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ADSORBED NATURAL GAS: FROM FUNDAMENTAL ADSORPTION DATA TO APPLICATION STUDIES

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Resumo

A adsorção de gases combustíveis em sólidos microporosos tem sido amplamente estudada como alternativa para armazenamento e transporte. O armazenamento de gás na forma adsorvida (GNA) é potencialmente mais barato e seguro que na forma comprimida (GNC). Para avaliar o desempenho do armazenamento de GNA em comparação ao GNC, é necessária a determinação de todas as propriedades de equilíbrio de adsorção do adsorvente com os componentes do GN. Este estudo apresenta os passos e metodologias a serem adotadas para uma apurada avaliação de sistemas de armazenamento de GNA a partir de dados e conceitos fundamentais. Um modelo matemático é desenvolvido e testado na intenção de demonstrar que simplificações devem ser assumidas, que experimentos devem ser realizados para fornecer *inputs* e que fenômenos estão envolvidos nesse processo de armazenamento.

Abstract

Adsorption of combustible gases on microporous solids has been intensely studied as an alternative for their storage and transportation. Storing gases in adsorbed form is thought to be safer and cheaper than in compressed form. In order to assess the performance of ANG as compared to CNG, it is necessary to fully determine the equilibrium adsorption properties of the adsorbent with the usual constituents of Natural Gas. This study presents most of the steps and methodologies that should be adopted for an accurate evaluation of ANG storage systems from fundamental data and concepts. A mathematical model is developed and tested in an attempt to demonstrate what simplifications should be assumed, what experiments should be carried out to obtain input values and what phenomena are involved in this type of storage process.

1. Introduction

The instability of the petroleum derivative fuels market, besides the increasing of environmental matters, has stimulated new researches regarding alternative fuels (Matranga et al., 1992). Within this background, natural gas (NG) is highlighted as a non-renewable resource still available in large amounts, inadequately used as for its energetic potential and e more attractive for its cleaner combustion.

As a consequence, the world began to encourage higher NG consumption levels. However, to make possible a large-scale use it is necessary that the gas is stored in a safe, practical and economical manner. A very promising system proposes natural gas storage at lower pressures (< 40 bar) in its adsorbed form (ANG), which is capable of supporting a positive storage cost/capacity relation (Mota et al., 1997a).

Since the efficiency of this type of system depends essentially on the used porous material, majority of the researches in this area are focused in the development of new materials with greater storage capacities. However, one

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knows that the phenomena involved in the storage process also play an important role in the system efficiency. Thus, the adequate scale study is essential to predict the system viability and to guide the ANG storage technology.

Some studies related to ANG storage vessels have been accomplished in the last years, being greater part estimations and simulations. Few of them presented experimental data using those vessels, almost all for vehicular purposes.

The main purpose of this study is to establish a set of methodologies to be followed for analyzing and predicting charge and discharge cycles behaviors in an ANG storage vessel designated for gas transportation to regions not provided by gas ducts.

2. Model

The mathematical model developed in this study is fundamentally based on material and energy balances in a proper differential volume. The first assumption considered is that natural gas may be represented by its main component, methane (~90%). This way, the very first model simplification is that pure methane enters and exits the vessel.

Pressure is assumed to be a variable, so that the continuity equation is needed besides an energy balance. It is also assumed that the gas flow in the adsorbent bed is laminar and that the fluid phase behaves like an ideal gas. Chang and Talu (1996) suggested that a radial flow would lead to more efficient heat and mass transport so that the vessel may be represented by Figure 1.

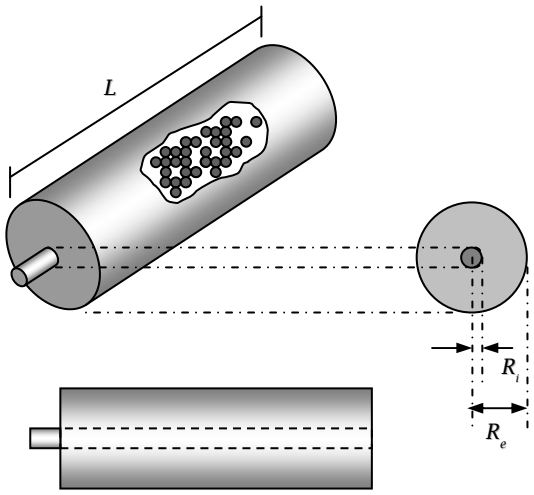

Figure 1. Model illustration

The model may be applied to either slow or fast charge or discharge.
Material Balance:

$$\frac{\partial}{\partial t}\left(\varepsilon_T c + \rho_b q\right) + \nabla \cdot c\vec{v} = 0 \tag{1}$$

