NUMERICAL ANALYSIS OF NATURAL GAS DESORPTION DYNAMICS IN AN ACTIVATED CARBON BED

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Abstract. *The present work performs a numerical study of natural gas desorption dynamics in a column packed with activated carbon. In the bed regeneration process, a stream of overheated natural gas is used. The influence of regeneration temperature in the desorption dynamics was invetisgated. A numerical code based on the finite volume method was developed to solve the mathematical model that describes the desorption process in the column. The numerical results revealed that the elevation of gas temperature entering the bed increases the desorbed mass, improving, as a result, the desorption performance. The time required to complete the gas desorption in the adsorbent column was about 500 seconds. Based on the numerical results obtained, a new methodology for discharge in natural gas storage vessels has been suggested aiming at reducing the detrimental effects of the adsorption heat along the process implementation. A vessel made up of several tubes, compacted with activated carbon, is proposed in this work. To facilitate gas desorption, a fraction of the desorbed gas is made to circulate through an external heat exchanger at the storage vessel, where the energy of desorption is supplied in order to avoid temperature drop in the bed. The vehicle exhaustion gases can be used as heating fluid in the heat exchanger.*

Keywords*: Adsorbed natural gas, desorption dynamics, activated carbon, natural gas vessels*

1. INTRODUCTION

There has been, at present, a worldwide mobilization aiming at reducing greenhouse gases emissions in the atmosphere on account of global warming. Carbon dioxide, considered the most noxious of the greenhouse gases, comes mainly from the burning of fossil fuel and deforestation. Natural gas (NG) is an excellent alternative fuel for application in automotive vehicles because it is cheaper than gasoline or diesel and emits less carbon dioxide as well as other air pollutants. An internal combustion engine using natural gas can be switched to gasoline through spark ignition without major engineering difficulties. Natural gas includes about 95% methane, which is a gas that cannot be liquefied at ambient temperature. Therefore, the storage of natural gas requires the use of high-pressure compression technology (20MPa) at a very high cost (Mota *et al.*, 1995). Compressed natural gas (CNG) vessels reduce vehicular space and may call for suspension reinforcement on account of their weight. All efforts to improve this technology have been focused on storage pressure reduction in order to decrease compression stations operating costs and make possible the use of lighter gas storage vessels. With the reduction of storage pressure, it is possible to develop other vessel geometries, allowing better design flexibility. Another benefit from pressure reduction storage is the use of lighter materials, such as aluminum, in the manufacturing of vessels, which reduces the system weight.

Adsorption offers a low-pressure alternative (3.5-4MPa) system for storing NG. The adsorbed natural gas (ANG) is 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 of adsorption isotherm (unfavorable to desorption), which prevents a linear response of the system relatively to the pressure (Mota *et al.*, 1995). The second problem is related to 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 in the process, thus increasing the residual amount of NG left in the tank at exhaustion pressure (Chang and Talu, 1996). Ridha *et al.* (2007a) and Ridha *et al.* (2007b) showed the detrimental effects of adsorption heat along the charge and discharge steps of ANG vessels.

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]
$\overline{q}$	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]
R_e	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]

Greek letters

ε	bed porosity
λ	thermal conductivity [W/m K]
ρ	specific mass [kg/m^3]

Subscripts

∞	Relative at the ambient conditions
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

Superscripts

*	Relative at the adsorption equilibrium

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

In this work, the desorption dynamics of natural gas in activated carbon is investigated. Based on the numerical results obtained, a new tank configuration is proposed to minimize the effects of adsorption heat in ANG systems. The proposed system uses the forced advection between the adsorbent and the gas fluid flow in order to 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 desorption process. Details of the natural gas adsorption dynamics in activated carbon can be found in our previous work (Santos *et al*., 2007).

2. MATHEMATICAL MODEL

Figure 1 shows the investigated configuration. An open adsorbent column in both sides is considered. The adsorbate flows through a steel column filled with activated carbon.

