Microporous Carbon Monolith Synthesis and Production for Methane Storage

T.A. Rash^{*a}, A. Gillespie^a, B.P. Holbrook^c, L.H. Hiltzik^c, J. Romanos^d, Y.C. Soo^a, S. Sweany^a, and P. Pfeifer^a

^a University of Missouri, 701 S College Ave, 223 Physics Building, Columbia MO 65211.

^b Department of Natural Sciences, Lebanese American University, Byblos, Lebanon

^c MeadWestvaco Corporation, 5255 Virginia Avenue, North Charleston, SC 29406

^d Department of Natural Sciences, Lebanese American University, Byblos, Lebanon

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.

Keywords: Storage; Adsorbents; Carbon; Methane; Natural Gas

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

*Corresponding author E-mail address: tar477@mail.missouri.edu (Tyler Rash)

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 ρ_{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 ρ_{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 $V_{\text{st,cryst}}$. When $V_{\text{st,cryst}}$ 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 impact the adsorbent’s storage capacity in a macroscale tank. This packing efficiency is monitored by the packing fraction f in equation 1. The volumetric storage capacity of a tank $V_{\text{st,tank}}$ filled with an adsorbent with capacity $V_{\text{st,cryst}}$ is governed by equation 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.

$$f = \frac{\rho_{\text{bulk}}}{\rho_{\text{cryst}}} \quad (1)$$

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

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

Experiments with MOFs in powder form have demonstrated crystalline storage capacities up to 161 g/L for HKUST-1 (reported as 225 cm³

STP/cm³ 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 equation 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 ($V_{st,cryst} = 133$ g/L, $\rho_{cryst} = 0.987$ g/cm³ [8,23]) has a bulk density of 0.4 g/cm³ (when sold as Basolite ® A100). 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 V/V) from a tank. This material has a tank storage capacity of 126 g/L (reported as 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/m³/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 grams of mixture were placed inside a 8.89 cm ID, steel, cylindrical, compaction die (see Figure 1) at ~27 °C in 100 gram 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 minutes at 305 °C and then the die was allowed to cool for ~16 hours while mechanical stress was maintained. Stress was applied with a metric ton press. Multiple green bodies were produced in parallel by maintaining the stress in multiple dies with the screws shown in Figure 1.

FIGURE. 1. The disassembled (left) and assembled (middle) die is shown here. A picture of one of the finished monoliths is also shown (right).

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 reached 700 °C/min where the temperature was maintained for 90 minutes before being allowed to cool naturally. The potentially harmful products of the carbonization (i.e. HCl, and the salts formed by its reaction with steel) were captured in a series of traps (0 °C, soda lime, and -78.5 °C.) Monoliths were then machined so that they could fit into the chambers of the flat panel tank. The size of the compaction die and machining of the monoliths were tailored to produce monoliths slightly smaller than the tank chambers. Several of these monoliths were measured independently to confirm quality control during synthesis. In order to compare structural characteristics, one of these monoliths was chosen as a representative sample and named Monolith-311.

2.3. Heat of Adsorption

In this work, the isosteric heat of adsorption was measured with the method of isosteres and equation 4 where R is the gas constant, T is temperature, and P is the pressure at which a constant number of molecules are present in the adsorbed state across adsorption isotherms measured at several temperatures.

$$\Delta H_{\theta} = R \frac{\partial \ln(P)}{\partial \left(\frac{1}{T}\right)} \quad (4)$$

In this work, isotherms at 273 K and 296 K were collected to compute the heat of

adsorption. For more details regarding these measurements, see the supplemental material.

3. Results

3.1 PAC and Monolith Performance and Structure

FIGURE. 2. Subcritical nitrogen isotherms are shown here for MWV-0260 and MSC-30. The black, solid data points correspond to the bottom logarithmic, x-axis and the red, open data points correspond to the top linear x-axis.

