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# Methane Adsorption Storage Using Microporous Carbons Obtained from Coconut Shells

MOISÉS BASTOS-NETO, A. EURICO B. TORRES, DIANA C.S. AZEVEDO* AND CÉLIO L. CAVALCANTE, JR.
*Universidade Federal do Ceará, Department of Chemical Engineering, Grupo de Pesquisas em Separações por Adsorção - GPSA, Campus Universitário do Pici, Bl. 709, 60455-760, Fortaleza, CE, Brazil*
dianacsa@ufc.br

**Abstract.** This paper presents an experimental and theoretical study of the adsorption equilibria of methane on activated carbon, focusing on the accurate determination of the absolute adsorbed mass from raw gravimetric measurements performed at high pressures (above 0.1 MPa). Two carbon samples were selected for these studies: a commercial sample (SRD-21) and a sample prepared in laboratory from coconut shells (CAQF-30). A gravimetric set up was used to measure the adsorption properties. Methane isotherms were obtained in the pressure range of 1 to 70 bar and under temperatures from 10 to 80°C. Equilibrium experimental data were evaluated with the aid of three approaches labeled as D, DD and DDA, the latter being proposed for the first time in this paper. The DDA approach provided consistent and physically meaningful results for the adsorbed phase density. The adsorption isotherm that was obtained following the DDA approach matched those obtained following an approach published in the literature. The results indicate that the CAQF-30 sample, despite being prepared from carbonaceous wastes, presents competitive values for the methane adsorption parameters when compared to the commercial sample.

**Keywords:** gas storage, carbon, adsorption, gravimetric measurements, buoyancy

## 1. Introduction

Natural gas has become a fuel of great industrial interest mainly because of its inherent clean burning characteristics (Inomata et al., 2002). It has a relatively lower price and larger abundance compared to other fuels. Methane, the main component of natural gas, has a superior octane number than other fuels; however, at the normal conditions of temperature and pressure, it is a supercritical gas and thus has low energy density. Therefore, the feasibility of the application of natural gas as a competitive fuel will depend on reservoir storage capacity. Compressed natural gas (CNG) is a popular storage method that involves higher costs with the vessel construction and pumping energy as compared to storing in adsorbed form.

Adsorbed natural gas (ANG) storage systems have been intensively studied in recent years (Mota, 1999; Vasiliev et al., 2000; Biloé et al., 2001; Lozano-Castelló, 2002). The keys to the design of ANG storage vessels lie on the discovery of adsorbent materials with high capacity and delivery and on the accurate determination of the adsorption isotherms. The gravimetric method is a traditional technique to measure adsorbed amounts in porous solids. However, when the adsorbate is a gas under supercritical conditions, determining the adsorbed phase density is not straight-forward. Furthermore, buoyancy effects become significant under pressures only slightly above 0.1 MPa (atmospheric pressure) and must be precisely taken into account.

In the present study, we have measured gravimetrically equilibrium adsorption data of methane in two samples of activated carbons: a commercial (SRD-21) one and another made from coconut shells (CAQF-30). Buoyancy effects present in gravimetric measurements

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*To whom correspondence should be addressed.

*Table 1.* Textural data for activated carbon samples studied in this work.

| Carbon | BET surface Area –($m^2/g$) | Micropore volume ($cm^3/g$) | Total pore volume ($cm^3/g$) | Mean pore diameter (Å) |
|---|---|---|---|---|
| SRD-21 | 1967 | 0.945 | 0.957 | 19.4 |
| CAQF-30 | 2114 | 1.142 | 1.304 | 24.9 |

at high pressures were taken into account by applying three methodologies: one proposed by Dreisbach et al. (2002), a second one proposed by Do and Do (2003), and a new approach that includes the Dubinin-Astakhov equation adapted for supercritical fluids (Biloe et al., 2002).