The flow velocity may be calculated, in general, by Ergun's equation:

$$\vec{v} = -\frac{2\nabla p}{\alpha' + \sqrt{\alpha'^2 + 4\beta' c\|\nabla p\|}} \tag{2}$$

This equation consists of laminar (α') and turbulent (β') terms. Pressure gradient is extended to two dimensions: radius and axis. Since our model considers laminar flow and radial flow, the pressure gradient will occur only through radius and term β' will be null. These assumptions lead us to Darcy's equation:

$$\vec{v} = -\frac{1}{\alpha'}\nabla p \tag{3}$$

where α' is the relation between the gas viscosity and the bed permeability, expressed Carman-Kozeny's equation:

$$\alpha' = \frac{150 \cdot (1-\varepsilon_b)^2 \cdot \mu}{4 \cdot \varepsilon_b^3 \cdot R_P^2} \tag{4}$$

Energy Balance:

$$\frac{\partial}{\partial t}((\varepsilon_T c + \rho_b q)c_{pg} T) + \rho_b \Delta H_{ad} \frac{\partial q}{\partial t} - \varepsilon_T \frac{\partial p}{\partial t} + \rho_b c_{ps} \frac{\partial T}{\partial t} + \nabla \cdot (c\vec{v} c_{pg} T - \lambda \nabla T) = 0 \tag{5}$$

Equilibrium relation is expressed by the Virial equation:

$$\frac{p}{q} = \exp\left(\left(k_1 + \frac{k_2}{T}\right) + \left(k_3 + \frac{k_4}{T}\right)q\right) \tag{6}$$

Initial conditions:

$$p = p_i, \quad \mathrm{T} = \mathrm{T_i}, \quad \mathrm{q} = \mathrm{q(p_i, T_i)} \quad \text{for } \mathrm{R_i} \le \mathrm{r} \le \mathrm{R_e}, \ \mathrm{t} = 0 \tag{7}$$

Boundary conditions:

$$\left.\frac{\partial p}{\partial r}\right|_r = 0 \text{ for } \mathrm{r} = \mathrm{R_e} \tag{8}$$

This condition represents the gas flow limit being no flow allowed through the cylinder outer wall.

$$p = p_{cg}, \text{ in } \mathrm{r} = \mathrm{R_i} \quad \text{(charge)} \tag{9}$$

$$p = p_{dg}, \text{ in } \mathrm{r} = \mathrm{R_i} \quad \text{(discharge)} \tag{10}$$

Equations 9 and 10 are the simplest and most commom experimental conditions to be admited for fast charge and discharge. Another way to represent this is, for exemple, by constant mass or volume flow as could occur in gas delivery for vehicular purposes.

$$\lambda \frac{\partial T}{\partial r} = c \cdot \frac{\alpha'}{\mu} \cdot \frac{\partial p}{\partial r} \cdot c_{pg} \cdot (T_w - T) \quad \text{for } \mathrm{r} = R_i \tag{11}$$

$$\lambda \cdot \nabla T + e_w \cdot C_w \frac{\partial T}{\partial t} = h_w (T - T_{amb}) \quad \text{for } \mathrm{r} = R_e \tag{12}$$

Equations 11 and 12 represent heat exchanges in the inner cylinder and the outer wall.

The algebraic-differential equations were solved by orthogonal collocation on finite elements using the solver gPROMS (Process System Enterprise Ltd., 1999).

Further information on the model description may be found elsewhere (Bastos-Neto et al., 2005).

3. Materials

Experimental runs with prototype were carried out with Mead Westvaco WV1050 granular activated carbon.