FIGURE. 3. The pore size distribution and cumulative pore volume (top right) for MWV-0260 and MSC-30 are shown here. The subcritical nitrogen isotherms featured in Figure 2 were analyzed using quenched solid density

functional theory (QSDFT)[37,38] to produce the plots shown here.

Material pore structures were characterized by collecting subcritical nitrogen isotherms using a Quntachrome Autosorb 1 C. MWV-0260 was found to have a specific surface area of 2600 m²/g (BET) while maintaining a relatively low specific pore volume of 1.54 cm³/g. For comparison, a commercially available material called MSC-30 was also analysed. MSC-30's specific surface area and pore volume is 2800 m²/g and 2.08 cm³/g respectively. The BET surface area of MSC-30 was computed over the pressure region 0.008 < P/P₀ < 0.033). MWV-0260's pores are much narrower than those of MSC-30 with 67% being less than 15 Å in diameter compared to 44% for MSC-30 (see Figure 3). Narrower pores display a significant overlap of the van der Waals potentials that extend from each pore wall[12,27,39,40]. This leads to MWV-0260's higher volumetric storage (see Figure 4.)

FIGURE. 4. The gravimetric (left axis and black

symbols) and volumetric storage capacities (right axis and red labels) of the adsorbents are shown here. The volumetric storage of a compressed gas is also shown. The gravimetric and volumetric storage capacities of Monolith-0311 are represented by one set of black/red triangles. MSC-30's gravimetric storage is not shown in order to emphasize the other materials.

FIGURE. 5. The gravimetric excess adsorption for MWV-0260 and MSC-30 are shown. The difference between gravimetric excess and $\rho_{\text{gas}}/\rho_{\text{skeletal}}$ can also be deduced so one may see the improvement in storage due to excess adsorption (see the first term in equations 5 and 6.)

The volumetric and gravimetric storage capacities in Figure 4 are given by equations 5 and 6 respectively. G_{ex} is the gravimetric excess adsorption[41]. For powders the pore volume was determined by measuring the subcritical nitrogen uptake at $P/P_0 = 0.995$ (see Figure 2). For monoliths ρ_{cryst} was determined by measuring the mass and

external dimensions of the adsorbent. The skeletal density of the materials produced and featured herein was determined to be 2 g/cm^3 via helium pycnometry (see the supplemental material.)

$$V_{\text{st,cryst}} = \left(G_{\text{ex}} - \frac{\rho_{\text{gas}}}{\rho_{\text{skeletal}}} \right) \rho_{\text{cryst}} + \rho_{\text{gas}} \quad (5)$$

$$G_{\text{st,cryst}} = \left(G_{\text{ex}} - \frac{\rho_{\text{gas}}}{\rho_{\text{skeletal}}} \right) + \frac{\rho_{\text{gas}}}{\rho_{\text{cryst}}} \quad (6)$$

The data in Figure 6 shows that Monolith-0311 has a similar pore structure to its precursor MWV-0260. The specific pore volume decreased slightly during the monolith production process from $1.54 \text{ cm}^3/\text{g}$ to $1.45 \text{ cm}^3/\text{g}$ due to minor pore clogging in $7 \text{ \AA}$ pores (see Figure 6). This small decrease in pore volume led to a slight increase (decrease) in volumetric (gravimetric) storage as the excess adsorption experienced little change as would be expected in adsorbents with similar pore structure (see equations 5 and 6, and Figures 4 and 5.) The flow of methane in and out of the monoliths is aided by the monolith's mesopore volume [30] that can be observed in Figure 6.

The storage capacity of PACs that is shown in Figure 4 is the crystalline storage capacity while those of the monoliths are defined by the external dimensions and thus include any internal void space that may be present. One of the principle findings of the work was the creation of an AC monolith (Monolith-0311) with a tank volumetric storage equivalent to the crystalline volumetric storage of its

precursor PAC (MWV-0260, see Figure 4). This is equivalent (in terms of storage capacity) to packing a tank with a packing fraction of 1 (see equations 1 and 3.) The average volumetric performance at 296 K and 35 bar for the 40 kg of monoliths created was 109 g/L based on volumetric adsorption measurements (method previously described by Gross [42]) carried out on 10% of the material produced. Monolith-0311 represents the aforementioned 10% in the figures below.