## 2. Experimental

### 2.1. Preparation of Activated Carbon Samples

Activated carbon (CAQF-30) was prepared from coconut shells by chemical activation with zinc chloride followed by physical activation. A commercial sample of activated carbon (SRD-21), kindly provided by Sutcliffe Speakman Carbons LTD (UK), was used as reference. Both samples were characterized for surface area and pore volume. Table 1 summarizes the textural data for both samples.

### 2.2. Equilibrium Measurements

Adsorption equilibrium studies were performed using a magnetic suspension balance by Rubotherm (Bochum, Germany). The gravimetric setup is shown in Fig. 1. Prior to the adsorption experiment, the sample was pretreated at 150°C, under vacuum, for 4 to 6 hours until no mass variations were observed. Then, methane pressure in the measuring cell was increased stepwise so that adsorption isotherms were measured in the pressure range of 0.1 to 7 MPa at temperatures from 10 to 80°C. For some runs, after reaching 7 MPa, pressure was decreased stepwise so as to measure the desorption branch of the isotherms.

The specific volume of the components of the measuring cell was measured from a blank experiment (no sample) using methane. The specific volume of the solid phase in the samples was measured from an experiment with Helium (which is a non-adsorbing gas up to 10 MPa).

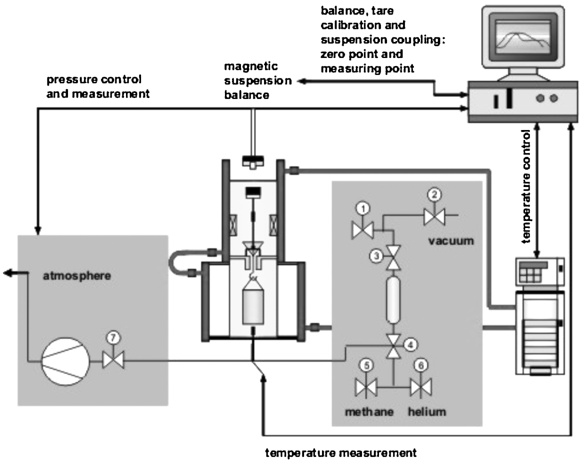

*Figure 1.* Experimental setup for gravimetric equilibrium measurements.

## 3. Theory

In gravimetric measurements, only the adsorbed excess mass is readily determined, as in Eq. (1).

$$m_{\mathrm{ex}}(p, T) = \Delta m + (V_{\mathrm{b}} + V_{\mathrm{s}})\rho = m - V_{\mathrm{ads}}\rho \qquad (1)$$

where $\Delta\, m$ is the mass difference measured by the balance, $m$ is the absolute adsorbed mass and $\rho$ is the gas density. $V_{\mathrm{b}}$, $V_{\mathrm{s}}$ and $V_{\mathrm{ads}}$ are the volumes occupied by the physical components of the measuring cell, the sample solid phase and the adsorbed phase, respectively. $V_{\mathrm{b}}$ and $V_{\mathrm{s}}$ are easily determined, which is not true for the determination of $V_{\mathrm{ads}}$, since methane is a supercritical fluid at the pressure and temperature conditions under study. Dreisbach et al. (2002) proposed the use of adsorption equilibrium model equations to represent m, so that the equation parameters and $V_{\mathrm{ads}}$ may be simultaneously estimated from experimental raw data. In that study, Toth and Unilan isotherm models were used:

$$\textit{Toth:} \quad m = m_{\infty} \frac{\rho}{(1/b + \rho^{\alpha})^{1/\alpha}} \qquad (2)$$

$$\textit{Unilan:} \quad m = \frac{m_{\infty}}{2\alpha} \ln\left[\frac{1 + \mathrm{b}e^{\alpha}\rho}{1 + \mathrm{b}e^{-\alpha}\rho}\right] \qquad (3)$$

The isotherm parameters to be estimated in both models are $m_{\infty}$, $b$ and $\alpha$. The absolute adsorbed mass and the adsorbed phase density ($\rho_{\mathrm{ads}} = m/V_{\mathrm{ads}}$) were determined by the following three different approaches.