Pure gases used in the determination of adsorption equilibrium isotherms were provided by White Martins Praxair Inc. (Brazil). Helium was used to calculate the adsorbent specific volume.

4. Equipments

The adsorbent textural and surface characteristics were evaluated through N2 isotherms at 77 K in an Autosorb-1 MP (Quantachrome). Some of these characteristics are input data for the model.

Equilibrium of adsorption studies were carried out in a magnetic suspension balance Rubotherm (Bochum, Germany).

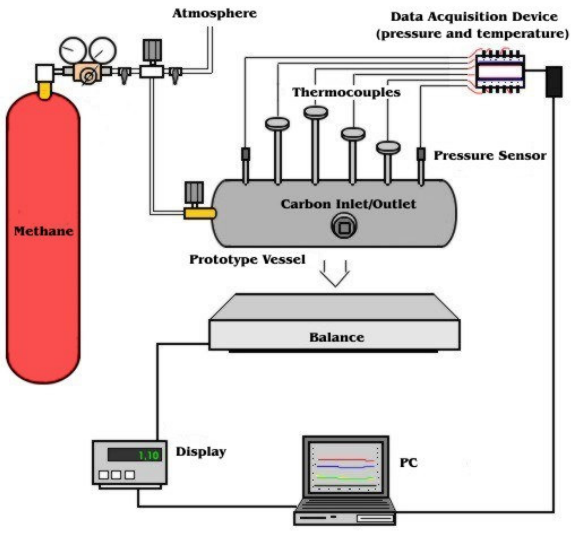

Figure 2. System illustration of prototype vessel.

The prototype vessel used in charge and discharge cycles, in a range of pressure from 0.1 and 4 MPa, was disposed in an experimental system as shown in Figure 2. Natural gas and pure methane was used in the cycles.

5. Methodology

The analysis of charge and discharge cycles in ANG storage reservoirs requires a series of adsorbent particle and bed proprieties. Such proprieties are related to the particle physical structure (textural characteristics), to the thermodynamic behavior of the phases involved in the adsorption phenomenon, to the vessel material, etc. One of the most important bed proprieties is the adsorption capacity, evaluated through equilibrium of adsorption isotherms, moreover, other proprieties are also extremely essential for the investigation of a NG storage process: bed packing density, heat of adsorption, bed porosity, particle porosity, solid (carbon) specific heat, gas specific heat, vessel material specific heat, bed thermal conductivity and coefficient of heat transfer by convection in the vessel outer surface.

To assist our explanation about how to acquire those data, the input parameters were arranged into four groups: (1) adsorption equilibrium data; (2) adsorbent and bed characteristics; (3) heat and mass transfer-related proprieties and (4) geometrical definitions and operational conditions.

The first group data is considered the most important one and it consists basically of determining pure component adsorbed amounts in a given pressure range. From this procedure methane isotherms are obtained according literature (Dreisbach et al., 2002; Do and Do, 2003).

These isotherms are fit by Virial equation with the objective of finding a relation of adsorption capacity, pressure and temperature in one single equation.

Those isotherms are also used for determining the heat of adsorption which is an entity that gives us an idea about the adsorbent-adsorbate affinity and will define the amount of heat liberated in the storage process.

The storage system efficiency depends strongly on the operational temperature. Adsorption is an exothermic phenomenon. Higher temperatures lead to lower efficiencies. For great rates of generated heat it is desired a bed with excellent transfer proprieties.

The second data group is acquired through nitrogen isotherms at 77 K in proper equipment. Specific area, pore volume, average pore size and pore distribution are determined according to assessments detailed in literature (Ruquerol et al., 1999). Particle and bed porosity are calculated from those data. Bed packing density is evaluated by dividing the adsorbent bed mass by the volume it fills.

The third group of data that consists of specific heat and conductivity proprieties could not be directly or indirectly calculated, so they were extracted from literature (Biloé et al., 2001; Mota et al., 1997; Chang and Talu, 1996).

The last input parameters are the vessel length, radius and its wall thickness. Also are the pressure and temperature conditions. All of them can be easily and directly measured.

6. Results

All the main textural and surface characteristics of the WV1050 sample evaluated through nitrogen isotherms at 77 K are summarized in Table 1.

