COBEM 2023 27TH INTERNATIONAL CONGRESS OF MECHANICAL ENGINEERING

ABCM Brazilian Society of Mechanical Sciences and Engineering
27th ABCM International Congress of Mechanical Engineering
December 04-08, 2023, Florianópolis-SC, Brazil

COBEM-2023-1368: A SIMPLE MODEL FOR THE SLOW STORAGE OF HYDROGEN USING PHYSICAL ADSORPTION

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Abstract. *Hydrogen is an advantageous energy source because it is renewable, and its use can reduce the emission of pollutants. However, the challenge is how to transport and store hydrogen safely and efficiently. There are some methods for hydrogen storage such as compressed hydrogen, liquid hydrogen, metal hybrids and adsorption in packed beds. In relation to constraints regarding mobile applications, the adsorption method has been a potential alternative because they require smaller volumes of gas. Due to a high average surface area, low cost and accessibility at industrial level, microporous activated carbons are good candidates for packed bed hydrogen storage in a commercial level. During the charging process of the reservoir, the exothermal adsorption may lead to high temperature values, reducing the adsorption capacity of the tank (do Nascimento* et al.*, 2014). Besides, the discharging process reduces the volume of available gas. This paper aims to investigate the thermal effects during the discharging of a packed bed hydrogen storage tank.. The GS and SAC02 activated carbon, which respectively had a specific surface area about 300 m2/g and 2074 m2/g, were selected as adsorbents.The absolute adsorption amounts were determined by Toth equation.The desorption dynamics was analyzed using a computational simulation code, developed using the Wolfram MATHEMATICA software. A simple lumped-capacitance mathematical model was used to predict the time-variation of the pressure in the storage tank. The main parameters involved in the thermal model are: heat absorption and amount of gas adsorbed, both essential to determine the amount of heat.The mass and energy balance equations that govern the system were solved for slow discharge of adsorbed hydrogen gas under ideal conditions of temperature and pressure. Comparisons made between simulations and results of previous experiments were made to seek a better understanding of the thermal performance of adsorption during hydrogen discharge.*

Keywords: *hydrogen, adsorption, discharging , packed bed .*

1. INTRODUCTION

1.1 Motivation

Hydrogen has great potential as a clean fuel produced from renewable sources. The great interest in the use of hydrogen as an energy source is due to the concern with the reduction of the environmental impact due to the use of fossil fuels, and to an increasing demand for clean and efficient energy sources, such as fuel cells. Despite the numerous advantages of using hydrogen as an energy source, problems with its safe storage and transportation still remain. Currently, hydrogen is stored in special tanks under very high pressure or in liquid form at cryogenic temperatures and high pressures, these two alternatives being unfeasible for economic and/or safety reasons (Hermosilla-Lara *et al.*, 2007). A possible solution to this problem is the storage of hydrogen adsorbed on carbonaceous structures, such as activated carbon.

1.2 Literature Review

Derived from the most abundant element in the universe, hydrogen fuel is clean, flexible, and energy-efficient.It has been considered as an ideal energy medium for replacing fossil fuels such as oil and coal. Hydrogen is currently used in industrial processes, as rocket fuel, and in fuel cells for electricity generation and powering vehicles. Operators of several natural gas-fired power plants are exploring the use of hydrogen to supplement or replace natural gas. Hydrogen has the potential for effectively storing energy for electric power generation(Mendonça and Fancello, 2019). Hydrogen can be used in fuel cells to generate electricity, or power and heat. Today, hydrogen is most commonly used in petroleum refining and fertilizer production, while transportation and utilities are emerging markets. Markets are emerging for industrial trucks and passenger cars powered by hydrogen fuel cells. Indoor and outdoor hydrogen fueling stations are being built in support of these vehicles. A fuel cell is a device that combines hydrogen with oxygen from the air in an electrochemical reaction to create electricity, which can power an electric motor and propel a vehicle. The challenge,however,is how to transport and storage hydrogen. Due to their microporous characteristics and low costs, microporous activated carbons appeared as a good candidate for the development of porous packed bed hydrogen storage tank for mobile applications.

During the charging and discharging processes of a packed bed reservoir , the exothermal adsorption may result in serious limitations of the storage bed capacity.Recent researches have shown that several parameters affect the storage capacity, the volume of gas retained at the exhaustion pressure of the reservoir. In this context, the following themes have been highlighted(SILVA):

- Dissipation of the heat of adsorption. As adsorption is a process that releases heat and, in turn, heating reduces the absorption capacity, associated with the insulating character of the adsorbent materials, lead to a longer charging time. A similar situation occurs with the cooling desorption, the temperature drops considerably, making the rate of slow desorption .
- Minimize the non-desorbed residual volume. Of equal importance is the amount of gas that can be released in the desorption. The adsorption on microporous systems entails the retention of a significant part of the15% gas stored, but up to 30% in microporous.