### 3.1. *Approach by Dreisbach et al. (2002): D-Approach*

The adsorbed phase volume in Eq. (1) is written as $V_{\text{ads}} = m(p, T)/\rho_{\text{ads}}(T)$, where $\rho_{\text{ads}}$ is the adsorbed phase density. The Toth and Unilan isotherm equations are used to express $m(p, T)$ as a function of $\rho(p, T)$. The raw experimental data $\Delta m$ versus $\rho$ are used to estimate $m_\infty$, $b$, $\alpha$ and $\rho_{\text{ads}}$. Note that a value of $\rho_{\text{ads}}$ is obtained for each temperature, which is an average value in the pressure range under study.

### 3.2. *Approach by Do and Do (2003): DD-approach*

The adsorbed phase volume $V_{\text{ads}}$ is assumed to be constant at a given temperature. Substituting the analytical isotherm expressions given either by (2) or (4) in Eq. (1), model parameters and $V_{\text{ads}}$ may be estimated from the experimental values $\Delta m \times \rho$. Note that, in this case, the adsorbed phase density ($\rho_{\text{ads}} = m(p, T)/V_{\text{ads}}$) is a function of temperature and pressure.

### 3.3. *New Approach Proposed in This Study: DDA-Approach*

The data of $m \times p$, as obtained from the approach of Dreisbach et al. (2002), may be plotted according to the linear form of the Dubinin-Astakhov equation, as follows:

$$\ln[m(p, T)] = \ln[W_o\rho_{\text{ads}}(T)] - \Omega \ln^n(p_o/p) \quad (4)$$

$$p_o = p_c(T/T_c)^2 \quad (5)$$

*Table 2.* Adsorbed phase densities (g/cm$^3$) obtained from the D-approach.

| | CAQF-30 | | | SRD-21 | | |
|---|---|---|---|---|---|---|
| | 40°C | 60°C | 80°C | 30°C | 40°C | 60°C |
| Toth model | 0.308 | 0.183 | 0.212 | 0.188 | 0.245 | 0.149 |
| Unilan model | 0.366 | 0.271 | 0.274 | 0.229 | 0.236 | 0.328 |

where $W_o$ is the sample micropore volume and $\Omega$ is a constant of the DA equation. $T_c$ and $p_c$ are the methane critical temperature and pressure. The parameter $n$ is related to the pore size distribution of the sample; it is 1.7 for the sample SRD-21 and 1.5 for CAQF-30. The slope of the line obtained from Eq. (4) allows the calculation of $\rho_{\text{ads}}$ if $W_o$ is known. Then a new procedure of estimation of isotherm parameters is performed using the methodology described by Dreisbach et al. (2002). The new data ($m \times p$) obtained are treated according to Eq. (4) and a new value for the adsorbed phase density is obtained. This iterative methodology proceeds until $\rho_{\text{ads}}$ converges within a given error tolerance.

## 4. Results and Discussion

Gravimetric experiments were performed in the pressure range from vacuum to 70 bar and temperatures of 10, 20, 30, 40, 60 and 80°C. Methane adsorption isotherms in samples CAQF-30 and SRD-21 were measured and compared. Figure 2 shows the recorded mass gains for CAQF-30 and SRD-21.

The absolute methane adsorbed mass ($m$) was estimated in each case following the approach proposed by

