



# A pilot study of activated carbon and metal–organic frameworks for methane storage



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## HIGHLIGHTS

- CH<sub>4</sub> storage of 2 metal–organic frameworks (MOF) and 1 porous carbon (AC) was tested.
- Samples were studied in a new 3 L testing vessel and on ~1 g samples.
- Results from the two measurements agreed well.
- The AC showed a higher heat-transfer rate than the MOFs.
- A correlation between intergranular porosity and gas flow velocity was proposed.

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## ABSTRACT

The methane storage of an activated carbon and two metal–organic frameworks (Cu<sub>3</sub>(btc)<sub>2</sub> and Al(OH) Fumarate) are compared for laboratory scale (~1 g of material) to pilot scale measurements (~1.5 kg of material). Excess adsorption and volumetric storage capacity uptakes agreed well between the two measurements. By decomposing the volumetric storage capacity into the contributions from the gas and adsorbed phases, the volumetric storage was evidenced to be dominated by the excess adsorption up to 100 bar. The volumetric storage is a function of both the excess adsorption uptake and the material's bulk density. The AC shows higher heat transfer rates than the metal–organic frameworks upon adsorption indicating a superior thermal conductivity. The mean flow velocity has been estimated from the pilot scale measurements and is discussed as it will strongly influence the adsorbed natural gas technology performance.

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## 1. Introduction

Since 1995, the United States has seen more than a fivefold increase in the amount of natural gas (NG) used in motor vehicles [1]. The low energy density of NG at atmospheric pressure (lower heating value of 0.031 MJ/L) compared to gasoline (32.2 MJ/L) requires that natural gas be stored at high pressure [2]. Compressed natural gas (CNG) vessels are thus constrained in their geometry, typically cylindrical. There are definitely benefits and compromises to having a CNG powered car as an alternative to gasoline. Compared to gasoline, CNG burns more cleanly and it provides similar fuel economy, performance, and drivability. Natural gas refueling, however, can be problematic as public access

to CNG filling stations is scarce and not available in some areas. Moreover, the trunk capacity is reduced to give space to bulky pressure vessels. Low pressure solutions such as adsorbed natural gas (ANG) storage systems could enable more widespread use of home refueling options and the capability of using conformable tanks. Ideas surrounding ANG storage systems have been around for quite some time, but research and development on the technology has ramped up with the discovery of potentially better performing adsorbent materials [3–8].

Adsorbent materials with a high surface area to volume ratio have been suggested as a medium for low pressure gas storage [5,9,10]. Because NG is supercritical above approximately –80 °C (depending on the exact composition [11]), it cannot be liquefied by increasing the pressure. In the presence of an adsorbent material, a high density monolayer forms on the adsorbent surface allowing for an increased storage capacity compared to compressed natural gas at same pressure and temperature ( $p, T$ ) operating conditions.

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Adsorbent materials performance evaluation and comparison are typically performed at laboratory scale on small amounts of materials (<1 g). Excess methane adsorption uptake is measured and the storage capacity, *i.e.* the total adsorption, is calculated from the excess adsorption and the material density. If the ANG technology is to be used for light duty vehicles, the storage vessel will be filled with kilograms of materials. By using measurements on small samples to predict the behavior of larger samples, we are assuming that the materials are completely homogeneous and that scaling-up the material synthesis does not significantly alter the adsorbent's properties. Thus it is essential to assess the behavior of the adsorbent materials at larger scale.

A first step to validating our assumption and projecting an adsorbent from the laboratory into the application is to complete a pilot study with near-industrial scale batches of adsorbent materials. Very few real-conditions vehicle demonstrations have either been conducted or are ongoing. The Atlanta Gas Light Adsorbent Research Group (AGLARG) tested shaped activated carbon monoliths in a flat panel storage tank in 1997 [12]. The University of Missouri also tested a storage system based on cylindrical carbon monoliths on a Kansas City, MO municipal vehicle [13]. Additionally, metal–organic frameworks (MOF) are currently being tested by BASF in a class 8 truck [14] and EnerG2 is partnering with Portland NW Natural, a gas distribution company, to evaluate advanced nano-structured activated carbon [15].

These vehicle level experiments cannot be avoided because they give significant information not only about the adsorbent material performance under real operating conditions but also about the overall ANG technology including the storage system. However, these experiments require very specific instrumentation set up to collect meaningful data and consequently significant monetary investment. These vehicle level demonstrations cannot be done systematically on each potential adsorbent, so pilot scale experiments can be a good compromise. There have been some laboratory studies that are designed to look at large scale properties of adsorbents such as gas discharge thermal properties [16,17], adsorbent performance during cycling [18], or used adsorption models to predict gas storage [19,20]. However, to the knowledge of the authors, no significant study has been published for adsorbed natural gas storage on large samples of metal–organic frameworks in a laboratory setting.

