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Letter

Deliverable Capacity of Methane: Required Material Property Levels for the Ideal "Holy Grail" Adsorbent

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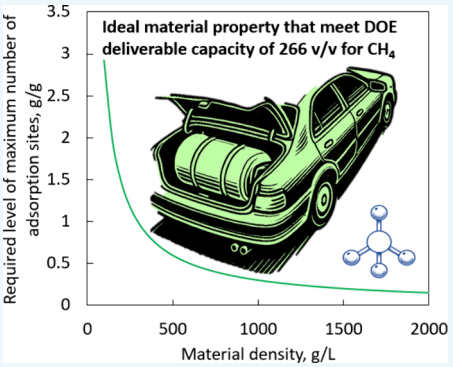
ABSTRACT: The Langmuir isotherm is used to determine the properties of a theoretical "holy grail" adsorbent that can meet the US Department of Energy's methane storage target of 0.5 g/g and 266 v/v. For a storage tank operating between 5 and 65 bar, the adsorbent requires a maximum adsorption capacity of 0.8388 g/g, a binding affinity of 0.05547 bar^{-1}, and a material density of 377 g/L. For a tank operating between 5 and 80 bar, the binding affinity should be 0.05 bar^{-1}, with the same capacity and density. The Langmuir isotherm is also applied to calculate the necessary adsorbent properties, including the number of adsorption sites and binding energies, to achieve the volumetric storage target of 266 v/v based on the material's density.



Methane is regarded as a promising and environmentally friendly alternative to gasoline due to its availability and clean-burning properties.[1−4] Natural gas offers several advantages over conventional fuels, and adsorption at ambient temperature is considered to be an effective and safe method for onboard methane storage. Current standards call for adsorbent materials capable of delivering up to 266 v/v at standard temperature and pressure. The US Department of Energy's (DOE) "Methane Opportunities for Vehicular Energy (MOVE)" program has set a target of 266 v/v and 50 wt % to store and release sufficient methane for long driving distances, such as cross-country journeys.[5] Since methane is supercritical at 298 K and cannot be liquefied, achieving the 266 v/v target requires high pressure, with storage pressures ranging from 65 to 80 MPa and a delivery pressure of 5 bar.[6,7] Researchers aim to meet these deliverable capacity targets by determining the required binding affinity of adsorbent materials. In this work, theoretical calculations are presented to identify the necessary material properties, including the concentration of adsorption sites as a function of material density, to meet the DOE's methane deliverable capacity targets.

Theoretically, higher the binding energy higher will be the adsorption capacity at higher pressures, but higher affinity will favor increased adsorption at delivery pressure (5 bar).[8−10] This means higher affinity though favors the adsorption capacity at higher pressures; it will penalize the deliverable capacity. If the binding affinity is lower, the adsorption will be low at both delivery pressure and storage pressure, and again, this will limit the deliverable capacity. Thus, there must exist an optimal binding affinity that will ensure the required level of deliverable capacity of 266 v/v, operating between a storage pressure, p_1 and delivery pressure, p_2. A Langmuir isotherm can be used to determine this crucial material design parameter. A Langmuir isotherm can be used to determine the required level of binding affinity in an adsorbent. The Langmuir isotherm is given by[11]

$$q = q_m k_L p / 1 + k_L p \tag{1}$$

where q is the amount adsorbed at equilibrium expressed in terms of grams of methane adsorbed per gram of adsorbent, p (bar) is the pressure at equilibrium, q_m is the maximum adsorption capacity usually expressed in terms of g of methane adsorbed/g of adsorbent, k_L is a parameter related to the affinity of the adsorbent and expressed in terms of 1/bar.

If the storage tank is operated between the delivery and storage pressures of p_1 and p_2, respectively, then the deliverable capacity, D_{cap} can be calculated using the Langmuir isotherm as follows.[12]

$$D_{cap} = \frac{q_m k_L p_1}{1 + k_L p_1} - \frac{q_m k_L p_2}{1 + k_L p_2} \tag{2}$$

For a storage tank operating between p_1 and p_2, the D_{cap} will be at this theoretical maximum, when k_L is at optimum. The

