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Research article

Biomass-derived carbon composites for enrichment of dilute methane from underground coal mines

Jun-Seok Bae [a, *], Yonggang Jin [a], Chi Huynh [b, 1], Shi Su [a, **]

[a] CSIRO Energy, 1 Technology Court, Pullenvale, Queensland 4069, Australia
[b] CSIRO Materials Science and Engineering, PMB 10, Clayton, Victoria 3168, Australia

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ABSTRACT

Ventilation air methane (VAM), which is the main source of greenhouse gas emissions from coal mines, has been a great challenge to deal with due to its huge flow rates and dilute methane levels (typically 0.3–1.0 vol%) with almost 100% humidity. As part of our continuous endeavor to further improve the methane adsorption capacity of carbon composites, this paper presents new carbon composites derived from macadamia nut shells (MNSs) and incorporated with carbon nanotubes (CNTs). These new carbon composites were fabricated in a honeycomb monolithic structure to tolerate dusty environment and to minimize pressure drop. This paper demonstrates the importance of biomass particle size distributions when formed in a composite and methane adsorption capacities at low pressures relevant to VAM levels. The selectivity of methane over nitrogen was about 10.4 at each relevant partial pressure, which was much greater than that (6.5) obtained conventionally (at very low pressures), suggesting that capturing methane in the presence of pre-adsorbed nitrogen would be a practical option. The equilibrium and dynamic performance of biomass-derived carbon composites were enhanced by 30 and 84%, respectively, compared to those of our previous carbon fiber composites. In addition, the presence of moisture in ventilation air resulted in a negligible effect on the dynamic VAM capture performance of the carbon composites, suggesting that our carbon composites have a great potential for site applications at coal mines because the cost and performance of solid adsorbents are critical factors to consider.

1. Introduction

Total greenhouse gas (GHG) emissions in Australia for 2017 were estimated at 550.1 Mt CO_2-e, of which 9% were from fugitive emissions (DEE Australia, 2017). Coal mining activities, including underground, open cut, post-mining and decommissioned mines contribute about 67% of fugitive emissions (DCCEE Australia, 2012). The primary methane-emitting source (60–70%) is ventilation air methane (VAM) from underground coal mines (Karakurt et al., 2011). The mitigation of VAM has been, however, an ongoing challenge as the ventilation air contains dilute methane (typically 0.3–1 vol%) with huge and variable volumetric flow rates (120–600 m^3/s in typical gassy mines in Australia). Thus, it is imperative to develop effective technologies for VAM mitigation and utilization, reducing GHG emissions and making practical and profitable use of VAM (GMI, 2012).

As of today, two approaches have been mainly applied to mitigate VAM. Since the global warming potential (GWP) of methane is 28 (IPCC, 2014), the first option is to directly convert the dilute methane to carbon dioxide by thermal or catalytic oxidation, which has been regarded as a major practical option for VAM mitigation. The other option is to enrich VAM to levels that conventional methane-fueled engines such as lean burn gas turbines can use as a principal fuel. For the first option, however, due to the presence of variable and low VAM concentrations, an additional energy input is typically required to retain stable and effective operation of oxidizers (Baris, 2013). In this regard, enriching VAM, while reducing fugitive emissions, can be a beneficial option to provide the required additional energy to the oxidizers as well as to act as a buffer to cope with fluctuations in methane concentrations.

Various technologies, including cryogenic and membrane separation (Chen et al., 2015; Yang et al., 2014), hydration separation (Sun et al., 2012; Zhong et al., 2013), ionic liquids (Anthony et al.,

* Corresponding author.
** Corresponding author.
E-mail addresses: jun.bae@csiro.au (J.-S. Bae), shi.su@csiro.au (S. Su).
[1] Current address: Lintec of America, *INC*. Inc. R&D Division, Nano-Science and Technology Center, 990 N. Bowser Road, Suite 800 Richardson, Texas 75081, U.S.A.

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2002; Uchytil et al., 2011) and adsorption with solid sorbents (Bae et al., 2014; Cavenati et al., 2006; Garcia et al., 2013; Liu et al., 2012; Shao et al., 2012; Thiruvenkatachari et al., 2009), have been applied to enrich methane concentration or to separate methane from its mixtures. Amongst them, adsorption technology with solid adsorbents has been demonstrated as a viable and effective option for VAM enrichment (Bae et al., 2014). For instance, with carbon fiber composites and combination of temperature and vacuum swing adsorption, 5–11 times VAM enrichment was achieved at room temperature and atmospheric pressure (Bae et al., 2014). In addition, as a practical option, VAM enrichment units can be combined with oxidation units to get mutual benefits at mine sites because the former can provide the captured methane to the later while receiving waste heat from the later to regenerate solid adsorbents. The VAM enrichment performance with adsorption technology mainly depends on the characteristics of solid adsorbents such as methane adsorption capacity and selectivity, and the desorption processes typically including vacuum, temperature and pressure swings. This paper deals with the former, focusing on development of carbon composites suitable for VAM enrichment.