These results points WV1050 as a high-area activated carbon reasonably good to methane storage due to its high average pore size.

Table 1. Summary of the WV1050 textural characteristics.

Specific Surface Area ($m^2.g^{-1}$)	1615
Total Pore Volume ($cm^3.g^{-1}$)	1.038
Micropore Volume ($cm^3.g^{-1}$)	0.761
Average Pore Size (Å)	25
Solid Specific Volume ($cm^3.g^{-1}$)	0.419
Particle Porosity	0.713

Table 2 presents the calculated bed proprieties. Packing density is the relation between the total adsorbent mass and the vessel total inner volume. Total porosity considers all accessible void volumes (including intra-particle) while bed porosity takes into account only inter-particle volumes.

Table 2. Bed proprieties.

Packing Density ($g.cm^{-3}$)	0.280
Bed Porosity	0.592
Total Porosity	0.883

Figure 3 illustrates methane adsorption isotherms fitted by Virial equation. The greatest advantage in using this isotherm model fitting is that by calculating its coefficients one can predict the adsorbed amount as a temperature-independent function of pressure.

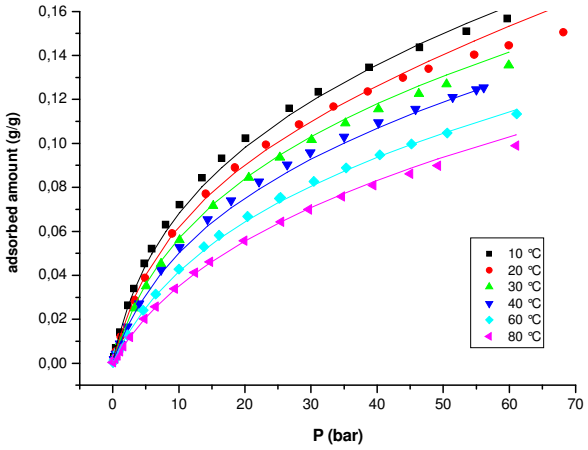

Figure 3. Adsorption isotherms of methane (10 – 80 °C). Lines represent the virial fit of the experimental data.

The calculated isosteric heat of adsorption was -975.31 J.g-1 which is in a range of values commonly reported in literature.

In a first stage, natural gas was used in the prototype cyclic experiments. It was expected that the model could finely fit experimental data since NG is constituted mainly by methane (c.a. 90 %) which is the only component taken into account by the model. However, poor agreement was found between NG experiments and pure methane simulations. Hence, new experiments were carried out with pure methane and then compared with simulations.

Nice agreements were found between experimental and simulation data for stored mass in charge (Figure 4) and discharge (Figure 5) cycles. Minor differences between model and experiment in the charge cycle may be explained by incomplete bed regeneration or lowly estimated packing density.

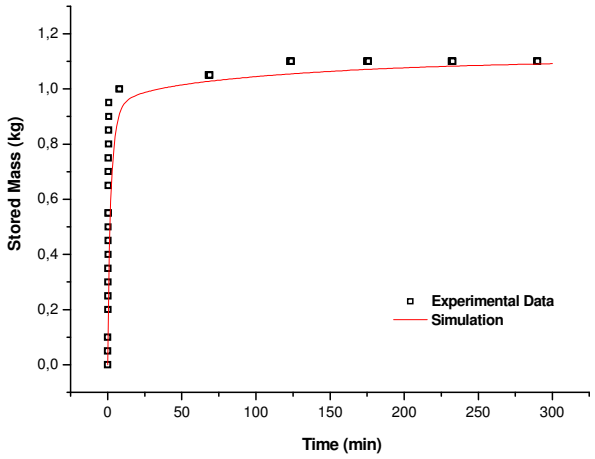

Figure 4. Experimental data and simulation for the amount of stored mass as function of time during the charge process.