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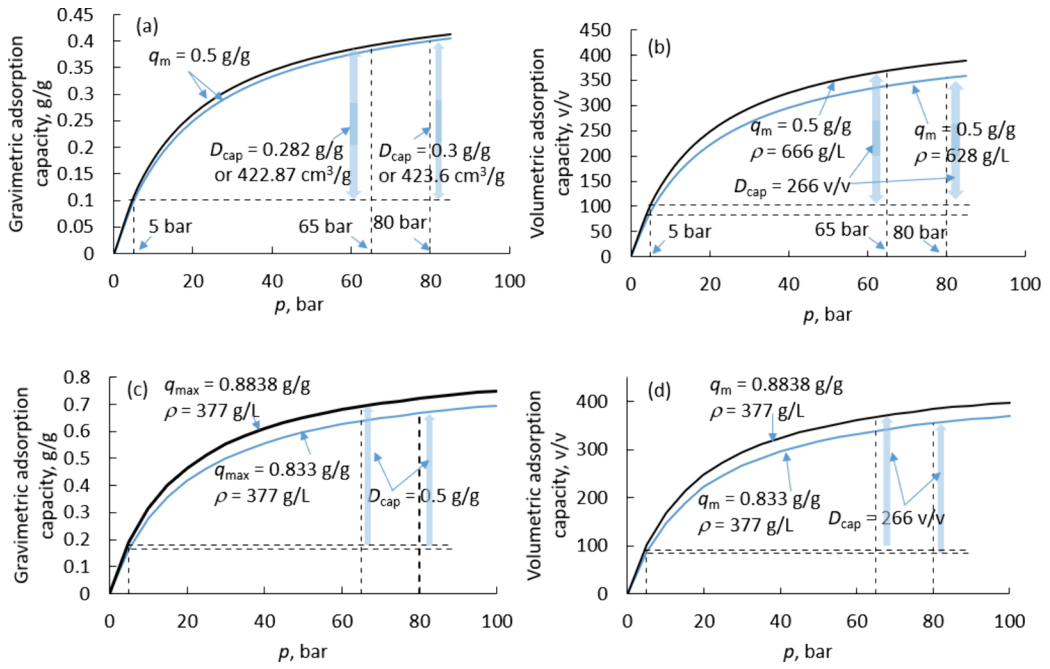

Figure 1. (a) Gravimetric adsorption capacity vs pressure for an adsorbent with adsorption site concentration of q_m = 0.5 g/g and $k_L = k_{L,optimum}$. The black line shows methane uptake in a storage tank operating between 5 and 65 bar, while the blue line shows uptake between 5 and 80 bar. (b) Volumetric adsorption capacity vs pressure for an adsorbent with q_m = 0.5 g/g, $k_{L,optimum}$, and material densities of 666 g/L (for 5−65 bar, black line) or 628 g/L (for 5−80 bar, blue line). (c) Gravimetric capacity of a theoretical "holy grail" material ensuring a deliverable gravimetric capacity of 0.5 g/g, regardless of storage pressure. The black line represents a tank operating between 5 and 65 bar, and the blue line represents 5−80 bar. (d) Volumetric capacity vs pressure for the same theoretical material, ensuring a deliverable capacity of 266 v/v, regardless of operating pressure. The black and blue lines represent the storage pressures of 5−65 bar and 5−80 bar, respectively.

optimum k_L value can be determined by differentiating D with respect to k_L and setting the resulting expressions to zero. This should mathematically allow one to obtain the optimum k_L value, and theoretically this should be equal to[10]

$$k_{L,optimum} = 1/\sqrt{P_1 . P_2} \tag{3}$$

Equation 1 and (3) are resourceful, and they can be used to identify the required level of material properties for different case scenarios based that ensures the DOE target in terms of the volumetric capacity or in terms of the gravimetric capacity or the combination of both.

Case 1: In this case study, eqs 1 and (3) were applied to estimate the gravimetric and volumetric storage capacity of a material with a maximum number of adsorption sites equivalent to the DOE's gravimetric target of 0.5 g/g. According to eq 1, for a fixed number of adsorption sites on the adsorbent per unit mass (q_m = 0.5 g/g), the optimal binding affinity can be calculated using eq 3 to ensure the desired methane delivery between operating pressures p_1 and p_2. Using the Langmuir expression in eq 1, we can determine the methane delivered by this material. In Figure 1a, the ideal Langmuir isotherm for q_m = 0.5 g/g and $k_L = k_{L,optimum}$ (from eq 3) is plotted for two scenarios: storage tanks operating between 5 and 65 bar and between 5 and 80 bar, with methane uptake expressed in gravimetric units (g/g). In Figure 1b, the corresponding material density required to achieve a deliverable capacity of 266 v/v is shown for both pressure cycles (5−65 bar and 5−80 bar).

For a storage tank operating between 80 bar (p_1) and 5 bar (p_2), the material delivers 0.3 g/g of methane, which, at STP conditions (where 1 g of CH_4 occupies 1.412 L), translates to a deliverable capacity of 0.4236 L/g or 423.6 cm^3/g. To meet the 266 v/v target, a material density of 628 g/L (0.628 g/cm^3) is required. Similarly, if the storage tank operates between 65 bar (p1) and 5 bar (p2), the delivered methane is 0.282 g/g, equivalent to 0.398 L/g or 398.18 cm^3/g. To achieve the 266 v/v target, a material density of 666 g/L (0.666 g/cm^3) is needed.

