# High volumetric and energy densities of methane stored in nanoporous materials at ambient temperatures and moderate pressures

Nuno Bimbo [a], Andrew J. Physick [a], Antonio Noguera-Díaz [a], Adam Pugsley [a], Leighton T. Holyfield [a,b], Valeska P. Ting [a], Timothy J. Mays [a,*]

[a] Department of Chemical Engineering, University of Bath, Claverton Down, Bath BA2 7AY, United Kingdom
[b] Centre for Doctoral Training in Sustainable Chemical Technologies, University of Bath, Claverton Down, Bath BA2 7AY, United Kingdom

## HIGHLIGHTS

- Methane isotherms for 3 materials were obtained from 250 to 350 K and up to 15 MPa.
- Analysis indicates a very high adsorbed density in the pores of the materials.
- Energy densities are 40% of gasoline and equal to methanol.
- All materials have high volumetric working capacities, in excess of $100 \text{ kg m}^{-3}$.

## GRAPHICAL ABSTRACT
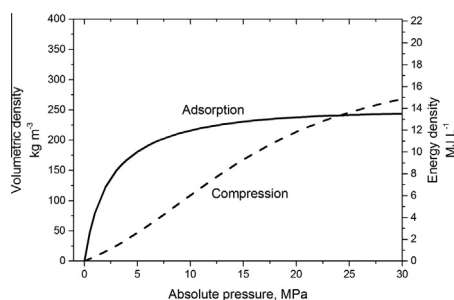
## ABSTRACT

Experimental results for methane adsorption on two high-surface area carbons (TE7-20 and AX-21) and one metal–organic framework (MIL-101(Cr)) are presented, with isotherms obtained at temperatures ranging from 250 to 350 K and at pressures up to 15 MPa. The isotherms were analysed to determine if these materials could be viable alternatives for on-board solid-state storage of methane. The results show a very high adsorbate density in the pores of all materials, which for some can even exceed liquid methane density. At moderate pressures below 5 MPa, the calculated total energy densities are close to the energy density of methanol, and are almost 40% of the energy density of gasoline (petrol). Compared with standard compression at the same conditions, the results show that adsorption can be a competitive storage alternative, as it can offer equal volumetric capacities at much lower pressures, hence reducing the energy penalty associated with compression. It is shown that the optimal conditions for adsorptive methane storage in these materials are at moderate pressure ranges, where the gains in amounts stored when using an adsorbent are more pronounced when compared to cylinders of compressed methane gas at the same operating conditions. Finally, a study on deliverable capacities for adsorbed methane was carried out, simulating two charging pressure scenarios of 3.5 and 6.5 MPa and discharge at 0.5 MPa. The results show that some of the tested materials have high working volumetric capacities, with some materials displaying more than $140 \text{ kg m}^{-3}$ volumetric working capacity for charging at 6.5 MPa and delivery at 0.5 MPa.

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## 1. Introduction

The predicted energy demand in the upcoming decades, mostly from less developed parts of the world, will entail a significant

* Corresponding author at: Department of Chemical Engineering, 9W Building, University of Bath, Claverton Down, BA2 7AY, United Kingdom.
*E-mail address:* t.j.mays@bath.ac.uk (T.J. Mays).

strain on primary energy sources worldwide [1,2]. This has prompted investment in alternative sources of energy, both from governmental and private sources, with renewable sources of energy gaining an increasing share of primary energy conversion [1]. Nowadays, as has been the case for the last two centuries, most of the primary energy comes from fossil fuels, which are finite and will eventually run out. Fossil fuels' popularity is due to their low price and their availability, high volumetric energy content and the ease in converting energy via simple combustion. One interesting and topical fossil fuel is natural gas, which is a mixture whose main component is methane (more than 90% of its molar composition). While it is hard to dispute that natural gas adds to energy security at a very affordable price in countries like the United States, due to the prospect of exploring shale gas reserves in their continental shelf, increasing methane usage as a strategy for mitigation of greenhouse gas emissions has raised several concerns. Despite methane's combustion emitting less carbon dioxide per unit of energy generated than other fuels (methane has the highest ratio of heat of combustion per carbon atom of any hydrocarbon), methane itself is a very potent greenhouse gas, with a global warming potential of 72 if a 20-year horizon is considered (methane has an atmospheric lifetime of 12.4 years) [3], and increased use will mean more emissions of methane to the atmosphere due to leakages [4]. Leakages are not a trivial matter and can mean that methane has a higher environmental footprint than oil or coal [5] and that its impact in coming decades will be minimal and possibly even negative in climate change [6]. Nonetheless, the exploration and production of natural gas and the prospect of producing shale gas mean that, as has been the case for the last decade, natural gas share in the energy mix has been on the rise and is predicted to continue to grow. This is due to its affordability and availability, and to the fact that it has many uses, as in electricity production in combined-cycle natural gas turbines, in domestic applications (domestic heating and cooking in developed countries are very reliant on natural gas) and as a commodity in the chemical industry, where it is a precursor to many chemical products.