FIGURE. 6. The pore size distributions and cumulative pore volumes are shown here.

FIGURE. 7. Subcritical nitrogen isotherms

for precursor PAC (MWV-0260) and the monoliths from that precursor (Monolith-0311) are shown here.

3.2. Isosteric Heat of Adsorption

Adsorption is an exothermic process, releasing heat during charging and absorbing heat during discharging. For a real world system, excess heat will need to be dissipated from the tank in proportion to the amount of adsorbed gas. The isosteric heat of adsorption for Monolith-0311 was determined to be less than 19 kJ/mol at 1 bar and greater than 16 kJ/mol at pressures up to 20 bar (see Figure 8). Between 0-35 bar, the weighted average (weighted by storage capacity) is approximately 17.4 kJ/mol. Though the isosteric heat should decrease slightly with increasing pressure, these values may serve as a benchmark to engineer storage tanks for optimal thermal conductivity.

FIGURE. 8. Isosteric heat of adsorption for Monolith-0311 is shown on the left axis in red. The temperature dependence of the volumetric

storage (i.e. a difference of 17 g/L at 28 bar) is shown on the right. Without thermal management during adsorption and desorption, the amount of gas stored (delivered) will be reduced by heating (cooling) in accordance with the isotherms in Figure 8.

3.3. 40 L Flat Panel ANG Performance

In addition to the previously mentioned volumetric measurements, a flat panel tank assembly (FPTA) was created to measure the temperature, pressure, and gas flow behavior of 20 kg of the monoliths inside of a 40 L conformable, flat panel tank. Here the volumetric performance was found to be 105 g/L (157 V/V) at 35 bar and 296 K with a mass flow meter meaning that the monoliths filled 94% of the internal tank volume. At 43 bar the volumetric storage capacity is 114 g/L (172 V/V). In this work, V/V is defined by the ideal gas law at 1.01325 bar and 20 °C i.e. 0.04157 mol/L.

In Figure 9, the discharge flow rate data is shown. Desorption cooled the tank to ~0 °C leading to a nonzero flow rate at atmospheric pressure. The nonzero flow is due to heat transfer into the system from the surroundings. Under such conditions, the discharge flow rate will decrease proportionally with the adsorbent's binding energy and increase with the rate of heat transfer. For an automobile going 60 mpg

with a fuel economy of 30 mpgge, 1.5 kW would need to be transferred to the adsorbent to discharge isothermally.

FIGURE. 9. The discharge flow rate from an ANG tank is plotted as a function of tank capacity in gallons of gasoline equivalent (gge) and pressure. It was assumed that the delivery flow rate from our 1.6 gge ANG system would scale with tank capacity to predict the delivery flow rate for the larger systems plotted (e.g. the 25 gge data in the plot.) 86 g/min corresponds to a vehicle traveling at 60 mph getting 30 mpgge. The ANG flow rate is primarily reduced by a 2-micron filter, check valve, and a 2 mm flow control orifice. Estimates regarding these restrictions suggest that the system was experiencing choked flow downstream from the adsorbent. The filter, check valve, and orifice have a combined flow coefficient of 0.054 (gallons/minute)[43]. An 8.5 minute, “fast fill” supplied by buffer storage (see Figure 10 for the system state)

resulted in a volumetric storage capacity of 80 g/L (120 V/V). During this experiment, the storage capacity was determined by weighing the tank after the aforementioned 8.5 minutes. Within 2 minutes of the start, the temperature at the center of the tank was 120 °C (see Figure 11.) These high temperatures during adsorption ultimately led to the observed reduction in storage capacity[30–32]. Before entering the tank the methane was cooled via adiabatic expansion to an average temperature of −11 °C.