Case 2: In Case 1, the analysis identified the material property required to achieve the DOE's volumetric deliverable capacity of 266 v/v but did not address the gravimetric deliverable capacity. By utilizing the Langmuir isotherm and eq 3, it is possible to determine the material properties that meet both the gravimetric target of 0.5 g/g and the volumetric target of 266 v/v at standard temperature and pressure. For a storage tank operating between 5 bar (p_1) and 65 bar (p_2), the optimal adsorption site concentration (q_m) can be calculated using a fixed binding affinity (k_L), derived from eq 3. The goal is to ensure that the difference in methane adsorption between these pressures matches the gravimetric target of 0.5 g/g. It was found that a material with q_m = 0.8388 g/g and a binding affinity of k_L = 0.05547 bar^{-1} meets this requirement, as illustrated in Figure 1c.

For a tank operating between 5 and 80 bar, a material with q_m = 0.833 g/g and the same binding affinity (k_L = 0.05547 bar^{-1}) is necessary, as shown in the corresponding Langmuir isotherm in Figure 1c. To also meet the volumetric deliverable capacity of 266 v/v, the adsorbent material must have a density of 377 g/L. Figure 1d presents the properties and volumetric deliverable capacity of such a material. The properties of the adsorbent and Langmuir isotherms in Figures 1c and 1d provide guidelines for designing adsorbents that can simultaneously achieve the gravimetric and volumetric deliverable capacity targets for methane set by the DOE.

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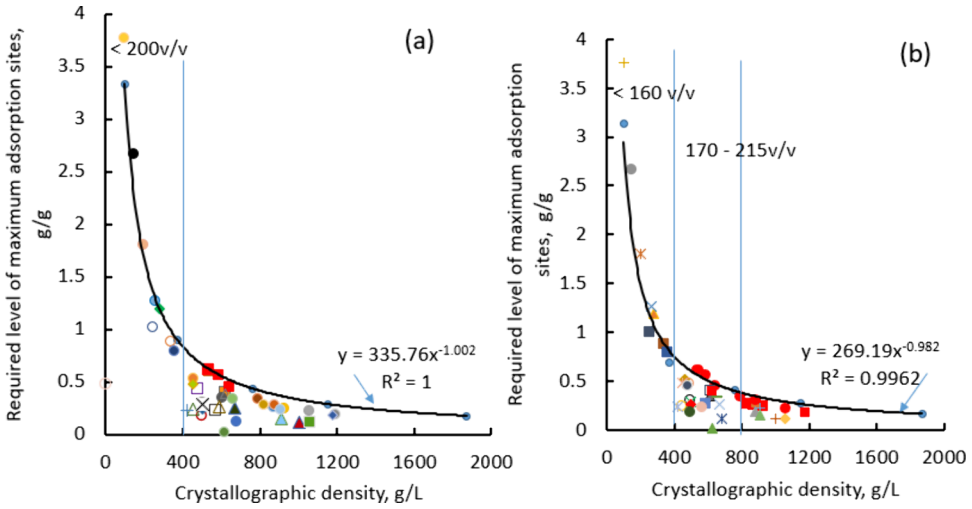

Figure 2. Plot shows the maximum adsorption sites for methane predicted using the Langmuir isotherm (black line) versus crystallographic density for (a) a storage tank with adsorbent material operated between 65 and 5 bar and (b) a storage tank operated between 80 and 5 bar. Also included are the q_m values of benchmark materials from the literature. Materials with a deliverable capacity of 260 v/v are shown as filled red squares in Figure 2a. In Figure 2b, filled red squares indicate materials exceeding the DOE target of 266 v/v, while filled red circles indicate materials with capacities between 250 and 266 v/v. The ideal material property line (black line in parts a and 2b) is temperature-independent, and materials on this line may exhibit high deliverable capacities. The q_m and k_L values were calculated based on the experimental data taken from the literature.[7,13−20] Note: The materials included in this figure include the following materials: Al-soc-MOF1,[7] HKUST (monolith),[21] NOTT-100a,[13] NOTT-101a,[13] NOTT-102a,[13] NOTT-103a,[13] NOTT-109a,[13] MOF-Lo to MOF-L7,[14] PCN-46,[15] ZJU-105a,[15] PCN-14,[16] HKUST-1,[17] Ni2(dobdc),[17] PCN-14,[17] Co2(dobdc),[17] MOF-5,[17] Mg2(dobdc),[17] AX-21,[17] HKUST-1,[18] HKUST-1_HP,[18] RGC30,[18] F400,[18] Maxsorb,[18] LMA405,[18] LMA726,[18] LMA738,[18] activated carbon monoliths,[19] MOF-210,[19] PY56−1:1_800,[20] DO100−3:1_700.[20]