1.3 Objectives

As adsorption is an exothermic process, an increase in temperature occurs during charging, which results in a lower gas storage capacity. In the discharge stage, there is a decrease in temperature, which reduces the amount of recovered gas. These thermal effects originate from the heat of adsorption, the global thermal capacity of the system and the heat transfer coefficient with the external environment. The objective is storage hydrogen at near-ambient temperatures and 'safe' pressures.As temperature values vary with location, the thermal system is made up of distributed parameters. In this way, the mathematical models would be constituted by partial differential equations, since the properties are distributed and not concentrated. However, in order to simplify the analysis of the problem, it is convenient to admit that a thermal system can be represented by a model of concentrated parameters, where the presented system has negligible resistance to heat flow, which leads to models governed by ordinary differential equations. The influence of important parameters on the behavior of the reservoir can be observed, and performance results of the hydrogen discharge process can be calculated. Due to the simplicity of such a formulation, only slow processes can be evaluated. To analyze the problem, values commonly found in a system containing hydrogen were assigned to the variables involved. Then, the solution of the presented model was made numerically. All simulations were performed using the Mathematica software.

2. PROBLEM FORMULATION

2.1 Reactor Configuration

The analyzed domain consists of a cylindrical reservoir containing an adsorbent material internally ,as shown in Fig: 1, equipped with a single opening for gas entry or exit and exchanges heat, by convection, with the surrounding air through its external area.

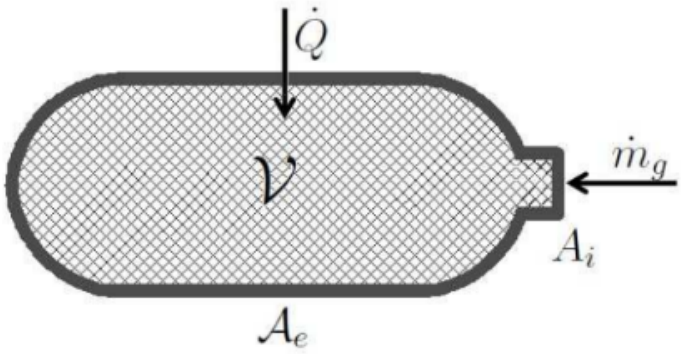


Figure 1: Packed bed of Hydrogen.

2.2 Simplifying assumptions

The adopted simplifying assumptions are:

- The wall temperature is assumed constant in the numerical model.
- Hydrogen is assumed to obey the perfect gas law.

- The solid and gas temperatures are assumed to be equal.
- The sites have equivalent energy and the adsorbed molecules do not interact with each other.

2.3 Conservation of Mass

As there is no variation in the mass of the adsorbent, only the variations of the gaseous and liquid phases or adsorbed phase, the term of mass accumulation is comprised by the fluid gaseous phase and the adsorbed phase:

$$\frac{\mathrm{d}m_g}{\mathrm{d}t} + \frac{\mathrm{d}m_l}{\mathrm{d}t} = (\dot{m}_g)|_{in} \tag{1}$$

The reservoir is loaded and unloaded through an opening located at one of its ends, thus being the net transfer rate of mass. In this way, the mass accumulation terms of the mass balance equation mass in the reservoir (Eq.(2)) are obtained by applying the concentration definitions of the gaseous and adsorbed phases:

$$(\varepsilon\frac{\mathrm{d}\bar{\rho_g}}{\mathrm{d}t} + \frac{\mathrm{d}\bar{\rho_l}}{\mathrm{d}t})\,\mathcal{V} = (\dot{m}_g))|_{in} \tag{2}$$

At this preliminary stage slow discharge at a constant mass flow rate is considered, for which $(\dot{m}_g)|_{in} = \rho_g v_g \mathcal{A}_{in}$ is negative constant.

