

PERFORMANCE ANALYSIS OF A NEW ADSORPTIVE SYSTEM APPLIED TO THE FAST CHARGE IN NATURAL GAS STORAGE VESSELS

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Abstract. *The present work performs a numerical study case of a new adsorptive system applied to the natural gas storage vessels. In order to eliminate the detrimental effects of the adsorption heat, and to make viable the fast charge of the gas in automotive tanks a vessel constituted of the several tubes compacted with activated carbon is proposed in the present work. In the charge process, the gas circulates through the tank and all non-adsorbed gas goes through an external heat exchanger to the vehicle, which is installed close to the gas station. Depending on the applied mass flow rate, the numerical results obtained in the present work showed that the charge time of the new system vary between 50 and 200 seconds. Another advantage of this new system is that there no need to include the usual accessories employed in traditional tanks that increase the complexity of the vessel design such as: fins, perforated tube in the center of the tank, and cooling external jacket.*

Keywords: *Adsorbed natural gas, fast charge, natural gas storage vessels*

1. INTRODUCTION

Actually, a great world mobilization exists in the sense of reducing the emissions of the greenhouse gases in the atmosphere in function of the global warming. The carbon dioxide emissions, considered the major greenhouse gas, are due principally to fossil fuels burning and deforestation. The natural gas (NG) appears as excellent alternative fuel for application in automotive vehicles because it is cheaper gasoline or diesel and emits less carbon dioxide and other pollutants air when compared with gasoline vehicles. Natural gas is constituted of about 95% methane, a gas that cannot be liquefied at ambient temperature. Its storage has required the use of high-pressure compression technology (20MPa) with elevated cost (Mota *et al.*, 1997). The compressed natural gas (CNG) vessels reduce space in the vehicles and can require reinforcement in the suspension because of its weight. All efforts to improve this technology have focused on the reduction of the storage pressure in order to decrease operating costs of compression stations, and allow the use of lighter gas storage vessels.

An alternative low-pressure (3.5-4MPa) system for storing NG is the storage by adsorption. The adsorbed natural gas (ANG) represents a good compromise between compression costs and storage capacity. Presently, microporous activated carbons are the most successful adsorbents for ANG technology (Lozano-Castelló *et al.*, 2002). The ANG technology presents two major problems not encountered in CNG systems. The first problem is related to the shape adsorption isotherm (desfavorable to desorption), which prevents a linear response of the system relatively to the pressure (Mota *et al.*, 1995). In adsorption systems, the greatest pressure drop occurs with the removal of the first 10% of the fuel and as much as 15%-18% of the fuel still remains in the vessel under depletion pressure, since is unfeasible to operate the reservoir under sub-atmospheric pressure. The second problem is related to both the heat of adsorption which is about 1100 kJ/kg for methane adsorption on activated carbons, and with the dependence of the adsorption equilibrium relatively to the temperature. The physical adsorption of a gas is an exothermic phenomenon. During the rapid filling of a storage system by adsorption under conditions in which the heat of adsorption is not dissipated, less methane is adsorbed as the adsorbent heats up. Conversely, in the discharge cycle, the temperature drops due to the heat of desorption consumed on the process, thus increasing the residual amount of NG left in the tank at the exhaustion pressure (Chang and Talu, 1996).

Differents solutions have been proposed to minimize the detrimental effects of the temperature fluctuations in the ANG vessels ((Mota *et al.*, 2004), (Vasiliev *et al.*, 2000), (Yang *et al.*, 2005)). However, all those solutions need the insertion of the accessories in the tank that they reduce the available space for gas storage, they increase the complexity of the vessel design and they present serious limitations in terms of the heat transfer due to the poor thermal conductivity to the adsorbent bed. The major problem of the proposed solutions is that practically all the generated heat on the adsorption process is dissipated by conduction.

In this work, a new tank configuration is proposed to minimize the effects of the heat of adsorption in ANG systems. This new system uses forced convection between the adsorbent and the gas itself in order increase the heat transfer rates

within the bed. A computational code based on the finite volume method was developed to solve the mathematical model that describes the dynamics of the charge process. The discharge process is in development.