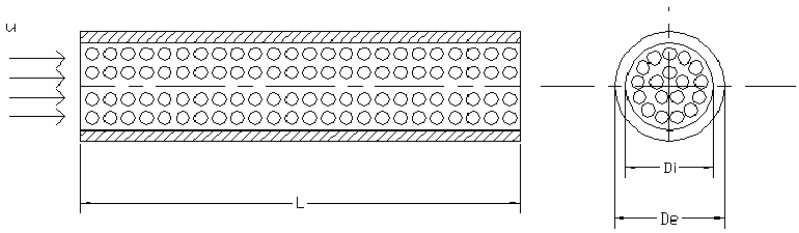


Figure 1. Adsorbate fluid flows in the open column.

2.1. Open column model

To model the fluid flow in the column, the following assumptions are considered:

- The flow velocity is constant;
- Radial gradients are neglected;
- The natural gas is constituted of the pure methane;

- The adsorbate behaves as ideal gas;
- Pellets are spherical particles uniformly distributed;
- The monodisperse model is used for the description of the adsorption kinetics in the adsorbent. The effective mass diffusion coefficient is considered constant;
- Temperature is uniform inside the adsorbent particles;
- Adsorption equilibrium is assumed on the external surface of the adsorbent particles.

Considering the above assumptions, the column model comprises the continuity equation, the energy equation and the ideal gas equation of state, respectively. More details can be found in Ruthven (1984).

$$\frac{\partial C}{\partial t}+\frac{\partial}{\partial x}(uC)=-\frac{1-\varepsilon}{\varepsilon}\frac{\partial \overline{q}}{\partial t} \tag{1}$$

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

$$p=C\,R_g\,T_f \tag{3}$$

The previous equations are subjected to the following initial and boundary conditions:

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

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

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

The mass and heat transfer resistance along the Pellets were modeled as follows:

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

$$C_s\frac{\partial T_s}{\partial t}=\frac{6h_P}{d_P}(T_f-T_S)+(-\Delta H)\frac{\partial \overline{q}}{\partial t} \tag{8}$$

The following initial and boundary conditions to the pellet equations were used:

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

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

$$q(R_P,t)=q^*(p,T_S) \quad \text{for} \quad t>0 \tag{11}$$

2.2. Determination of the heat transfer coefficients

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

$$Nu_p=\frac{h_p d_p}{\lambda_f}=2+1.1\,\mathrm{Pr}^{1/3}\mathrm{Re}^{0.6} \tag{12}$$

The overall heat transfer resistance in the column wall is given by the sum of the inner advective resistance, wall conductive resistance, and the outside advective resistance. Therefore, the overall heat transfer coefficient U_g is given by

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

The inner convective coefficient is given by Ruthven (1984)

$$Nu_i = \frac{h_i D_i}{\lambda_f} = 0.813\,\mathrm{Re}^{0.19}\,\mathrm{e}^{-6 d_p / D_i} \tag{14}$$

To evaluate the external convective coefficient, forced advection conditions were assumed. The external advective coefficient is given by the following correlation described by Incropera and DeWitt (1996)

$$Nu_e = \frac{h_e D_e}{\lambda_{air}} = 0.193\,\mathrm{Re}^{0.618}\,\mathrm{Pr}^{1/3} \tag{15}$$

3. 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 at a given time step. The tridiagonal matrix algorithm (TDMA) was employed to solve the linear systems. The iterative process to obtain the numerical solution implied in the following steps:

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

The following convergence criterion was used to stop the iterations at each time step

$$\left|\frac{\phi_P^{k+1} - \phi_P^k}{\phi_{\max} - \phi_{\min}}\right| \le 10^{-5} \tag{16}$$

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

5. NUMERICAL RESULTS

Details of the numerical validation of the computational code used in this work can be found in Santos (2005). The column geometric dimensions and other data used in the simulations are illustrated in Tab. 1. The G216 carbon from North American Carbon Inc. of Columbus, Ohio was used as adsorbent. The adsorption equilibrium is given by a relationship of the Langmuir type. The adjustmental parameters were obtained from the experimental data published by Remick and Tiller (1996).