The pressure inside the buffer storage tanks (data not shown) shows that roughly half of the total amount of methane flowed into the tank within the first 45 s. The temperature data in Figure 11 shows that the thermal response at the center of the tank trails the pressure at the tank inlet by less than 3 s demonstrating that methane is able to reach throughout the tank almost instantaneously. This demonstrates that the amount of methane that can be rapidly stored is limited by the tanks ability to dissipate the heat generated due to adsorption and that the flow of methane into and around the monoliths is largely unrestricted.

FIGURE. 10. A schematic of the FPTA is shown here. Green signifies a path that gas can flow through while red signifies a closed path. The “fast fill” state is shown in which methane bypasses the mass flow meter and flows directly into the flat panel ANG tank from buffer storage. The check valves force gas to flow the correct direction through the flow meter during adsorption (bypassed during fast fill) and desorption. The FPTA can also operate with NG. The NG compressor is off during fast fill experiments and internal check valves in the NG compressor prevent backflow.

FIGURE. 11. The pressure and temperature of flat panel tank during and after the 8.5 minute fill are shown here. The inflection points in pressure data are due to input from experimenter with flow being stopped at the inflection point shown at 8.5 minutes. Data was recorded every 3 s. The pressure and temperature during the first 24 s of the experiment is shown in the lower right.

FIGURE. 12. The steel, 40 L, flat panel tank with a machined monolith (i.e. the monolith was cylindrical prior to machining) is shown here. The small gap for convective, axial flow around the monoliths is featured. Convective, radial flow occurs in surface roughness gaps between successive monoliths (not shown).

FIGURE. 13. A photo of the FPTA is shown here. The flow meter/controller, electro-pneumatic valves, data acquisition & recording, and methane detectors are controlled with a LabVIEW user interface.

4. Discussion and Conclusion

The deliverable amount of methane with a sufficiently high flow rate is perhaps the most important performance metric for this application. The deliverable amount from an ANG system will be determined by the difference in storage capacity between the maximum operating pressure and the minimum operating pressure. While the ARPA-E targets call for a minimum engine inlet pressure of 70 psig (5.8 bar), they also call for the mitigation of “methane losses stored below 70 psig[44,45]”. In this work we assume that the losses have been mitigated elsewhere. Because of this we have opted to define deliverable capacities between 35-1 bar. This relatively low delivery pressure (1 bar) will especially benefit high binding energy, narrow pore, carbonaceous adsorbents.

For adsorption in carbonaceous materials, the binding energy is greatest in sub 1 nm pores where the potential from both pore walls can overlap[12,27,39,40]. In addition to reduced working capacity, increased binding energies will also reduce the desorption flow rate in real systems (i.e. non-isothermal) for a fixed heat transfer rate because of the additional heat per mole of gas that is required for desorption (see Figure 9 and the surrounding text). Lastly, a lack of mesopore volume (pores larger than 1 nm) will lead to slower

diffusion of gas through the adsorbent. All of these factors will reduce the effective working capacity for applications that require a large minimum flow rate.

For comparison with the featured material, an adsorption isotherm for a monolith (A3-48, data from Marco-Lozar et al[15]) with a pore volume that is almost exclusively composed of pores that are less than 1 nm[15] is shown in Figure 14. This isotherm is steep at low pressure which has the effect of a reduced deliverable capacity. The volumetric delivery between 35-1 bar is shown graphically on the left side of Figure 14 for both A3-48 and Monolith-0311. The Redlich Peterson Isotherm model[46] was used out of convenience to fit the isotherms and extrapolate the A3-48 data[15] from 30 bar to 35 bar so that the delivery could be estimated graphically. The deliverable capacity of Monolith-0311 is 151 V/V.

FIGURE. 14. Volumetric and gravimetric storage and delivery comparisons between the monoliths created here (Monolith-0311) and a

FIGURE. 15. Tank gravimetric and volumetric storage capacities from literature and from this work are shown here. Squares represent monoliths and circles represent powders. Red stars represent MU samples discussed here, blue represents MOFs, and black represents activated carbons made elsewhere. All of the data quoted here was taken near 35 bar and 25 °C with precise conditions, values, and references reported in Table 1.

