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Microporous carbon monolith synthesis and production for methane storage

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ABSTRACT

The synthesis, characterization, and performance of a new low pressure, monolithic, activated carbon adsorbent developed for methane storage is discussed and compared to other adsorbents. The effect of particle packing density on the storage capacity of tanks filled with commercially available and developmental adsorbents is quantified. 20 kg of the developed monolithic material is tested using a custom built, 40 L, space conformable tank test assembly. The performance is found to be superior to metal organic frameworks and other activated carbons reported in literature based on high tank volumetric and gravimetric storage capacities. The developed material has a pore structure and external dimensions that allow for rapid adsorption/desorption with gas being able to reach the center of the 40 L tank within ~3 s. The developed material delivers 151 V/V of methane between 35 bar and 1 bar in the 40 L tank. A continuous discharge flow rate of 2 g/s at 5 bar for a 10 gge system was demonstrated.

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1. Introduction

The full economic and environmental benefits of natural gas [1,2] (NG) are not being realized by its numerous energy applications [3,4] due to its relatively low energy density compared to petroleum and coal. For many applications, the energy density of NG can be improved by utilizing adsorption with metal-organic frameworks (MOFs) and carbonaceous adsorbents in powder or monolithic form [5–18]. Adsorption based storage removes some of the costs associated with densifying NG that are present due to CNG or LNG systems (high pressure and low temperature capital and operating expenses) while adding costs associated with producing and operating adsorption based systems. The amount of performance that a particular adsorbent delivers will determine if its benefits outweigh its costs.

The performance of an adsorbent is often measured by collecting an excess adsorption isotherm and converting that into total amount stored by knowing the pore volume V_{pore} of the adsorbent. V_{pore} can be described as the intraparticle pore volume. In the case of MOFs, V_{pore} can be determined by studying crystal structure. Due to the disordered nature of powdered activated carbon (PAC), V_{pore} needs to be measured experimentally by measuring the volume that is accessible to a probe molecule which can be determined by collecting a supercritical nitrogen adsorption isotherm or using pycnometry, mercury porosimetry etc. [19].

In this work, we characterize the adsorbents (and their adsorptive capacity) in terms of three distinct densities, ρ_{bulk} which is the bulk density [20], ρ_{cryst} which is the crystalline density [8,19], and $\rho_{skeletal}$ which is the skeletal or "true" density [20] which is needed in order to determine the aforementioned excess adsorption. All of these densities are defined by unique volumes (see below) and a common mass which is that of an adsorbent free of any adsorbate.

The volume defining $\rho_{skeletal}$ is the skeletal volume ($V_{skeletal}$) which is defined by the method in which it is determined which in this work is helium pycnometry (see the Supporting material). $V_{skeletal}$ can be described by the volume inaccessible to helium or, alternatively the volume of the carbon in the adsorbent plus the volume contained in the adsorbent's closed pores should any such pores exist. ρ_{cryst} is defined by the sum of $V_{skeletal;}$ and V_{pore}. ρ_{bulk} is defined by the sum of the volume between particles contained in a particle bed, $V_{skeletal}$, and V_{pore}.

The total amount stored, when it is expressed volumetrically, is the crystalline volumetric storage capacity $V_{st,cryst}$. When $V_{st,cryst}$ is measured by these methods is that of an ideal crystal in that is defined by the same volume as ρ_{cryst}. The extent in which interparticle voids exist between the grains of an adsorbent will greatly

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impact the adsorbent's storage capacity in a macroscale tank. This packing efficiency is monitored by the packing fraction f in Eq. (1). The volumetric storage capacity of a tank $V_{st,tank}$ filled with an adsorbent with capacity $V_{st,cryst}$ is governed by Eq. (3) where ρ_{gas} is the gas density given by NIST [21]. To achieve large tank volumetric storage capacities adsorbents will have to display large crystalline volumetric storage capacities and packing fractions.

$$f = \frac{\rho_{bulk}}{\rho_{cryst}} \tag{1}$$

$$\rho_{cryst} = \left(\frac{V_{skeletal}}{V_{pore} + V_{skeletal}}\right)\rho_{skeletal} \tag{2}$$

$$V_{st,tank} = fV_{st,cryst} + (1-f)\rho_{gas} \tag{3}$$

Experiments with MOFs in powder form have demonstrated crystalline storage capacities up to 161 g/L for HKUST-1 (reported as 225 cm^3 STP/cm^3 at 35 bar by Mason et al. [8]) but this material has a fragile pore structure making it difficult to pack efficiently. In Mason's work [8], STP is defined by 0 °C and 1 atm giving a molar density of 0.0446 mol/L. HKUST-1 tablets have a storage capacity of 67 g/L [8] which translates to an effective packing fraction (i.e. calculated by using Eq. (3) and assuming the pore structure is unchanged) of 0.31. Tap density measurements (measured according to [22]) on commercially available HKUST-1 produce a packing fraction of 0.51. MIL-53 ($V_{st,cryst}$ = 133g/L, ρ_{cryst} = 0.987g/cm^3 [8,23]) has a bulk density of 0.4 g/cm^3 (when sold as Basolite ® A100[1,2]). This equates to a packing fraction of 0.41 and a tank storage capacity of 55 g/L. It can be deduced that Tagliabue et al. [24] experienced similar packing results (effective packing of 0.34) when trying to densify Ni-MOF-74. Collectively, these results suggest that many MOFs have large crystalline storage capacities (e.g. 161 g/L) but improved material packing methods are required to improve the useable storage capacity of these materials.