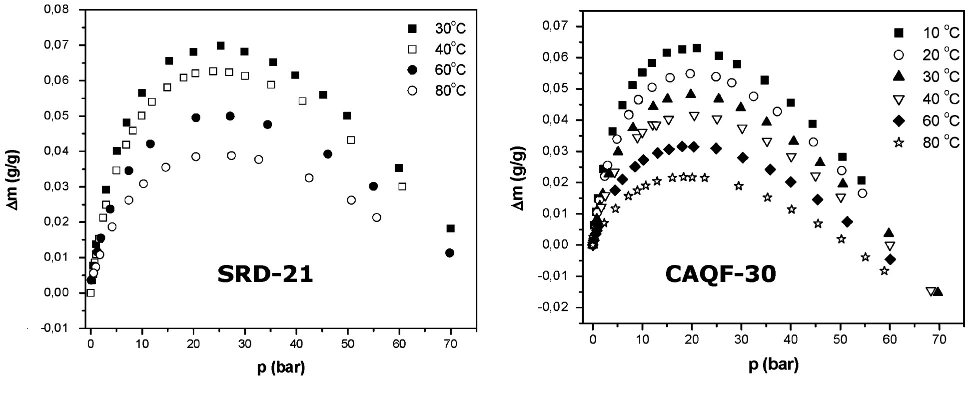

*Figure 2.* Registered mass variation as a function of the gas pressure in different temperatures for SRD-21 and CAQF-30.

*Table 3.* Adsorbed phase densities (g/cm$^3$) obtained from the DDA-approach.

| | $T$ (°C) | $\rho_{ads}(1)$ | $\rho_{ads}$ (2) | $\rho_{ads}$ (3) | $\rho_{ads}$ (4) | $\rho_{ads}$ (5) |
|---|---|---|---|---|---|---|
| CAQF-30 | 30 | 0.15781 | 0.17558 | 0.17037 | 0.17176 | 0.17139 |
| | 40 | 0.14888 | 0.16851 | 0.16266 | 0.16422 | 0.16379 |
| | 60 | 0.13168 | 0.15227 | 0.14635 | 0.14783 | 0.14745 |
| SRD-21 | 30 | 0.20950 | 0.20880 | 0.21501 | 0.21383 | 0.21405 |
| | 40 | 0.18995 | 0.18376 | 0.19857 | 0.19632 | 0.19625 |
| | 60 | 0.17051 | 0.17280 | 0.17232 | 0.17243 | 0.17240 |

Dreisbach et al. (2002). Figure 3(a) shows the isotherms at 20 and 30°C obtained for the commercial sample (SRD-21) and those obtained for the carbon made from coconut shells (CAQF-30). In spite of the larger surface area and micropore volume, the coconut shell carbon sample (CAQF-30) showed a smaller capacity for methane. This is possibly due to a narrower pore size distribution for the commercial sample, which may be verified by the DR plots of the samples obtained from adsorption experiments with $N_2$ at 77 K, see Fig. 3(b).

Table 2 shows the values obtained for the average adsorbed phase density according to the D-approach. Most values lie in the range of densities for saturated liquid methane, which is 0.43 down to 0.16 g/cm$^3$ for pressures 46 down to 0.05 bar, resp. However, there is no consistent behavior with temperature and the values vary randomly from one sample to another.

The DDA approach was applied in an attempt to find more consistent values for the adsorbed phase density values. Table 3 summarizes the values obtained for $\rho_{ads}$ in each of the iterate steps involved in the methodology. Not only the values converge to a finite value, but they also vary with temperature in a physically meaningful fashion. At a given temperature, the adsorbed phase density is larger for SRD-21 than for CAQF-30, which is in agreement with the larger methane adsorption capacity obtained for that sample. The isothermal experimental curves obtained following the D-approach (q1) as compared to those obtained from the DDA-approach (q2) are shown in Fig. 4. After the correction applied on the values of adsorbed phase density (DDA-approach), the absolute adsorbed mass is slightly higher than that calculated using the DA approach. To ensure the reliability of these data, the DD-approach (Do and Do, 2003) was applied to find the absolute adsorbed mass from the raw experimental data. Figure 4(b) shows the isothermal curves obtained using the three approaches. The results provided by the DDA approach match those found from the DD-approach, indicating the validity of the proposed DDA methodology.