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

with

$$q_m = 55920\; T_s^{-2.3} \tag{18}$$

$$b = 1.0863 \times 10^{-7}\; e^{806/T_s} \tag{19}$$

where q is the adsorbed phase concentration (kg/kg), p is the pressure (Pa) and T_s is the solid phase temperature (K). Regarding the adsorption kinetics, activated carbons have high diffusional time constants, $D_{ef}/R_p^2 \cong 10^{-1}\ s^{-1}$, for methane adsorption (Cess, 1973). Therefore, activated carbon generally offers low resistance to the mass diffusion process occurring inside adsorbent particles. The results presented next will refer to a column with adiabatic wall.

Figure 2 shows the natural gas desorption dynamics in activated carbon bed. Figure 2a shows the temperature profiles as regards the time obtained from the numerical solution along the column length. The discharge flow rate is considered equal to 15 l/min, while the gas temperature in the inlet end is assumed equal to 400 ºC. The curves are registered according to its axial position in the column. For nx volumes used in the discretization of the computational domain, the vol. [1] corresponds to the first volume of the mesh, whereas vol. [nx] corresponds to the last volume. Figure 2a shows the thermal front displacement due to the hot gas flow inside the adsorbent column. Another interesting factor in Fig. 2a is that the thermal equilibrium between the gas and the column is attained in approximately 500s.

Table 1. Data and properties used in the discharge process simulations.

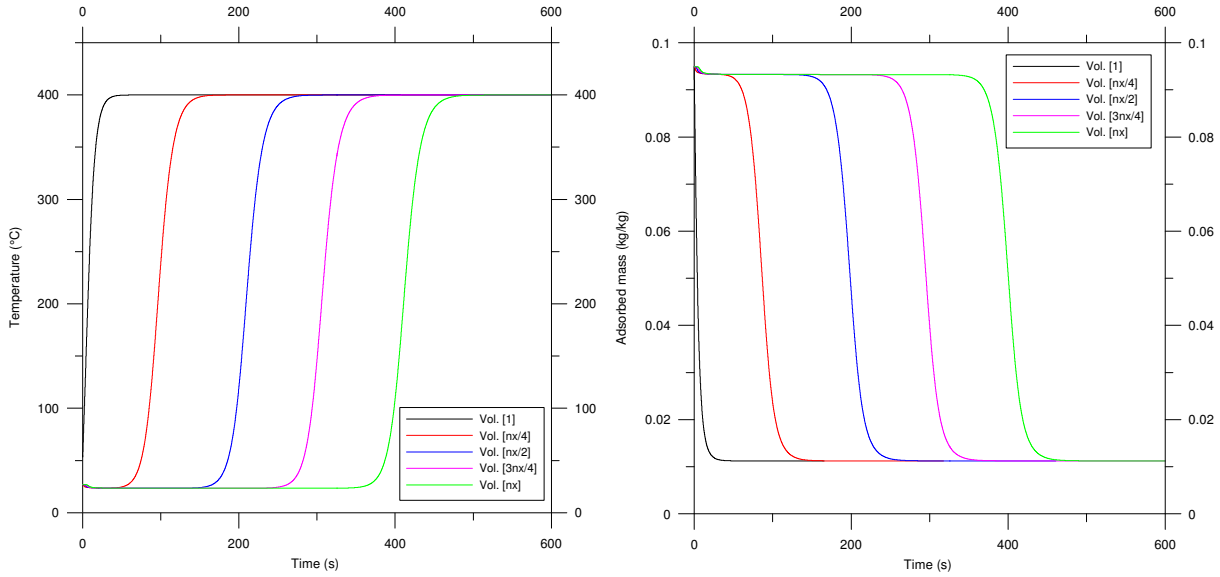
Particle radius, Rp	0,5 mm
Column lenght, L	0,5 m
Column inner radius, R_i	2.5 cm
Initial pressure, p_0	3.5 MPa
Initial temperature, T_0	300.3 K
Inlet pressure, p_{in}	5 MPa
Inlet temperature, T_{in}	373.3, 473.3, 573.3, 673.3 K
Mass diffusion coefficient, D_{ef}	2.5×10^{-8} m^2/s, Cess(1973)
Ideal gas constant, R_g	518.35 J/kg K
Bed porosity, ε	0.4
Adsorbent density, ρ_s	2150 kg/m^3, (Mota *et al.*, 1995)
Adsorbent specific heat,C_{ps}	648 J/kg K, (Mota *et al.*, 1995)
Effective thermal conductivity of the bed, λ_{ef}	0.2 W/m K, (Mota *et al.*, 2004)
Adsorbate specific heat, C_{pg}	2450 J/kg K, (Mota *et al.*, 1995)
Surrounding temperature, T_∞	300 K
Flow velocity, u	0.1273 m/s
Adsorption heat, ΔH	$-1{,}1 \times 10^6$ J/kg , (Mota *et al.*, 1995)
Discharge flow rate	2.5×10^{-4} m^3/s (15 l/min)
Wall thickness	0.4 cm
Wall thermal conductivity	15.1 W/m K

