Adsorbed methane storage for vehicular applications

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HIGHLIGHTS

- Methane storage of 5 materials were studied at ambient temperature up to 250 bar.
- Materials were evaluated for use in a 110 L pressure vessel.
- At low pressure, all materials can deliver more fuel than compressed methane.
- At 250 bar, only high skeletal density materials outperform compressed methane.
- Activated carbon in a 50 bar, 110 L tank could have a driving range of 140 miles.

ARTICLE INFO

ABSTRACT

The methane storage properties of five benchmark high surface area adsorbent materials were studied at ambient temperature and up to 250 bar service pressure. Using adsorption and sample density data, we evaluated the potential of these materials to store methane in a 110 L pressure vessel. At 50 bar, the adsorbent materials significantly outperformed traditional compressed gas storage. Two materials, an activated carbon and a copper based metal–organic framework (Cu-BTC), also showed improvement over compressed gas storage at 250 bar. Driving ranges calculated from storage data show that with an adsorbent, a 110 L tank filled to 50 bar could have a driving range of up to 140 miles, more than three times the range offered by a plug-in hybrid electric vehicle when operating as a pure battery electric vehicle.

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1. Introduction

Recent improvements in natural gas extraction coupled with an increase in gasoline prices has driven a renewed interested in natural gas vehicles (NGV) (Fig. 1) [1–3]. NGVs in North America typically store natural gas (NG) in cylindrical containers at 250 bar. Because 250 bar CNG's energy content per unit of volume is approximately one third of gasoline, a CNG fuel tank must be three times larger than a gasoline tank to allow a vehicle the same driving range. Because CNG tanks are cylindrical, their conformability factor, defined by the outer tank volume divided by the enclosing rectangular cuboid volume, is about 50–60%. This leads to some wasted space, especially when the pressure vessel is installed within the trunk of a vehicle. The sparse distribution of NG filling stations in the US [4] compounded with the price and availability of compressors for at-home refueling limits the widespread use of compressed natural gas (CNG) in the US to light-duty trucks and larger vehicles.

Because NG is supercritical and cannot be liquefied at ambient temperature, high-surface area adsorbents have been proposed as an alternative method for storing NG [5–7]. In the presence of a gas, a high-density film develops on the surface of an adsorbent. An adsorbed natural gas (ANG) tank has the potential to store more gas at a lower pressure than CNG because of this higher density adsorbed film. A lower operating pressure opens the door for more conformable (>90% conformability factor) non-cylindrical storage tanks and new options for home refueling.

While conformable tanks with ANG materials may (or may not) be the future of natural gas storage, it can take years for a new tank design to be certified by the National Traffic Safety Board [8]. A logical first step to make an ANG tank commercially available is to take current 250 bar CNG technology and simply add an adsorbent. However, most research in other laboratories has focused on low pressure (<100 bar) storage in adsorbents [9–15] or focused on material adsorption properties only both experimentally [16,17]

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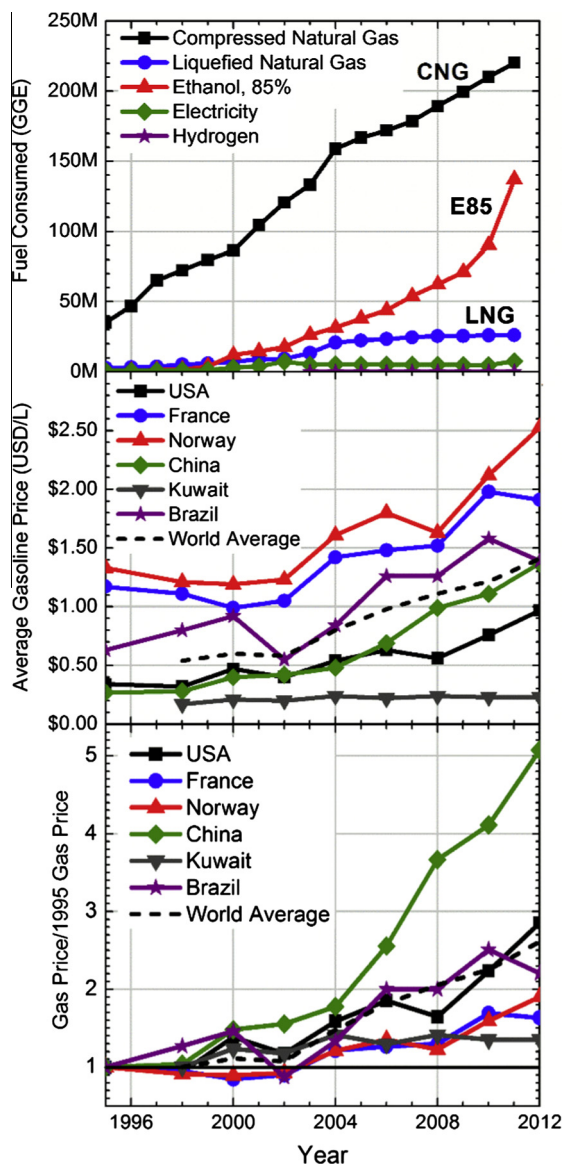   E-mail addresses: matthew.beckner@gm.com, beckner.matthew@gmail.com (M. Beckner).