2.4 Conservation of Energy

The global energy balance for the considered control volume is given by Eq.(3), where the energy accumulation is equal to the sum of energy transfer terms associated with charge and discharge , heat exchange with the external medium and the energy generation term due to the latent heat of adsorption.

$$(\varepsilon\bar{\rho_g}\frac{\mathrm{d}\bar{i_g}}{\mathrm{d}t} - \varepsilon\frac{\mathrm{d}\bar{p}}{\mathrm{d}t} + (\bar{i_l} - \bar{i_g})\frac{\mathrm{d}\bar{\rho_l}}{\mathrm{d}t} + \rho_b\frac{\mathrm{d}\bar{i_s}}{\mathrm{d}t})\,\mathcal{V} = -h(\bar{T} - T_0)A_e + (i_g\dot{m}_g)|_{in} \tag{3}$$

Where the parameters $\bar{i_g}$, $\bar{i_l}$ and $\bar{i_s}$ are the values of the average enthalpy of the gas, liquid and solid, respectively.

2.5 Constitutive Equations

2.5.1 Gas phase equation of state

The specific mass of the gaseous phase $\bar{\rho_g}$ will be expressed in terms of temperature and pressure with the aid of the Ideal Gas Law :

$$\bar{\rho_g} = \frac{\bar{p}}{RT} \tag{4}$$

For an isothermal process, the charge and discharge cycles start and end at the same temperature T_0. The minimum pressure ($P_{min} = p_0$) is the phase pressure gaseous at the beginning of the charge and, also, at the end of the discharge, measured at T_0. The pressure maximum (pmax) is the pressure of the gaseous phase at the end of the load and also at the beginning of the discharge, measured at T_0:

$$p_{\max} = \rho_{g,\max}\,RT_0 \tag{5}$$

$$p_{\min} = \rho_{g,\min}\,RT_0 \tag{6}$$

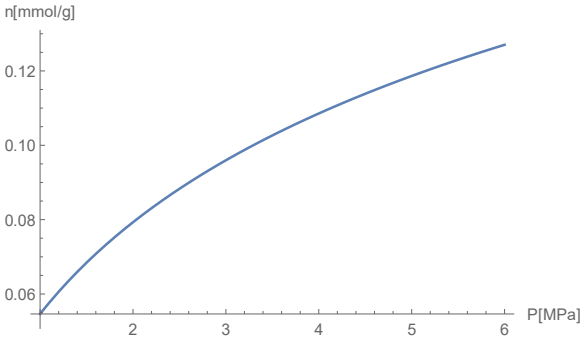
2.5.2 Adsorption equilibrium relations

The absolute adsorption amount can be described by the Toth equation:

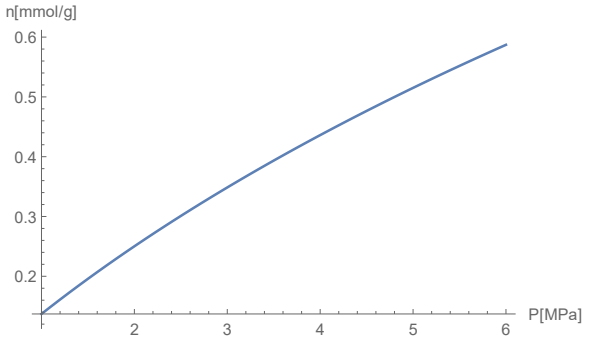
$$n = \frac{n_0(bf)}{(1 + (bf)^t)^{1/t}} \tag{7}$$

Where n is the number of moles of solute adsorbed per grams of adsorbent at equilibrium with the solid , n_0 is the saturated adsorption capacity , f is the bulk gas fugacity , t characterizes the heterogeneity of the adsorption system and b is a experimental parameter.

The parameters of the equations were taken from the studies of Q. Zheng et al.



(a) Toth prediction of hydrogen adsorption on SAC-02 activated carbon.



(b) Toth prediction of hydrogen adsorption on graphene sheets(GS).

Figure 2: Toth predictions

Table 1: Input parameters.

T(K)		**293**
adsorbent	**GS**	**SAC-02**
n_0(mmolg^{-1})	3.27	0.32
b (mmol$g^{-1}Mpa^{-1}$)	0.049	0.52
t	0.71	0.49

2.6 Initial conditions

As initial conditions the reservoir is considered to be at its maximum pressure and at minimum temperature (ambient) temperature, such that:

$$p(0) = p_{\max} \tag{8}$$
$$T(0) = T_0 \tag{9}$$

2.7 Other properties

The particle density is defined by t he ratio between the particle mass and the particle volume including the micro pores.