Figure 2b shows the displacement of the desorption front inside the column. It is worth mentioning that the inverse behavior of the adsorbed mass profiles relative to temperature profiles is due to the inverse dependence of the adsorption equilibrium properties on temperature. When the bed average temperature reaches its maximum value, the minimum value of the adsorbed mass is registered in the adsorption column. This value is different from zero, since it is impossible to operate the column under sub-atmospheric pressure conditions and also is uneconomic to use high regeneration temperatures in the column. It has been observed that about 500s are needed in order to obtain full discharge in the column.

5.1. Influence of the regeneration temperature on the desorption process performance

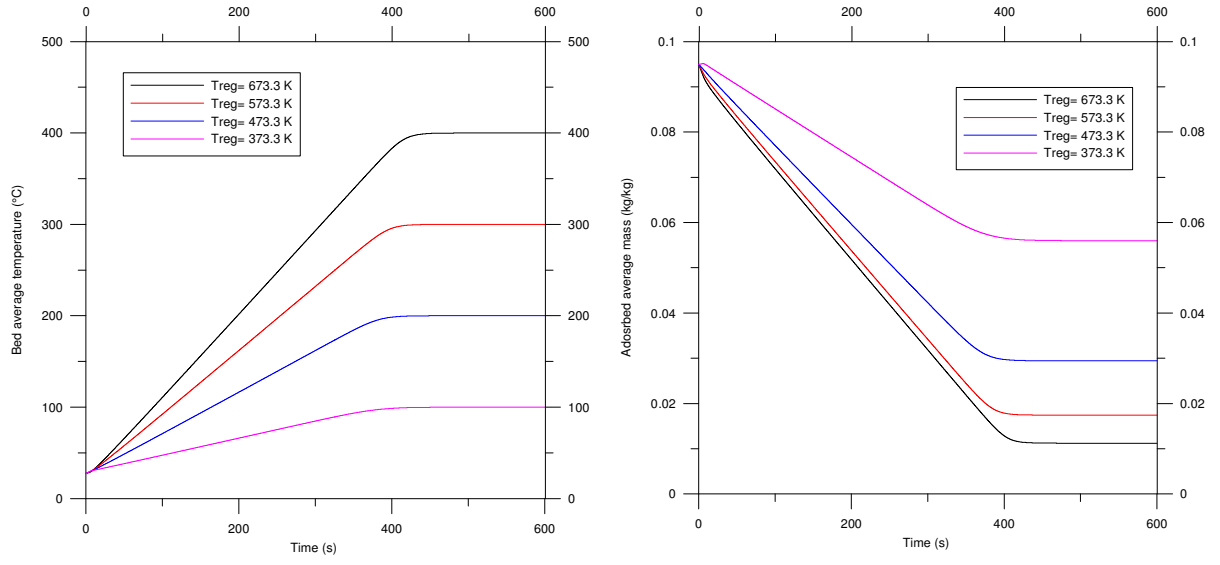
Figure 3 shows the influence of the regeneration temperature on the desorption process. Four distinct values are considered for the regeneration temperature: 373.3, 473.3, 573.3 and 673.3 K. Figure 3a shows that the bed average temperature increases linearly with the time until the steady-state is reached. It has also been observed that a higher

regeneration temperature increases the bed average temperature. Therefore, as shown in Figure 3b, a higher regeneration temperature increases the desorbed mass in the column. For natural gas fuelled vehicles, the exhaustion gas temperature can reach 500ºC. As a result, exhaustion gases have an elevated potential to provide the energy required at the regeneration process. However, the regeneration maximum temperature is limited by the exhaustion gases exergy in the combustion engine and by the effectiveness of the heat exchanger employed. Another interesting fact shown in Figure 3a is that the temperature-drop problem during the discharge step using the traditional ANG vessels does not occur here.