The purpose of this investigation is to demonstrate the scalability of adsorbents for natural gas storage without significant monetary and time investments in vehicle level testing. As a first study, we have selected three benchmark adsorbent materials that are of interest to natural gas storage: the MOF  $\text{Cu}_3(\text{btc})_2$  [8], the MOF Al(OH) Fumarate [21], and an activated carbon [22]. Because of the unique design of our experiment, mass and thermal transport properties were evidenced which would be impossible to demonstrate on a single, typical adsorption laboratory experiment.

Here the adsorption of methane, the main component of NG, on the three materials named above is investigated. We compared adsorption and material density measurements on small samples (~1 g) to measurements on ~1.5 kg of adsorbent material. To measure the 1.5 kg samples, we have used a new instrument that allows for temperature measurement at different points throughout the samples. This unique instrumentation setup allows for characterizing of the dynamic adsorbent properties that are not typically measureable on small samples.

## 2. Materials and methods

### 2.1. Materials

The materials investigated were a high surface area activated carbon (AC) (~2600 m<sup>2</sup>/g) and the metal–organic

frameworks (MOF) Al(OH) Fumarate and  $\text{Cu}_3(\text{btc})_2$  (btc = 1,3,5-benzenetricarboxylate). All materials were synthesized as indicated in our previous study [22], with the exception of the size of the synthesis batch. All materials were obtained from near-industrial scale batches. We have chosen these particular materials because they are of interest in natural gas storage, they represent a diverse variety of pore structures and surface chemistries, and they are available at the size of our target volume (~3 L). All of the materials were in powdered form.

### 2.2. Instrumentation and measurement procedure

Two types of measurements were performed, known here as laboratory scale and pilot scale measurements. The laboratory scale measurements refer to measurements on small samples (approximately 1 g or less) while pilot scale measurements refer to measurements in a 3 L pressure vessel on a large sample (greater than 1 kg).

#### 2.2.1. Laboratory scale measurements

Methane adsorption isotherms were measured up to 100 bar on a custom-built adsorption instrument described previously [23]. This instrument is capable of measuring adsorption isotherms up to 300 bar, but such high pressure isotherms were not required for comparison to the pilot scale measurements (see Section 2.2.2). The pressure was measured with three transducers with scales of 1000, 3000, and 5000 psi and uncertainties of 0.4, 1.2, and 2 psi respectively. The sample and reservoir temperatures were measured using two *t*-type thermocouples.

The skeletal density was measured on the same instrument using helium as a non-adsorbing gas. Subcritical argon adsorption isotherms were measured at 87 K using a Quantachrome Autosorb-1. The pore volume was determined from the argon adsorption isotherms at a pressure of 0.995  $p/p_0$ . The bulk densities were measured using a Micromeritics GeoPyc 1360 tap density analyzer using a compression force of 8 N (0.6 bar).

Prior to measurement, all samples were degassed under 10<sup>-5</sup> mbar vacuum for 24 h at 150 °C for the AC and 100 °C for the MOFs. After degassing, the samples were transferred to and stored in an argon glove box. All measurements were completed without exposing the materials to the laboratory atmosphere.

#### 2.2.2. Pilot scale measurements

For the pilot scale measurements, the methane adsorption isotherms, skeletal density, and bulk density measurements were all completed on a custom-built adsorption instrument. The instrument is a volumetric type adsorption instrument with a 3.07 L sample chamber and a 2.5 L reference volume. A schematic representation of the setup is found in Fig. 1. The temperature of the reservoir was monitored using a resistance thermometer (RTD) placed on the outside of the reservoir. A total of seventeen RTDs were placed within the sample cell at various positions. A quarter-turn, high flow coefficient plug valve was used to dose the sample from the reservoir. As the powder was added to the sample cell, the sample cell was agitated periodically to remove larger voids in the powder. The entire sample cell was filled to its maximum capacity. The activated carbon and Al(OH) Fumarate were added to the sample cell in the laboratory atmosphere. The  $\text{Cu}_3(\text{btc})_2$  was added in an argon glove box. The materials were degassed at room temperature for 24 h prior to each adsorption measurement.

The bulk density was determined using the measured sample mass and the usable volume of the sample cell (3.07 L). Additional details on the pilot scale isotherm measurement and instrument calibration may be found in Appendices A and B respectively.

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