2. PROPOSED SYSTEM TO THE CHARGE CYCLE

An efficient ANG system should be capable to compensate the temperature fluctuations in the charge and discharge processes. In the traditional ANG systems the adsorbent bed is connected to a gas source at one end and is closed at the other end. The gas may enter or leave the tank through the open end. In this systems, the equilibrium between the external and the internal pressure is reached instantly. In this moment, the gas flow is stagnated and the heat transfer mechanism inside of the adsorbent bed is dominated by the conduction in the radial direction. Due to the low effective thermal conductivity of the adsorbent bed, these systems presents great temperature oscillations in the charge and discharge steps, being limited for application in fast charge situations. In order to minimize adsorption heat effects in ANG systems, a new tank configuration constituted of the several tubes compacted with activated carbon is suggested in this work. The idea is to use forced convection between the adsorbent pellets and the gas itself, in order to improve the heat transfer within the bed. Depending of the applied gas flow rate, high heat transfer rates can be obtained in the adsorbent bed. In Fig. 1 the charge cycle is shown. The natural gas enters in the tank with the temperature of the gas source and it leaves with high temperature due to the heat of adsorption generated in the charge process. After, all the non adsorbed gas that is hot passes through of a heat exchanger where the heat of adsorption is fully eliminated. Finally, the cold gas is recirculated for entrance of the tank through the use of a compressor. Depending of the work conditions of the heat exchanger the gas can enter sub-cold, increasing the adsorbed mass in the column. This study will be object of future publication.

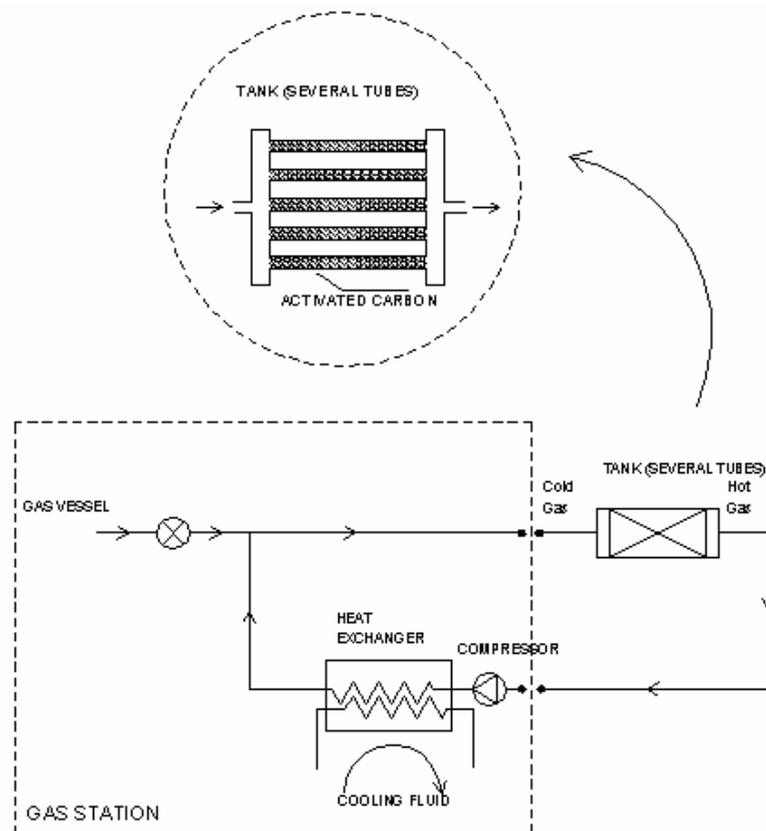


Figure 1 – Charge cycle

3. MATHEMATICAL MODEL

The Figure 2 shows the configuration of the problem under investigation here. A open column in both sides is considered in the analysis of the adsorbate flow in each individual tube. The adsorbate flows through of a steel column filled with activated carbon. The gas enters for an end of the column and it leaves for the other. The conservation laws that describes the column dynamics can be found in Ruthven (1984).