The results for NaOH activated Anthracite in Figure 15 and Table 1 suggest that it is the best material reported in literature due to high volumetric and gravimetric storage capacities. However, the need for mechanical stress to be applied to the sample for this level of storage

to be achieved is an additional constraint whose implications need to be understood. The vessel holding this material will have to be capable of sustaining the internal stresses brought on by the mechanical stress applied to the sample. At 98 bar of methane pressure, Monolith-0311 stores 159 g/L. In addition, AGLARG[47] was unable to achieve the same PAC packing density with their adsorbents when going from the mL to L scale. Lastly, applying a uniform mechanical stress of 98 bar may not be economically feasible for many large scale applications. Pellets made of AX-21 produced by Bose et al[48] are 9% better than the MU materials volumetrically but 24% worse gravimetrically. For light duty vehicle applications, this would add about 50 kg more adsorbent to a vehicle with a 10 gge tank meaning this vehicle's fuel economy would be 1-2% worse^I than one with MU materials. Due to its large density and as a result, low pore volume, the AX-21 pellets would need to have a pore size distribution similar to A3-48 (sub 1 nm pores) to achieve this level of volumetric storage which suggests that the deliverable storage will drop considerably due to the shape of the isotherm, slow diffusion through the material, and large binding energy/temperature swings during charging and discharging.

^I U.S. Dept. of Energy, <http://www.fueleconomy.gov/feg/driveHabits.jsp>, Accessed 9/19/2014, 2014.

Table 1. The tank storage capacity data shown in Figure 15 is listed along with the measurement conditions and the source of the results here.

Description	Ref.	P (bar), T (°C)	$V_{st,tank}$ (g/L)	$G_{st,tank}$ (g/kg)
Monolith-0311	This Work	35, 23	113	195
FPTA (40 L tank measurement of MU monoliths)	This Work	35, 23	105	199
2.5K-700 PAC	[27] (tap density; this work)	35, 23	85	224
NaOH and Anthracite PAC, after a mechanical stress of 98 bar	[11,17]	35, Room Temp	126	189
AX-21 Pellet	[48]	34.5, 25	123.3	148
A3-48 Monolith	[15]	30, 25	110	138
AGLARG AC Monolith	[47]	35, 25	98	163
CFC74, Steam Activated Carbon Fiber	[13]	40, 25	110	148
H KUST-1 Tablet	[8,49]	35, 30	67	116
MIL-53	[8,23]	35, Room Temp	55	137
Basolite C300 (H KUST-1 powder)	[50]	35, Room Temp	78	99
Ni-MOF-74 Compacted powder	[24]	34, 30	66	85

The inherently low density of methane has been overcome to the greatest extent with the monolithic adsorbents developed and tested in this work. By binding a precursor PAC with 33% PVDC, an effective packing fraction of ~1 with minimal pore clogging was achieved. The precursor PAC was selected because of its large crystalline volumetric storage capacity in the presence of mesopores which aid in the deliverable storage capacity and flow kinetics of the resulting monolith. The production of 40 kg of monoliths and the testing of 20 kg in a 40 L system has also demonstrated the potential for real world applications. The results from the 40 L system were consistent with those collected on the individual monoliths. The results also demonstrate a lack of significant flow restrictions within the adsorbent bed as methane was able to reach the center of the tank within 3 s of the pressure being applied.

^{II} Sigma-Aldrich, Basolite A100, <http://www.sigmaaldrich.com/catalog/product/aldrich/688738?lang=en®ion=US>, Accessed 6/9/2015, 2015.

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Notes and References

^d The crystalline storage capacity was taken from Mason et al[8]. The tank storage capacity was calculated using equation 3 and a bulk density of 0.4 g/cm³ (which is reported for Basolite ® A100^{II}).

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