Another application of methane gas is as an energy fuel in vehicles. Methane is extremely popular in some parts of the world, along with other alternative fuels like Liquefied Petroleum Gas (LPG), to power internal combustion engines. It is a gas at normal pressures and temperatures, so it has poor volumetric density, which is detrimental for on-board storage in vehicles. In addition, methane storage is a relevant issue outside mobile applications, as it is usually obtained from natural gas and transported as LNG at 111 K and atmospheric pressure. This carries some downsides – large tanks are needed to transport LNG (usually a 70 m diameter tank, 45 m high, which can hold 100,000 m$^3$), which require large and expensive infrastructure [7]. Long term storage is also difficult for LNG, as significant losses occur due to boil-off [7]. Alternatively, natural gas can be compressed at high pressures, with natural gas mixtures rich in ethane and propane compressed at around 12.2 MPa and pure methane gas compressed at twice that pressure (24.4 MPa) [7]. Compression and liquefaction both carry energy penalties and safety issues, so the challenge is to find storage alternatives that are competitive in terms of price and can offer high volumetric densities.

Adsorption of methane in porous materials has been considered as a viable storage alternative precisely because it can increase volumetric densities at moderate conditions [8]. High-surface area materials with porosity in the micropore range can store significant amounts of methane under moderate pressures [9]. The goal is to keep the energy penalty at a minimum, so adsorptive storage should occur as close to ambient conditions as possible, meaning that it will be above its vapour-liquid critical temperature of 190 K. It has been suggested that high capacities for methane adsorption are a result of a complex interplay of factors, including BET surface areas, enthalpies of adsorption and pore morphologies and distributions [10]. A number of recent reviews highlighted the main materials challenges, which include purity of methane gas, kinetics and enthalpies of the system [11–14]. The kinetics can be an issue since short charging and discharging times are needed. The thermodynamics of the system mean that high enthalpies are beneficial for room temperature methane storage, although they also mean that adsorption of methane will release heat into the system. Adsorption is highly sensitive to temperature, so the thermal management of the storage system becomes an issue. It has been reported that, for storage and delivery of methane at 3 and 0.15 MPa, respectively, the optimum temperature for storage in porous carbons is 254 K and the optimum enthalpy change is 18.8 kJ mol$^{-1}$ [15]. It has also been recently observed that methane adsorbed at high pressures in a zeolite template carbon can have an increasing isosteric enthalpy with coverage [16].

Many adsorbent materials have reported high volumetric and gravimetric methane uptakes at moderate pressures and ambient temperatures. The materials that have showed the highest gravimetric and volumetric uptakes for methane at ambient temperatures and moderate pressures are summarised in Table 1.

In this work, experimental isotherms measured at temperatures from 250 to 350 K and at pressures up to 15 MPa for the activated carbon AX-21, metal–organic framework MIL-101 (Cr) and activated carbon beads TE7-20 are presented, with the analysis of the results showing high adsorbate densities. The optimum conditions for adsorptive storage and the working capacities for all three materials were also determined.

## 2. Experimental and modelling methodology

The materials used in this work are the activated carbon AX-21, the metal–organic framework MIL-101 (Cr) and the activated

**Table 1**
Methane gravimetric and volumetric uptakes for different materials. Except where otherwise noted, uptake refers to excess amount.

| Material | Volumetric uptake | | Gravimetric uptake | Temperature | Pressure | References |
|---|---|---|---|---|---|---|
| | kg m$^{-3}$ | cm$^3$ cm$^{-3}$ | wt.% | K | MPa | |
| PCN-14 | 163[a] | 230[a] | 18.7[a] | 290 | 3.5 | [17] |
| PCN-61 | 102 | 145 | 18.6 | 298 | 3.5 | [18] |
| PCN-68 | 78 | 99 | 18.6 | 298 | 3.5 | [18] |
| NOTT-109 | 139[a] | 196[a] | 17.6[a] | 300 | 3.5 | [19] |
| NU-111 | 145[a] | 205[a] | 36.0[a] | 298 | 6.5 | [20] |
| DUT-23 (Co) | 107 | 152 | 26.8 | 298 | 10 | [21] |
| DUT-49 | 167 | 236 | 30.8 | 298 | 11 | [22] |
| HKUST-1 | 160[a] | 226[a] | 18.4[a] | 298 | 3.5 | [23,24] |
| MOF-210 | 119[a] | 84[a] | 47.6[a] | 290 | 3.5 | [25] |
| MIL-101 (Cr) | 96 | 135 | 21.8 | 303 | 6 | [26] |
| AX-21 | 109[a] | 154[a] | 22.3[a] | 298 | 3.5 | [11] |

[a] Calculated total amount.