Notation	
C	concentration in the fluid phase [kg/m ³]
C_p	specific heat at constant pressure [J/kg K]
C_s	volumetric heat capacity of the solid [J/m ³ K]
d_p	pellet diameter [m]
D_{ef}	effective mass diffusion coefficient [m ² /s]
q	concentration in the solid phase [kg/m ³]
\bar{q}	volumetric average concentration over pellet [kg/m ³]
u	interstitial velocity [m/s]
h	convection heat transfer coefficient [W/m ² K]
ΔH	heat of adsorption [J/kg]
L	column length [m]
Nu	nusselt number
p	gas pressure [Pa]
Pr	Prandtl number
r	pellet radial coordinate [m]
R	column radius [m]
Re	Reynolds number
R_g	ideal gas constant [J/kg K]
t	time [s]
T	temperature [K]
U_g	Overall heat transfer coefficient [W/m ² K]
x	axial coordinate in the column [m]
<i>Greek letters</i>	
ε	bed porosity
λ	thermal conductivity [W/m K]
ρ	specific mass [kg/m ³]
<i>Subscripts</i>	
∞	Relative at the ambient ditions
0	Relative at the initial conditions
e	Relative at the external surface
f	Relative at the fluid phase
i	Relative at the internal surface
in	Relative at the column inlet
p	Relative at the pellet
S	Relative at the solid phase
w	Relative at the column wall
<i>Superscripts</i>	
*	Relative at the adsorption equilibrium

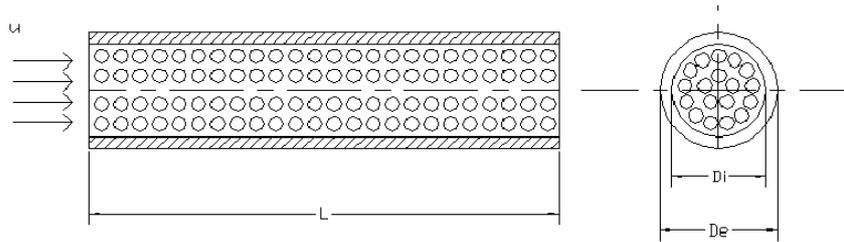


Figure 2 – Adsorbate flow in the open column.

3.1. Open column model

To the column model, the following assumptions are considered:

- The flow velocity is constant;
- Radial effects are neglected;
- The natural gas is considered constituted of the pure methane;
- The adsorbate behave as ideal gas;
- Pellets are considered as spherical particles and uniformly distributed;
- The monodisperse model is used to the description of the adsorption kinetics in the adsorbent and the effective mass diffusion coefficient is considered constant;
- Temperature is uniform inside the adsorbent particles;
- Adsorption equilibrium is assumed in the external surface of the adsorbent particles.

Under above assumptions, the column model is constituted by the continuity equation, energy equation and the perfect gas equation, respectively:

$$\frac{\partial C}{\partial t} + \frac{\partial}{\partial x}(u C) = -\frac{1-\varepsilon}{\varepsilon} \frac{\partial \bar{q}}{\partial t} \quad (1)$$

$$\frac{\partial}{\partial t}(C T_f) + \frac{\partial}{\partial x}(C u T_f) = \frac{\partial}{\partial x} \left(\frac{\lambda_f}{c p_f} \frac{\partial T_f}{\partial x} \right) + \frac{6 h_p}{d_p} \frac{(1-\varepsilon)}{\varepsilon c p_f} (T_s - T_f) + \frac{2 U_g (T_\infty - T_f)}{\varepsilon R_i c p_f} \quad (2)$$

$$p = C R_g T_f \quad (3)$$

The bed equations are subjected at the following initial and boundary conditions:

$$C(x,0) = C_0 \quad ; \quad T_f(x,0) = T_0 \quad \text{for} \quad 0 < x < L \quad (4)$$

$$C(0,t) = C_{in} \quad ; \quad T_f(0,t) = T_{in} \quad \text{for} \quad t \geq 0 \quad (5)$$

$$\frac{\partial C(L,t)}{\partial t} = 0 \quad ; \quad \frac{\partial T_f(L,t)}{\partial t} = 0 \quad \text{for} \quad t \geq 0 \quad (6)$$

To the Pellet, the mass and energy balances, can be written, respectively, as follows:

$$\frac{\partial q}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 D_{ef} \frac{\partial q}{\partial r} \right) \quad (7)$$

$$C_s \frac{\partial T_s}{\partial t} = \frac{6h_p}{d_p} (T_f - T_s) + (-\Delta H) \frac{\partial \bar{q}}{\partial t} \quad (8)$$