$$\rho_p = \frac{\rho_s}{1 + \upsilon_\mu \rho_s} \tag{10}$$

Where υ_μ is the volume of activated carbon microspores. The adsorbent porosity is calculated by:

$$\varepsilon = 1 - \frac{\rho_a}{\rho_s} - \upsilon_\mu \rho_a \tag{11}$$

Where the term $\frac{\rho_a}{\rho_s}$ is the volume occupied by the solid , the term$\upsilon_\mu \rho_a$ the volume of microspores.
The thermal conductivity of the adsorbent particles (k_p) will not only be that of the solid adsorbent (k_s) , but will also depend on the amount of adsorbed hydrogen (q). Porous media is made by:

$$k_{eff} = \varepsilon k_g + (1 - \varepsilon) k_p \tag{12}$$

The heat capacity of the adsorbent particle $c_{p,p}$ depends on the heat capacity of the solid adsorbent $c_{p,s}$ and on the heat capacity of the solid adsorbate considered in liquid phase $c_{p,l}$, as in the Eq.13:

$$cp, p = c_{p,s} + q c_{p,l} \tag{13}$$

Furthermore, the heat capacity of the porous medium is given by:

$$(\rho c_p)_p = \varepsilon \rho_g c_{p,g} + (1 - \varepsilon) \rho_p c_{p,p} \tag{14}$$

The permeability (α) and the coefficient of inertial losses (C) are calculated from Ergun's semi-empirical equations:

$$\alpha = d_p^2 \varepsilon^3 \frac{150}{(1-\varepsilon)^2} \tag{15}$$

$$C = \frac{3,5(1-\varepsilon)}{d_p \varepsilon^3} \tag{16}$$

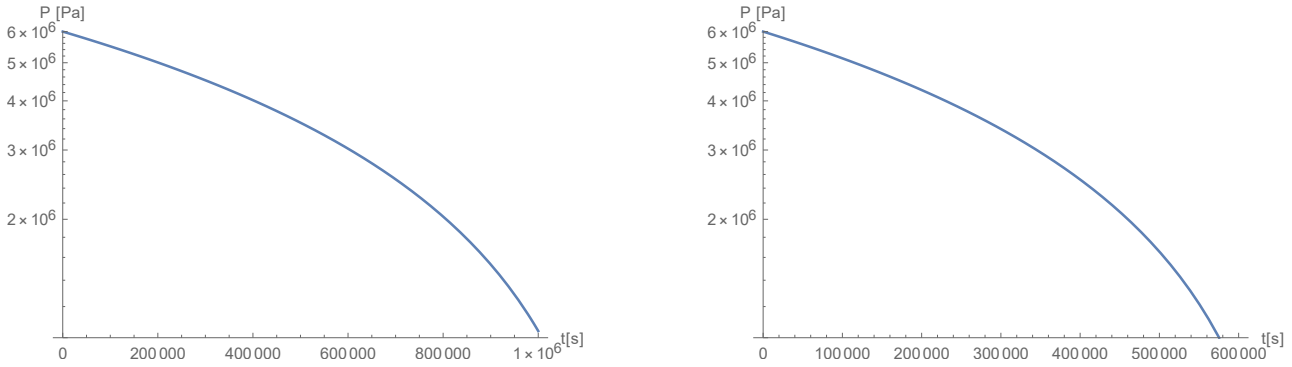
3. RESULTS

This section presents preliminary results for the simulated problem. At this stage an isothermal operation is considered. Table 2 presents input values used in the simulations. As mentioned, the inlet mass flow rate is negative as a discharge

Table 2: Input parameters.

Symbol	Quantity	Value
ε	porosity of SAC-O2 activated carbon	0.49
ε	porosity of graphene sheet	0.28
ρ_d	density of SAC-O2 activated carbon (kg/m^3)	517.6
ρ_d	density of graphene sheet (kg/m^3)	1800
$\rho_{l,\max}$	Maximum sorption capacity (kg/m^3)	103.5
$\mathcal{V}$	reservoir volume (m^3)	1.0
$\dot{m}_g\|_{in}$	inlet mass flowrate (kg/s)	-10^{-3}
$p_{\max}$	maximum pressure (MPa)	6
T_0	temperature (K)	293
β	Thermal Expansion of hydrogen (K^{-1})	3.5x10^{-3}

condition is being simulated. The simulation of the input data until the total depletion of the reservoir under isothermal operation is presented in figures 3a and 3b. The variation of gas concentration in the tank during discharge is demonstrated



(a) Pressure evolution on SAC- 02 activated carbon.

(b) Pressure evolution on graphene sheets

Figure 3: Pressure evolution for isothermal operation at a constant outlet mass flow rate.

by the figures 4a and 4b.