Having almost 100% relative humidity, ventilation air from some Australian underground coal mines contains dust loadings of 0.13–4.47 mg/m^3 with a maximum particles size of 5 μm (Su et al., 2008). Based on the huge flow rate of ventilation air, the daily dust loading ranges from 1.35 to 232 kg/day, which may result in a significant impact on the following treatment processes. Thus, apart from separation characteristics such as the adsorption capacity and selectivity of methane, for VAM enrichment with fixed bed applications, the solid adsorbents should be less sensitive to moisture, having a low flow resistance (i.e. pressure drop) and a high dust tolerance in dealing with high volumetric flow applications (Bae et al., 2014). In this regard, monolithic carbon composites (Burchell et al., 2005; Liu et al., 2007; Macias-Garcia et al., 2012; Moreno-Castilla and Perez-Cadenas, 2010; Thiruvenkatachari et al., 2009) can be a viable and suitable option, particularly in a honeycomb monolithic (HM) structure (Bae et al., 2014; Macias-Garcia et al., 2012; Thiruvenkatachari et al., 2009) for VAM enrichment. Honeycomb monolithic carbon fiber composites (HMCFCs) based on petroleum pitch were found to possess twice as high methane adsorption capacity as a commercially available activated carbon at ambient pressure (Thiruvenkatachari et al., 2009). In addition, it has been demonstrated that the HMCFCs have high cyclic stability through vacuum and temperature swing processes (Bae et al., 2014; Thiruvenkatachari et al., 2013).

As part of our continuous endeavor to further improve the methane adsorption capacity of HMCFCs, this paper presents new carbon composites derived from macadamia nut shells (MNSs) and carbon nano tubes (CNTs). Among agricultural bio wastes, nut shells are very attractive candidates as precursors for carbon composites because they have high cracking pressure with very low ash and high fixed carbon contents. About 39% of the world's macadamia nuts were produced in Australia (Le Lagadec, 2009) and thus the shells are locally available and low-cost biomass. In addition, CNT-added composites can possess a hierarchical structure in the composites, resulting in an easy accessibility of methane molecules to pore space (Jin et al., 2013). It was identified in an earlier study that addition of 5 wt % of single wall nanotube (SWNT) to pitch fibre, improved its strength, modulus, and electrical conductivity by about 90, 150 and 340%, respectively (Andrews et al., 1999). In this paper, new carbon composites for VAM enrichment were developed with various blend ratios of MNSs and CNTs over a binder, particle sizes of MNSs and activation time. And they were characterized in terms of methane adsorption capacities, pore size distributions and breakthrough tests. In addition, the effect of moisture on VAM capture performance, which is an important step prior to site trials at coal mines, was investigated.

2. Experimental

2.1. Composite fabrication

MNSs were obtained from a local farm in Australia and used as a biomass template to fabricate carbon composites. The proximate and ultimate analysis results can be found elsewhere (Bae and Su, 2013). The ash content of MNS is about 0.4 wt % (a.d.), which is lower than that of other nut shells such as kukui nut shell (3.27 wt %), coconut shell (2.78 wt%) (Antal and Gronli, 2003) and oil palm shell (Arami-Niya et al., 2012). When carbonized and activated, MNSs yield a higher surface area than other nut shells (pecan, hazelnut, walnut, almond, pistachio nut and palm shell) (Arami-Niya et al., 2012; Strezov et al., 2007; Wartelle and Marshall, 2001). As-received MNSs were crushed to a few mm in size using a roller crusher. The crushed MNSs were then carbonized under nitrogen flow (5 L/min) in a tube furnace at a pre-determined temperature (873 K). The carbonized MNSs (MNS-Cs) were sieved down to a few size ranges to study the particle size effect on methane capture when formed as composites. Then, the MNS-Cs were mixed with a binder (phenolic novolac resin from Durez Corporation, United States) and water, and molded to form a honeycomb monolithic structure (20 mm in diameter with 500 mm long). The molded mixture was dried and cured at 408 K in an oven, followed by carbonization under nitrogen flow at 923 K and activation with CO_2 at 1223 K in a tube furnace. The experimental flowchart can be found in Fig. S1.

Although it is common that physical activation may yield lower surface areas and methane capture capacities than chemical activation, the former process was adopted in this paper because it has been widely used for commercial production, being simple with no chemical washing or treatment steps (Islam et al., 2017) but still resulting in well-developed microporosity with good physical strength (Reddy et al., 2012; Yang et al., 2010). The blend ratios (0.5, 1, 2 and 3 by weight) of MNS-Cs over phenolic resin are named BR1, BR2, BR3 and BR4, respectively. Carbonized samples at 923 and 1223 K are denoted as C923 and C1223, respectively. Activated samples at 1223 K for 15, 30 and 60 min are denoted as A15, A30 and A60, respectively.

Also, as an additive to composite formation, commercial CNTs (L-MWNT-1020, purity > 97%, Ash < 3 wt %, Nanotech Port Co. Ltd, China) were used, having 5–15 μm in length and 10–20 nm in diameter (aspect ratio: 400–1500). Prior to incorporating the CNTs in composites, a mild oxidation method (Jin et al., 2013) was applied to separate individual CNT clusters due to the tendency of CNTs to entangle and agglomerate. And a 2% methyl cellulose (MC) hydrogel solution was added to keep the resultant CNTs dispersed. The MNS-CNT composites are denoted as MCC.

2.2. Composite characterization and performance tests

The adsorption isotherms of CH_4, CO_2, N_2 and H_2O were measured using a gas adsorption analyzer (ASAP2020HD, Micromeritics). The micropore size distributions (MPSDs) of composites were obtained from the adsorption isotherms of CO_2 and N_2 at 273 and 77 K, respectively with a density functional theory (DFT). A helium pycnometer (AccuPyc 1340, Micromeritics) was used to measure the solid density (helium density). The morphologies of samples were examined using a scanning electron microscopy (SEM) (Philips FEG-SEM XL-30) at an operating voltage of 10 kV. The particle size distributions of carbonized MNSs were obtained using a Malvern particle sizer.

Breakthrough tests at ambient temperature and pressure were