.%)				Ultimate analysis (daf, wt.%)		
Moisture	Volatile	Ash	Fixed Carbon	C	H	O (diff)
7.8	73.2	0.1	18.9	50.7	5.9	43.4

2.2. Preparation and characterization of the carbon adsorbents

The coconut shell chars were ball-milled for 3 h to get the char powder of less than 10 μm. The char powder was mixed with a water solution of polyethylene glycol (PEG) and a certain amount of thermosetting phenolic resin as binder and then extruded to 2–6 mm length × 1.4 mm diameter cylindrical pellets. The ratio of PEG to char powder was kept at 0.1 g/g. After drying at 110 °C for 3 h, the pellets with a mass of 300 g were loaded into the rotary kiln, heated up to 800 °C at a heating rate of 10 °C/min, and kept for 1 h at this temperature under N_2 of 270 cm^3/min. Then the rotary kiln was cooled to room temperature under flowing N_2 before the carbon adsorbent product was removed. The carbon adsorbent prepared with a phenolic resin/char powder ratio of 0.3, 0.4, 0.5, 0.6 and 0.7 g/g is denoted as AC0.3, AC0.4, AC0.5, AC0.6 and AC0.7, respectively.

The BET surface area and porosity of the chars and the carbon adsorbents were examined by nitrogen adsorption at −196 °C using a JW-BK122W surface area analyzer. The total pore volumes (V_t) of the activated carbons are determined from the liquid volume of nitrogen adsorbed at relative pressure $P/P_0 = 0.99$. The micropore volumes (V_{mic}) are calculated by constructing the t-plots. The most probable micropore size of carbon adsorbents, D_{opt}, is obtained from the micropore size distribution calculated by the Horvath–Kawazoe (H–K) method. The separation factors of CH_4/N_2 of the carbon adsorbents were determined in a fixed bed column by the dynamic method [16], which is defined by the following equation:

$$\alpha_{12} = \frac{x_1/x_2}{y_1/y_2}$$

where x_i and y_i are the mole fraction of component i (1 or 2) in adsorbed phase and fluid phase, respectively. During the process, a gas mixture composed of 10 vol.% CH_4, 10 vol.% N_2 and 80 vol.% He passed through a column packed with the carbon adsorbents with an inlet flow of 100 cm^3/min at 25 °C and 0.2 MPa (absolute pressure). The column is 17 mm in internal diameter and 500 mm in length, the same as that of the VPSA experimental unit as will depicted in Section 2.3. The compressive strengths of the carbon adsorbents were measured with an YHKC-2A pellet hardness tester.

2.3. VPSA for VAM enrichment

The schematic diagram of a two-column VPSA experimental unit is showed in Fig. 1. The specifications of the adsorption columns are: 17 mm in internal diameter and 500 mm in length. A four-step VPSA cycle consisting of pressurization, adsorption, pressure equalization and desorption steps was studied for the enrichment of the model VAM, which consists of 0.42 vol.% CH_4 and 99.58 vol.% N_2. The methane in the product gas and off-gas was measured by an on-line GC-920 gas chromatograph with a FID detector. The temperature of the adsorption column was kept at 25 °C. Before experiments, the adsorbents were dried in a vacuum drying oven at 150 °C for 10 h.