The initial and boundary conditions to the pellet equations are:

$$q(r,0) = q^*(p_0, T_0) \quad ; \quad T_s(0) = T_0 \quad \text{for} \quad 0 < r < R_p \quad (9)$$

$$\frac{\partial q(0,t)}{\partial t} = 0 \quad \text{for} \quad t > 0 \quad (10)$$

$$q(R_p, t) = q^*(p, T_s) \quad \text{for} \quad t > 0 \quad (11)$$

3.2. Determination of the heat transfer coefficients

The fluid-particle heat transfer coefficient h_p is given by the following correlation described in Ruthven (1984)

$$Nu_p = \frac{h_p d_p}{\lambda_f} = 2 + 1.1 Pr^{1/3} Re^{0.6} \quad (12)$$

The overall heat transfer resistance in the column wall is given by the sum of the inner convective resistance with wall conductive and outer convective resistances. Therefore, the overall heat transfer coefficient U_g is given by

$$U_g = \frac{1}{\frac{1}{h_i} + \frac{R_i}{\lambda_w} \ln\left(\frac{R_e}{R_i}\right) + \frac{R_i}{R_e} \frac{1}{h_e}} \quad (13)$$

The inner convective coefficient is given by Ruthven (1984)

$$Nu_i = \frac{h_i D_i}{\lambda_f} = 0.813 Re^{0.19} e^{-6d_p/D_i} \quad (14)$$

To evaluate the external convective coefficient, forced convection conditions were assumed. The external convective coefficient is given by the following correlation described in Incropera and DeWitt (1998)

$$Nu_e = \frac{h_e D_e}{\lambda_{air}} = 0.193 Re^{0.618} Pr^{1/3} \quad (15)$$

4. NUMERICAL PROCEDURE

The equations of the column model have been discretized by the finite volume method (Maliska, 2004). To evaluate the properties and their gradients on the faces of each control volume, the upwind scheme was used. The non-linearities and couplings between the different equations are treated by linearization and internal iteration in a given time step. To solve the linear systems formed by the discretized equations of the column model, the tridiagonal matrix algorithm (TDMA) was employed. The iterative process to obtain the numerical solution implied the following steps:

- 1) To supply the initials values of the variables C , T_f , q and T_s ;
- 2) To solve the Eq.(7) in each control volume of the column;
- 3) To solve the Eq.(8) in each control volume of the column;
- 4) To solve the Eq.(1) to obtain the concentration field in the column;
- 5) To solve the Eq.(2) to obtain the temperature field in the column;
- 6) To calculate the pressure field through the Eq.(3);
- 7) To return at the step 2 and to iterate until which the convergence is obtained in the current time level;
- 8) To progress to the next time level.

The following convergence criterium was used for to stop the iterations in the solution procedure above

$$\left| \frac{\phi_P^{k+1} - \phi_P^k}{\phi_{\max} - \phi_{\min}} \right| \leq 10^{-5} \quad (16)$$

where $|\phi_{\max} - \phi_{\min}|$ represents the maximum variation of the fluid phase concentration at the k iteration. When the Eq.(16) was not verified for every volume, another iteration was required.

5. NUMERICAL RESULTS

Details of the numerical validation of the computational code developed in this work can be found in Santos (2005). To the simulations with natural gas a reservoir in column form was considered. The column geometrics dimensions and other data used in the simulations are illustrated in Tab. 1. The adsorbent compacted in the column is the G216 carbon from North American Carbon Inc. of Columbus, Ohio. The adsorption equilibrium is given by a relationship of the Langmuir type. The adjustment parameters were obtained through of the experimental data published by Remick and Tiller (1996)

$$q^*(p, T_s) = \frac{q_m b p}{1 + b p} \quad (17)$$

with

$$q_m = 55920 T_s^{-2.3} \quad (18)$$

$$b = 1.0863 \times 10^{-7} e^{806/T_s} \quad (19)$$

where q is the adsorbed phase concentration (kg/kg), p is the pressure (Pa) and T_s is the solid phase temperature (K). With relation at the adsorption kinetics, activated carbons have high diffusional time constants, $D_{eff}/R_p^2 \cong 10^{-1} s^{-1}$, to the methane adsorption (Cess, 1973). Therefore, activated carbons generally offers low resistance at the mass diffusion process which occurs inside adsorbent particles.