Case 3: Using the Langmuir isotherm, the combination of material properties (such as the maximum adsorption sites and material density) required to achieve a volumetric deliverable capacity of 266 v/v can be determined. If the volumetric capacity is fixed at 266 v/v, then the gravimetric storage capacity can be estimated based on the adsorbent density. For instance, if the adsorbent density is 100 g/L, and the deliverable capacity is 266 v/v, then the amount of methane adsorbed per unit mass of the adsorbent is 266/100 = 2.66 L/g. At standard temperature and pressure, 1 g of methane occupies 1.412 L; thus, 2.66 L of methane weighs 1.884 g. Therefore, for a density of 100 g/L, the material should have a gravimetric deliverable capacity of 1.884 g of methane per gram of adsorbent.

Using this, the q_m value that ensures a gravimetric capacity of 1.884 g/g and a volumetric capacity of 266 v/v can be estimated through iteration to optimize q_m for a fixed k_L value. For a storage tank operated between 65 and 5 bar, the Langmuir model and k_L from eq 3 indicate that a material with q_m = 3.329 g/g, k_L = 0.00547 bar^{-1}, and density of 100 g/L can meet the DOE target of 266 v/v at standard temperature and pressure.

For a storage tank operating between 5 and 80 bar, an adsorbent with q_m = 3.314 g/g and k_L = 0.05 bar^{-1} is required to achieve a volumetric deliverable capacity of 266 v/v. Figure 2a shows the predicted maximum adsorption sites (q_m) using eqs 1 and (3), which meet the 266 v/v target, plotted as a function of material density ranging from 100 to 1870 g/L for a storage tank operating between 65 and 5 bar. The solid black line in Figure 2a serves as a guideline for the design of methane storage materials. Similarly, Figure 2b shows the required q_m as a function of material density to meet the DOE target of 266 v/v for a storage tank operating between 80 and 5 bar.

Figures 1c and 1d indicate that regardless of the operating pressures the relationship between q_m and material density follows a power-law trend. Figures 2a and 2b also plot q_m values of benchmark methane storage materials against their crystallographic density. The trend observed from experimental data follows the same trend as predicted by the Langmuir isotherm, termed the "ideal material property line". For storage tanks operating between 5 and 80 bar, none of the materials with a crystallographic density below 200 g/L exceed a deliverable capacity of 160 v/v, as shown in Figure 2b. Materials with densities between 200 and 400 g/L show deliverable capacities ranging from 160 to 215 v/v.

Materials that align with the ideal material property line (black line in Figure 2b), as predicted by the Langmuir isotherm, exhibit deliverable capacities exceeding the DOE targets. Similarly, for adsorbent materials storing methane at 65 bar and delivering at 5 bar, some benchmark materials intersect the ideal material property line in Figure 2a, with deliverable capacities exceeding 260 v/v. Additionally, Figure 2a shows that materials with densities below 400 g/L do not exceed a deliverable capacity of 200 v/v. This indicates that the material properties required to meet DOE targets, as predicted by the Langmuir isotherms, are reliable for materials with densities of >400 g/L and can serve as a guideline for designing porous materials for methane storage.

In conclusion, the Langmuir isotherm was employed to theoretically estimate the material properties required to achieve the DOE target of 266 v/v methane deliverable capacity. A theoretical "holy grail" material was identified that satisfies both the DOE's deliverable gravimetric capacity of 0.5 g/g and volumetric deliverable capacity of 266 v/v. This corresponds to an adsorbent material with adsorption capacity of 0.84 g/g and binding affinity of 0.056 bar with a material density of 377 g/L. The results obtained from the theoretical analysis in this work were based solely on material density, binding affinity, and the maximum number of adsorption sites, while excluding pore properties such as surface area, pore

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volume, and adsorption isosteric heat, which are critical factors in determining the storage capacity of porous materials. Although surface area, pore volume, and isosteric heat were not explicitly considered, these parameters were indirectly accounted for through their correlation with the maximum number of adsorption sites, material density, and binding affinity. The correlations that directly link storage capacity and excess adsorption of small molecules, including methane, as a function of pore volume and the pore volume that ensures the DOE target can be found in the works of Li et al. and Zhang et al.[22,23] The correlations proposed in this study can serve as a guideline for identifying or designing materials with the required properties to meet the Department of Energy's (DOE) targets for methane storage.

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Notes

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