Experiments on PACs suggest that they can be efficiently packed. Corn cob based KOH PACs produced at the University of Missouri (MU) [12,25,26] demonstrate tank volumetric storage capacities of 85 g/L ($V_{st,cryst}$ of 120 g/L [27]) with a packing fraction of 0.63 (tap density measured according to [22]). No attempt was made to optimize the particle size distribution of the MU material for more efficient packing which contributed to its packing fraction matching that of random close packing of spheres [28,29]. By utilizing a bimodal particle size distribution (sieving the material) and applying 98 bar of mechanical stress to the sample, Celzard et al. [11,17] developed an anthracite based PAC capable of delivering 107 g/L (reported as 163 V/V) from a tank. This material has a tank storage capacity of 126 g/L (reported as 193 V/V [11]) which is similar to crystalline storage capacity results collected on MU materials [27]. In Celzard's work [11], V/V (i.e. volume of gas in some reference state per volume) is defined at 1.01325 bar, 25 °C, and the ideal gas law. While these results show that PACs can be efficiently packed, there are still inherent problems with granular adsorbed natural gas (ANG) storage and subjecting the adsorbent to large mechanical stresses.

Depending on the scale and type of storage application, subjecting the ANG storage vessel to a sufficient level of uniform mechanical stress to pack the PAC may not be practical. Also, in the event of an ANG tank rupture, the adsorbent would be immediately transported out of the tank by the expelled methane and the adsorbent itself will likely be flammable due to its high surface area. In the case of monolithic materials, they would likely remain inside the tank and slow the release of the adsorbate from the system. Densely packed PAC can present a significant resistance to gas flow that can prolong charging and discharging times and exacerbate the reduction in effective storage capacity that is primarily caused by thermal effects [30–32]. Diffusion problems can also be caused by adsorbents that do not have a sufficient amount of pores larger than ~1 nm. While monoliths may display similar behavior, they can be arranged in a way that allows for several monoliths to be charged/discharged in parallel by a single, relatively small, convective path that is machined into the monoliths.

In Section 2.2 we present the production process for both the precursor PAC and for binding the PAC into monoliths utilizing the binder poly(vinylidene chloride-co-vinyl chloride) (also known as Saran® or PVDC). The materials performance, structure, and isosteric heat of adsorption will be compared to that of other adsorbents. To our knowledge, the performance of the monoliths featured here is superior to materials reported elsewhere. A flat panel ANG storage system containing 20 kg of the featured monoliths will be introduced to demonstrate material performance.

2. Methods

2.1. PAC production

Powdered activated carbon was produced by MeadWestvaco according to U.S. Patents 5,416,056 [33] and 5,965,483 [34]. A two-stage activation process was conducted using wood sawdust as the starting material. The first stage of activation was performed according to (U.S. Patent RE31,093 [35]and Baker et al. [36]) to produce a commercially available product Nuchar™ WV-A 1100. The second activation was completed by mixing a 60 wt.% potassium hydroxide solution with Nuchar™ WV-A 1100 at a KOH/carbon ratio of 2:1 (dry weight basis). The mixture was heated in a rotary kiln to a temperature of 840 °C. The alkali laden product was water washed at 80 °C until the eluent had a pH of 7.5. The wet activated carbon was dried at 110 °C. The washed and dried material was named MWV-0260 and it was used as the precursor PAC material in the subsequent monolith production.

2.2. Monolith production

Monoliths were produced in a batch process by mixing MWV-0260 PAC with the binder, PVDC powder, partially thermally decomposing the binder while subjecting the mixture to compressive stress, and carbonizing the resultant green body under nitrogen flow. The monolith production process demonstrated a space time yield (kg of monolith produced per volume of reaction mixture per time) of 300 kg/m^3/day. The details of the production process are below.

PAC was mixed with binder with a 0.5:1 binder: carbon mass ratio in rock tumblers for a minimum of 7 hours using 0.635 cm ball bearings. 500 g of mixture were placed inside a 8.89 cm ID, steel, cylindrical, compaction die (see Fig. 1) at ~27 °C in 100 g increments with 760 bar of compressive stress applied after each increment. The temperature of the die was then increased 3 °C/min until it reached 305 °C while pressure was maintained. The temperature was maintained for 90 min at 305 °C and then the die was allowed to cool for ~16 h while mechanical stress was maintained. Stress was applied with a 45 metric ton press. Multiple green bodies were produced in parallel by maintaining the stress in multiple dies with the screws shown in Fig. 1.

After removal from the die, the green bodies were carbonized under nitrogen flow in a quartz tube sealed with PTFE end flanges containing FKM o-rings. The tube was heated at 2 °C/min until it

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[1] The crystalline storage capacity was taken from Mason et al. [8]. The tank storage capacity was calculated using Eq. (3) and a bulk density of 0.4 g/cm^3 (which is reported for Basolite® A100).

[2] Sigma-Aldrich, Basolite A100, http://www.sigmaaldrich.com/catalog/product/aldrich/688738?lang=en&region=US, Accessed 6/9/2015, 2015.

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