Table 1 – Data and properties used in the charge process simulations.

Particle radius, R_p	0,5 mm
Column length, L	0,5 m
Column inner radius, R_i	2,5 cm
Initial pressure, p_0	0,1 MPa
Initial temperature, T_0	300 K
Inlet pressure, p_{in}	3,5 MPa
Inlet temperature, T_{in}	300 K
Mass diffusion coefficient, D_{ef}	$2,5 \times 10^{-8} \text{ m}^2/\text{s}$, Cess(1973)
Ideal gas constant, R_g	518.35 J/kg K
Bed porosity, ε	0,4
Adsorbent density, ρ_s	2150 kg/m^3 , (Mota <i>et al.</i> , 1995)
Adsorbent specific heat, C_{ps}	648 J/kg K, (Mota <i>et al.</i> , 1995)
Effective thermal conductivity of the bed, λ_{ef}	0,2 W/m K, (Mota <i>et al.</i> , 2004)
Adsorbate specific heat, C_{pg}	2450 J/kg K, (Mota <i>et al.</i> , 1995)
Surrounding temperature, T_∞	300 K
Flow velocity, u	0,5; 1,0; 1,5; 2,0 m/s
Adsorption heat, ΔH	$-1,1 \times 10^6 \text{ J/kg}$, (Mota <i>et al.</i> , 1995)

The Figure 3 shows temperature profiles in function of the time obtained of the numerical solution, along the column length. The gas velocity is considered equal to the 0.5 m/s while the gas inlet temperature is assumed equal to the 300 K. The curves are registered according your axial position in the column. For n_x volumes used in the discretization of the computational domain, the vol. [1] corresponds to the first volume of the mesh while the vol. [n_x] corresponds to the last volume. Three stages in the temperature profiles are observed. The rapid initial temperature increase (stage 1) is followed by a period in that the temperature stays constant (stage 2) and gradually falling toward at the gas inlet temperature (stage 3). At the beginning of the filling adsorption zone, the adsorbed amount increases very sharply and, as adsorption is an exothermic process, the temperature increases rapidly. The flat zone is a consequence of the fact that the quantity of the heat removed in the adsorbent becomes of order of magnitude of the generated heat inside adsorbent. In the last stage, the removed heat by the gas surpass the generated heat in the adsorbent and the temperature falls gradually until the equilibrium state. Activated carbons offers little resistance at the methane diffusion. Therefore, due to the high rates of adsorption verified in the adsorbent, the system can reach maximum temperatures of the order of 120°C. Other fact interesting in the Fig. 3 is that the equilibrium state was attained in only 200s. This is due to the fact that the heat exchange between the adsorbate and the adsorbent occurs by forced convection. All generated heat inside system is removed by the gas that flows in the column. Depending of the applied gas flow rate, high heat transfer rates can be obtained inside column.

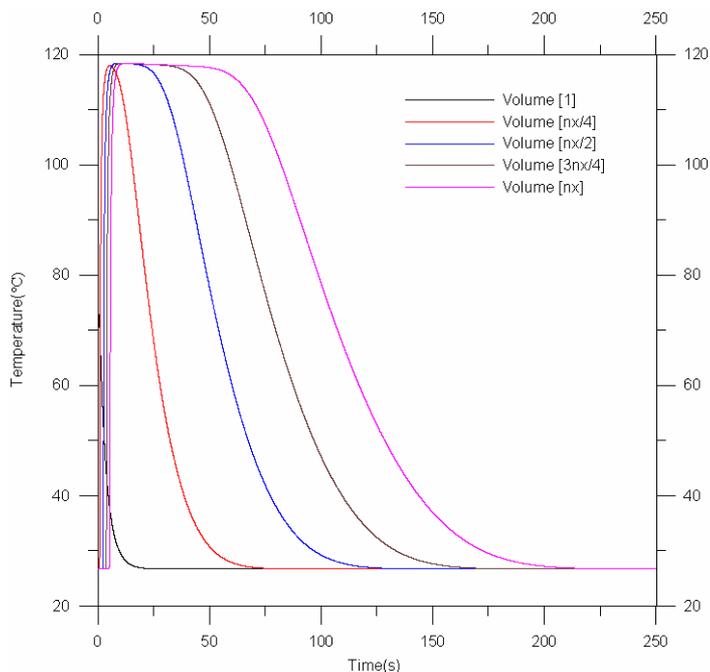


Figure 3 – Temperature profiles in five different points of the column ($u=0.5$ m/s, $T_{in}=300$ K).