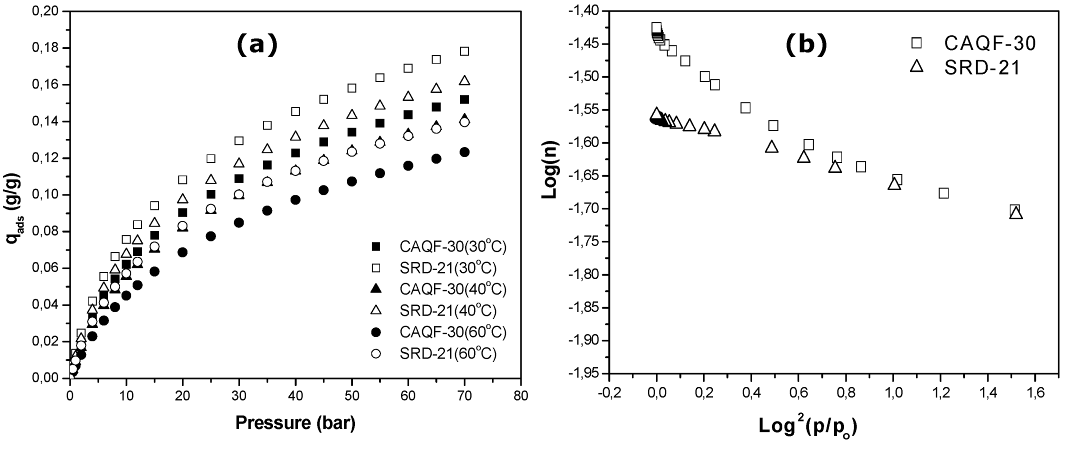

*Figure 3.* Absolute adsorbed mass ($m$) for commercial and CS samples at 20 and 30°C (a) and DR plots for nitrogen adsorption at 77K (b).

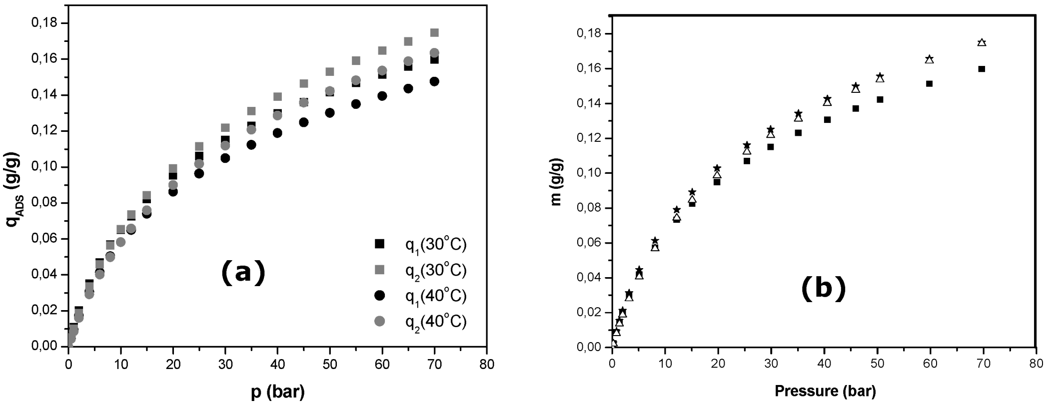

*Figure 4.* Absolute adsorbed mass for CAQF-30 calculated (a) following de *D*-approach (q1) as compared to the *DDA*-approach (q2) and (b) following the *D*-approach (squares), the *DDA*-approach (triangles) and the *DD*-approach (stars).

## 5. Conclusions

This study shows experimental data for methane adsorption on activated carbon prepared from coconut waste (CAQF-30) and on a commercial activated carbon sample (SRD-21). The equilibrium adsorption isotherms were comparable and yield similar adsorption capacities. A study on the method used for correction of the buoyancy effect in the measurements has been presented, using an iterative approach that proposes the use of the linear form of the Dubinin-Astakhov equation along with the methodology proposed by Dreisbach et al. (2002). The results here obtained present values for the adsorbed phase density more significant physically than the previous approach using Toth and Unilan isotherms. A comparison with results obtained from an approach proposed by Do and Do (2003) indicate good agreement for the results obtained with the new proposed DDA approach.

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