Fig. 1. (top) Alternative fuel usage in the United States from [2] (millions of GGE). For comparison, gasoline (petrol) consumption in the United States ranged between 117 and 134 billion gallons per year between 1995 and 2012 [1]. (middle) Historic gasoline prices as reported by the World Bank [3] showing the price increase in non-oil-exporting countries over the last decade. (bottom) Graph showing the ratio of the gasoline price to the gasoline price in 1995 to show the relative price increases.

and theoretically [18]. It is also common for researchers to calculate material storage capacity using a material's crystal density. Using the crystal density gives an idealized maximum storage capacity as the crystal density does not include space between adsorbent powder grains, the inter-granular pore space. This can lead to significant differences between a calculated storage and the storage of a real tank [19].

To this end, we have investigated the adsorption of methane, the main component of NG, on several benchmark adsorbents up to 250 bar. We then combined this adsorption data with measurements of the materials' bulk density, which includes the inter-granular pore space, to calculate the total storage of a 110 L test tank. By using purely experimental data to calculate the packing-independent storage gain of ANG over CNG and estimating the driving range of an ANG vehicle, we have evaluated the efficacy of using adsorbents in a 110 L test tank with the aim of answering

these questions: (1) Does ANG show advantages compared to CNG? (2) What can be learned from current benchmark materials to drive the development of the next generation of storage materials? and (3) Does ANG make home refueling an attractive option to circumvent the problem of public NG station scarcity?

We use the terms ANG and CNG in place of adsorbed methane and compressed methane, respectively, throughout. Natural gas is a gaseous mixture of hydrocarbons consisting predominantly of methane (70–90% for typical composition at the pipeline). In the following study, we are essentially making the assumption that any natural gas has been purified and all non-methane components have been removed before filling the fuel tank.

2. Materials and methods

Five benchmark materials were chosen for measurement: one activated carbon (AC), three metal–organic frameworks (MOFs), and one porous polymer (PP). The AC was a microporous carbon with a specific surface area greater than 2000 m^2/g. The MOFs chosen were $Cu_3(1,3,5$-benzenetricarboxylate$)_2$, Al(OH) Fumarate, and $Zn_4O(1,3,5$-benzenetribenzoate$)_2$ commonly known as Cu-BTC, MIL-88a, and MOF-177 respectively. All MOFs were synthesized via standard reactions [14,20,21]. The PP was a developmental hypercrosslinked polymer (HCP) material produced by Merck. A sample of HCP from a near-industrial scale batch of the material was used for this study. The samples were degassed under 10^{-5} mbar vacuum for 24 h and transferred to an argon glove box prior to any sorption measurements. During degassing, the activated carbon was heated to 150 °C while all other samples were heated to 100 °C.

Excess adsorption isotherms were measured at ambient temperature (~25 °C) up to 250 bar using a custom built volumetric adsorption instrument described previously [22]. Ultra-high purity (UHP) methane was used as the adsorbate (99.999% CH$_4$). UHP methane is not readily available at any pressure greater than 180 bar (2600 psi). A gas booster was added to the instrument to provide the additional pressure to 250 bar (Fig. 2). All samples were massed and loaded into the sample holder in an argon glove box to prevent exposure of the samples to oxygen or moisture. The post-degas mass was used for all calculations. Sample masses ranged from 0.4 g (MOF-177) to 1.1 g. (AC). The skeletal density of each sample was determined on the volumetric instrument using helium expansion assuming that helium was non-adsorbing.

The bulk density was measured for each sample using a Micromeritics GeoPyc 1360 tap density analyzer. The GeoPyc measures the bulk density by compressing a sample of known mass with a plunger to 8.0 N of force (~63 kPa). The volume of the sample is determined by measuring the displacement of the plunger. Since both the sample holder and the plunger are removable from the instrument, the oxygen and moisture sensitive samples could
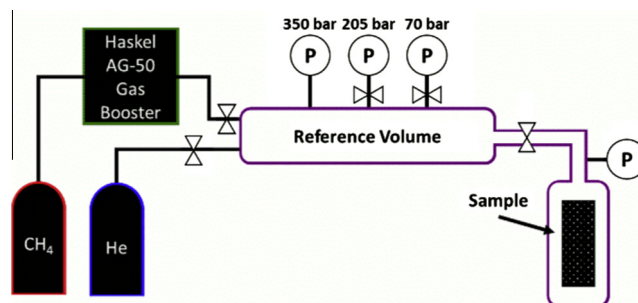

Fig. 2. Custom built Sievert apparatus and set-up schematics for methane sorption measurements up to 250 bar.