The Figure 4 shows the adsorbed mass profiles in distinct points along of the column length. Since the mass diffusion resistance is little, the thermal resistance controls the adsorption kinetics. The effects of the thermal front lead to inverse influence on the adsorbed mass profiles because of the temperature influence on the adsorption equilibrium. When the temperature decreases and the thermal resistance vanishes, the adsorption capacity increases until to attain the equilibrium loading. The flat zone in the Fig.4 corresponds at the period in that the temperature stays constant in the Fig. 3. Observe that only 200s are necessary to the total filling of the column.

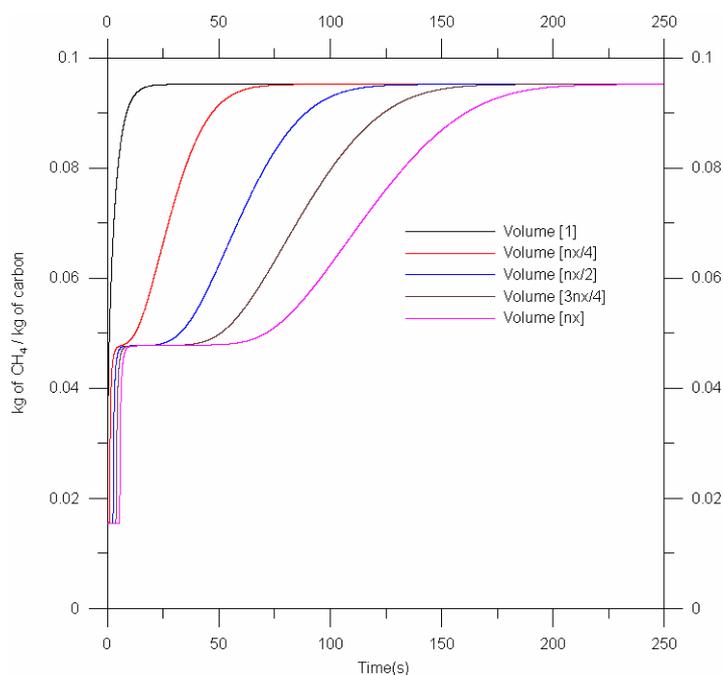


Figure 4 – Adsorbed mass profiles in five different points of the column ($u=0.5$ m/s, $T_{in}=300$ K).

The Figures 5 and 6 shows the influence of the flow rate in the column adsorption dynamics. In this case, four distinct values to the gas velocity are assumed, 2, 1.5, 1 and 0.5 m/s. The gas inlet temperature is considered equal to the 300 K. In the Figure 5 is verified that a progressive increase in the gas velocity causes a progressive reduction in the maximum average temperature and a reduction in the time necessary for to attain the equilibrium state. Those times can

to vary between 50 and 200s depending of the flow rate applied. The reduction in the maximum temperature occurs in function of the increase in the global transfer heat coefficient when the gas velocity increases. In the Figure 6 is verified that a increase in the gas velocity has as consequence a reduction in the column saturation time. The saturation time can to vary between 50 and 200s depending of the flow rate. In the Figure 1 we can to control the applied flow rate changing the work conditions of the compressor.