Since we are considering an isothermal process ,the internal energy of the gas phase only depends on the pressure :

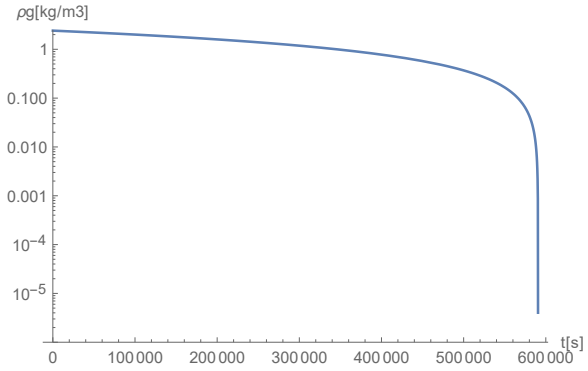
$$h_g = \frac{1}{\rho_g} dP - \beta T \frac{1}{\rho_g} dP \tag{17}$$

$$\beta = \frac{1}{\upsilon} \frac{\partial \upsilon}{\partial T} \tag{18}$$

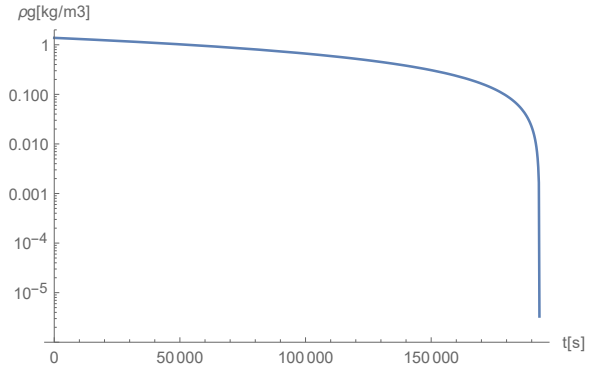
As the thermal expansion coefficient depends on the temperature variation, this term is disregarded from the equation.

$$h_g = \frac{1}{\rho_g} dP \tag{19}$$

In this case, as the enthalpy of the liquid varies only with temperature and the process is isothermal, the heat of adsorption will be the internal energy of the gas:



(a) Gas density on SAC- 02 activated carbon.

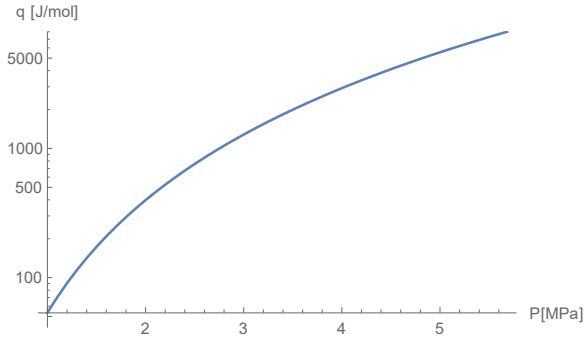


(b) Gas density on graphene sheets

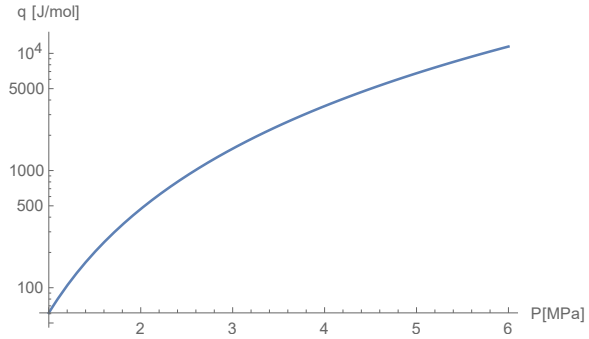
Figure 4: Gas density on adsorbent materials

$$q_{ads} = h_g - h_l \tag{20}$$

$$q_{ads} = h_g \tag{21}$$



(a) Adsorption heat on SAC- 02 activated carbon.



(b) Adsorption heat on graphene sheets

Figure 5: Adsorption heat on adsorbent materials

4. Conclusions

The adsorption mechanism of hydrogen on the adsorbent materials is the physisorption, and both adsorption isotherms of the GS and the activated carbon are Type I.The Toth equation was selected to analyze the adsorption data.During the discharging process, the pressure drop in the tank can be observed in figures 3a and 3b.Comparing with the activated carbon,the storage density of hydrogen on the GS is smaller than that of hydrogen on the activated carbon SAC-02, as shown in figures 4a and 4b.The heat of hydrogen adsorption on the activated carbon and the GS is respectively about 0.05–8.12 kJ/mol and 0.06–11.11 kJ/mol .It shows that interaction between hydrogen molecules and the graphene layer is stronger than that of hydrogen and carbon surface, as also demonstrated in the work of Q.Zheng et al.

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