(a) (b)

Figure 2. Natural gas desorption dynamics in activated carbon bed. (a) Temperature profiles. (b) Adsorbed mass profiles.



(a) (b)

Figure 3. Influence of the regeneration temperature on the desorption process. (a) Bed average temperature (b) Adsorbed average mass.

6. PROPOSED SYSTEM FOR DISCHARGE IN ANG VESSELS

An efficient ANG system should be capable of compensating for temperature fluctuations during the charge and discharge processes. In the traditional ANG systems, the adsorbent bed is connected to a gas source at only one end. The gas can enter or leave the tank through the same opened end. In these systems, the equilibrium between external and internal pressure is reached instantaneously. At that point, the gas flow stagnates and the heat transfer mechanism inside the adsorbent bed is dominated by conduction in the radial direction. Due to the low effective thermal conductivity on the adsorbent bed and the thermal resistance imposed by the vessel wall, the system presents great temperature oscillations in both the charge and discharge process. From the numerical results obtained in the present work, we verified that the regeneration temperature elevation in the adsorbent open column did improve the performance of the desorption process. Therefore, in order to minimize adsorption heat effects in ANG systems during the discharge cycles, a new tank configuration made up of the several tubes compacted with activated carbon is suggested. The idea is to use forced advection between the adsorbent pellets and the adsorbate in order to improve the heat transfer within the bed. The discharge cycle is shown in Fig. 4. The natural gas leaves the tank at low temperature due to the desorption heat consumed during the discharge process. Next, similar to the procedure accomplished in TSA separation plants, a fraction of the cold desorbed gas is extracted and made to circulate through an external heat exchanger, where the desorption energy required to regenerate the bed is supplied. Here, the exhaustion gases of the internal combustion engine can be used as heating fluid in the heat exchanger. Finally, the hot gas is pushed through into the other end of the column by means of a compressor so as to facilitate the discharge process in the adsorbent column. Depending on the work conditions of the heat exchanger, the gas can enter overheated, increasing the desorbed mass in the column. The mathematical model of the discharge system showed in the Fig. 4 is undergoing further development.

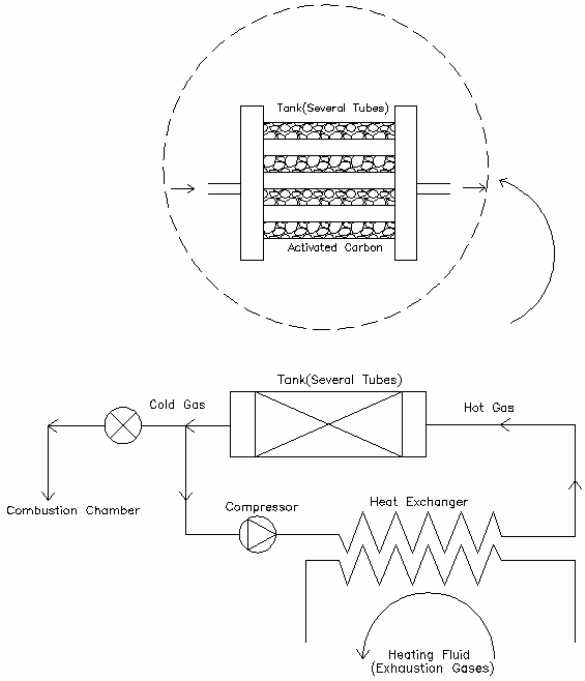


Figure 4. Proposed system for discharge in ANG vessels.