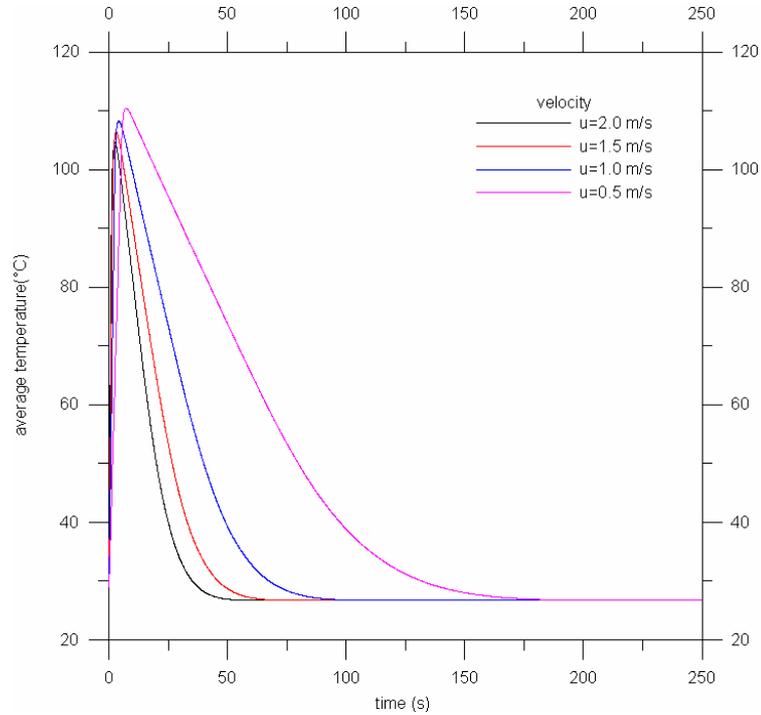


Figure 5 – Effect of the flow rate in the column cooling rate ($T_{in}=300$ K).

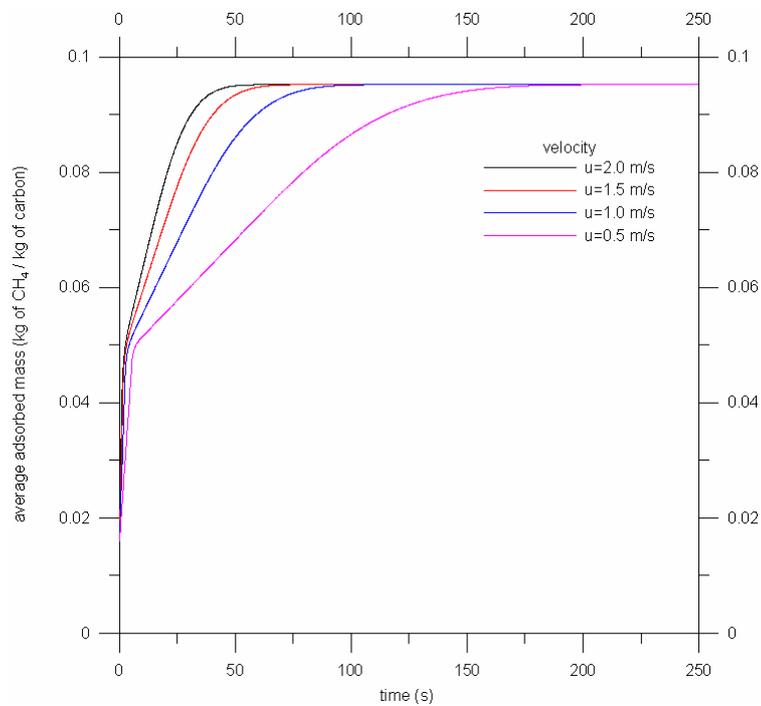


Figure 6 – Effect of the flow rate in the column saturation time ($T_{in}=300$ K).

6. CONCLUSIONS

A new tank configuration to the application in gas natural storage systems by adsorption was proposed with objective of to minimize the adsorption heat effects and to make viable the fast charge of the gas in automotive tanks. The proposed system uses forced convection between the adsorbent and the gas itself in order to increase the heat transfer rates within the adsorbent bed. A computational code based on the finite volume method was developed to solve the equations system that describes the charge process dynamics. The study of the discharge process is in development. The numerical results obtained in the present work showed that the charge time of the new system is a function of the prescribed mass flow rate and can vary between 50 and 200 seconds, depending of the applied flow rate. Those times are considered satisfactory for fast charge conditions. The second advantage of this new system is the possibility of the feed gas sub-cooling before it enters in the adsorbent bed. This study will be object of the future publication. Another advantage of this system is that there is no need to include accessories employed in traditional tanks such as: fins, perforated tube in the tank center and cooling external jacket which increases the complexity of the ANG vessel design.

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