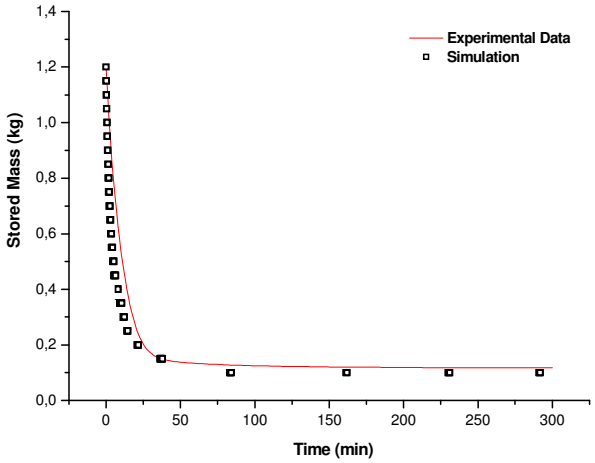

Figure 5. Experimental data and simulation for the amount of stored mass as function of time during the discharge process.

As previously discussed, the storage vessel efficiency depends essentially on the porous material that constitutes the adsorbent bed. To illustrate this statement another simulation was executed using input parameters of another carbon sample, SRD-21, formerly studied by Araújo (2004).

The stored amount profile for both samples simulations are exposed in Figure 6.

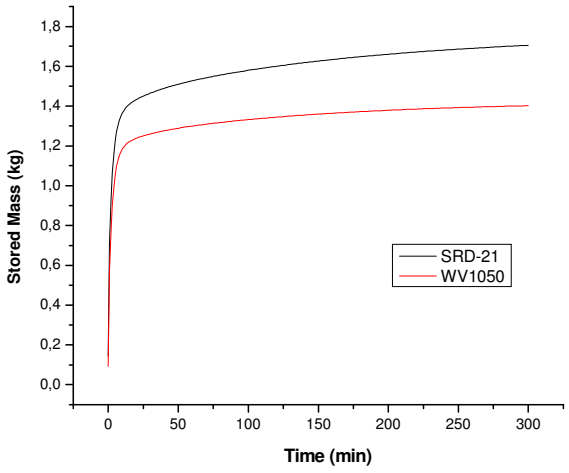

Figure 6. Stored amount as a function of time simulations for SRD-21 e WV1050.

One can note that the stored mass difference is about 22%, a considerable value that points SRD-21, from the British company Sutcliffe Speakman Carbons LTD, as a better sample for methane storage purposes.

7. Conclusions

This study showed experimental loading and delivery tests of methane performed with a prototype storage vessel filled with microporous activated carbon. Equilibrium adsorption data were measured for the range of pressure and temperature of the system and used as the input information to a dynamic model for charge and discharge of the storage vessel. The experimental results were compared to simulated curves in terms of pressure, temperature and stored mass histories. There was a reasonably good agreement between simulation and experimental results despite possible heat effects not considered in the model: variation of heat of adsorption with loading and changes in room temperature throughout the experimental runs. It was also verified that the porous material used in the adsorbent bed plays an important role on the storage process efficiency.

8. Nomenclature

c - fluid phase concentration, kg/m^3
c_{pg} - methane specific heat, J/kg K
c_{ps} - carbon specific heat, J/kg K
C_w - thermal capacity of the vessel wall, J/m^3 K
e_w - vessel wall thickness, m
h_w - coefficient of heat transfer (convection), W/m^2 K
k_1, k_2, k_3 e k_4 - virial isotherm parameters
L - vessel length, m
p - pressure, Pa
p_{atm} - atmospheric pressure, Pa
p_{cg} - final pressure on charge, Pa
p_{dg} - final pressure on discharge, Pa
p_i - initial pressure, Pa
q - adsorbed amount, kg/kg
R_e - outer radius of the vessel, m
R_i - inner radius of the vessel, m
R_p - adsorbent particle radius, m
t - time, s
T - temperature, K
T_w - wall temperature, K
T_{amb} - environment temperature, K
T_i - initial temperature, K
$\vec{v}$ - superficial velocity, m/s
ΔH_{ad} - adsorption heat, kJ/kg

Greek Symbols
α' - gas viscosity and bed permeability ratio
β' - Ergun's equation parameter, m^{-1}
ε_b - bed porosity
ε_T - porosity (void + macropores)
λ - thermal conductivity of the adsorbent, W/m K
μ - viscosity, kg/m s
ρ_b - packing density, kg/m^3

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