6. CONCLUSIONS

The present work proposes a numerical study of natural gas desorption dynamics in an opened adsorbent column packed with activated carbon. A computational code based on the finite volume method was developed to solve the system of equations describing the regeneration process dynamics. The numerical results demonstrated that the temperature elevation of the gas entering the column increases the desorbed mass, improving the regeneration process performance. The time required for the desorption process in the bed was about 500 seconds. The numerical results showed further that the temperature-drop problem during the discharge phase, observed in traditional ANG vessels, has not been registered here. Based on the numerical results obtained, a new discharge methodology for ANG vessels has been recommended in order to reduce the detrimental effects of the adsorption heat during the process. A vessel made

up of several tubes compacted with activated carbon is proposed. This system uses forced advection between the adsorbent and the gas itself in order to increase the heat transfer rates within the adsorbent bed. The proposed methodology for the discharge cycle in ANG vessels employs the energy of exhaustion gases to stimulate natural gas desorption in the adsorbent bed. Since the exhaustion gas temperature can reach 500ºC in natural gas fuelled vehicles, the proposed system has high potential to make ANG technology viable in automotive vehicles.

7. ACKNOWLEDGEMENTS

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8. REFERENCES

Cess, R. D., 1973, "Handbook of heat transfer", McGraw-Hill, New York.

Chang, K. J. and Talu, O., 1996, "Behavior and performance of adsorptive natural gas storage cylinders during discharge", Applied Thermal Engineering, Vol.16, pp. 359-374.

Incropera, F. P. and DeWitt, D. P., 1996, "Fundamentals of Heat and Mass Transfer", Wiley & Sons, 4ª Edition.

Lozano-Castelló, D., Monge-Alcañiz, J., Casa-Lillo, M. A. and Cazorla-Amorós, D., 2002, "Advances in the study of methane storage in porous carbonaceus materials", Fuel, Vol. 81, pp. 1777-1803.

Maliska, C. R., 2004, "Computational Fluid Mechanics and Heat Transfer", LTC, Rio de Janeiro, Brazil.

Mota, J. P. B., Esteves, I. A. A. C. and Rostam-Abadi, M., 2004, "Dynamic modelling of an adsorption storage tank using a hybrid approach combining computational fluid dynamics and process simulation", Computers and Chemical Engineering, Vol. 28, pp. 2421-2431.

Mota, J. P. B., Saatdjian, E. and Tondeur, D., 1995, "A Simulation model of a high-capacity methane adsorptive storage system", Adsorption, Vol.1, pp.17-27.

Remick, R. J. and Tiller, A. J., 1996, "Heat generation in natural gas adsorption systems", Gaseous Fuels for Transportation International Conference, Vancouver, Canada.

Ridha, F. N., Yunus, R. M., Rashid, M. and Ismail, A. F., 2007, "Thermal analysis of adsorptive natural gas storages during dynamic charge phase at room temperature", Experimental Thermal and Fluid Science, Vol. 32, pp. 14-22.

Ridha, F. N., Yunus, R. M., Rashid, M. and Ismail, A. F., 2007, "Thermal transient behavior of an ANG storage during dynamic discharge phase at room temperature", Applied Thermal Engineering, Vol. 27, pp. 55-62.

Ruthven, D. M., 1984, "Principles of adsorption and adsorption processes", Wiley Interscience, New York, 1984.

Santos, J. C., 2005, "Numerical analysis of the adsorption dynamics in column applied to the natural gas storage", Doctor thesis, Federal University of Paraiba, Joao Pessoa, Paraiba, Brazil.

Santos, J. C., Marcondes, F. and Gurgel, J. M., 2007, "Performance analysis of a new adsorptive system applied to the fast charge in natural gas storage vessels", Proceedings of the 19th International Congress of Mechanical Engineering, in CD-ROM, Brasilia, Brazil.

Vasiliev, L. L., Kanonchik, L. E., Mishkinis, D. A. and Rabetsky, M. I., 2000, "Adsorbed natural gas storage and transportation vessels", Int. J. Therm. Sci. , Vol. 39, pp. 1047-1055.

Yang, X. D., Zheng, Q. R., Gu, A. Z. and Lu, X. S., 2005, "Experimental studies of the performance of adsorbed natural gas storage system during discharge", Applied Thermal Engineering, Vol. 25, pp.591-601.

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