NUMERICAL ANALYSIS OF THE EFFICIENCY IN ADSORBED NATURAL GAS RESERVOIRS SUBMITED TO CONSTANT AND VARIABLES DISCHARGE PROCESSES

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Abstract. *With the exponential growth of market of natural gas for automotive refueling use, several researches have been developed for a better use of that technology. One of those arrivals consists of the application of microporous materials (adsorbents) inside the reservoirs that store the referred fuel. The adsorption benefits in the storage of the natural gas, for vehicles use, is many advantages on the storage viewpoint, principally respecting moderated pressure value necessary to storage an amount of gas approximately equivalent that one obtained only by compression. Therefore, there is stress reduction on the reservoir wall during adsorption storage process. Although, some problems relatives to adsorbed natural gas (ANG) employ has been described in specialized literature. Among everyone arguments contrary to adoption of this alternative, the most critical is the reservoir efficiency loss due to thermal effects, characteristics of the gas flow in porous media. Several studies has been developed objecting to minimize the temperature either rise or drop, observed in the charge and discharge gas process, respectively, once such variations is decisive factors to not provisioning of all storage capacity into ANG tanks. In present study is proposed a comparison between the boarded methodology (experimental or numerical) in literature, where in the first, the discharge rate flow is considered constant, and a second methodology (present work), apply a numerical approaching of discharge process interspaced by periods of no rate flow, proportioning a thermal equilibrium in the porous media and hence improvement in the adsorption system efficiency. Such pauses in the discharge process simulate the utilization, day by day, of a reservoir into a popular automotive vehicle.*

Keywords*: natural gas, adsorption, numerical simulation, reservoir efficiency.*

1. INTRODUCTION

The elevated cost of the traditional fuel, associate to environment preservation matter, encourages the search of alternatives manner to automotive refueling. The natural gas (NG) has represented a considerable section of that market, with growth participation, principally in the great world metropolitan area. According Alcañiz *et al*. (2002), the NG can be commercially available into different storage media, where each one to present characteristic cost and performance.

The consequence of the feasibility of this fuel is reflected in the storage under elevates pressure values, with range between 16 to 25 *MPa* (Mota *et al*., 1997), where, for this, is necessary tanks with stronger shape, usually cylindrical to support the stress level produces. In face to necessity of minimize the troubles caused by compressed natural gas (CNG), some materials, denominates adsorbents, has been utilized inside the cylinders, proportioning a pressure reduction necessary to gas compression, with no storage capacity loss. However, researches derived of the specialized literature describes problems as for utilization of that technology, once the thermal effects of the adsorption compromises the adsorbed natural gas system efficiency, infeasible, in some cases, its application (Mota *et al*., 1997).

The major of those problems is the decrease of the storage capacity in the reservoirs during charge and discharge process. According Chang and Talu (1996), the heat of adsorption produced concomitant to charge process can be minimized with a slow refueling (overnight), where the moderate gas velocity minimize the exothermal reaction featured of the referred process. By other side, the desorption (gas consumption), supply a substantial refresh of the ANG system, once that heat does not is replaced during the discharge process. This temperature drop favors the permanence of a residual amount gas inner of the reservoir. This represents up to 35 % of the maximum capacity (Matranga *et al*., 1991).

Among the solution presented on the literature (Vasiliev *et al*., 2000; Biloe *et al*., 2001), the forced convection around tank is a better to reduction of the already cited temperatures changes. This device is utilized to supply the heat requested to the adsorptive system during the engine gas consumption and can be made by either passing of the gases of combustion or compressed air produced in a compressor.

Although, in such board is considered the gas consumption as a constant currence, where the fuel flow out of the reservoir until has not any more discharge rate flow. In this case, the efficiency loss is evaluated at its extreme values, once the thermal effects growth during the gas consumption. In the present study the valuation of the discharge is proposed by numerical simulation and has a goal forthcoming of the real application in vehicle, that is, discharges variables (vehicles moving) interspaced by periods of not discharge (vehicle stopped), where the thermal effects is minimizes due absence of the discharge and thermal equilibrium of the porous media.

2. MODEL AND NUMERICAL STUDY

In the present study the analysis object is a reservoir (69 *liters*) whose dimensions is 356 *mm* of diameter, 920 *mm* of length and 6 *mm* of thickness, as viewed on the Fig. 1. This tank is filled with adsorvent material and the gas mass is conduct through diffuser (holed pipe) inside the cylinder. Thus, the discharge is done only in radial direction. The forced convection (h_w = 30 W/m^2K) is promoted by air circulation across the galleries around cylinder while the engine is working, such as proposed by Biloé *et al.* (2001). When the engine stop, h_w = 5 W/m^2K (natural convection).

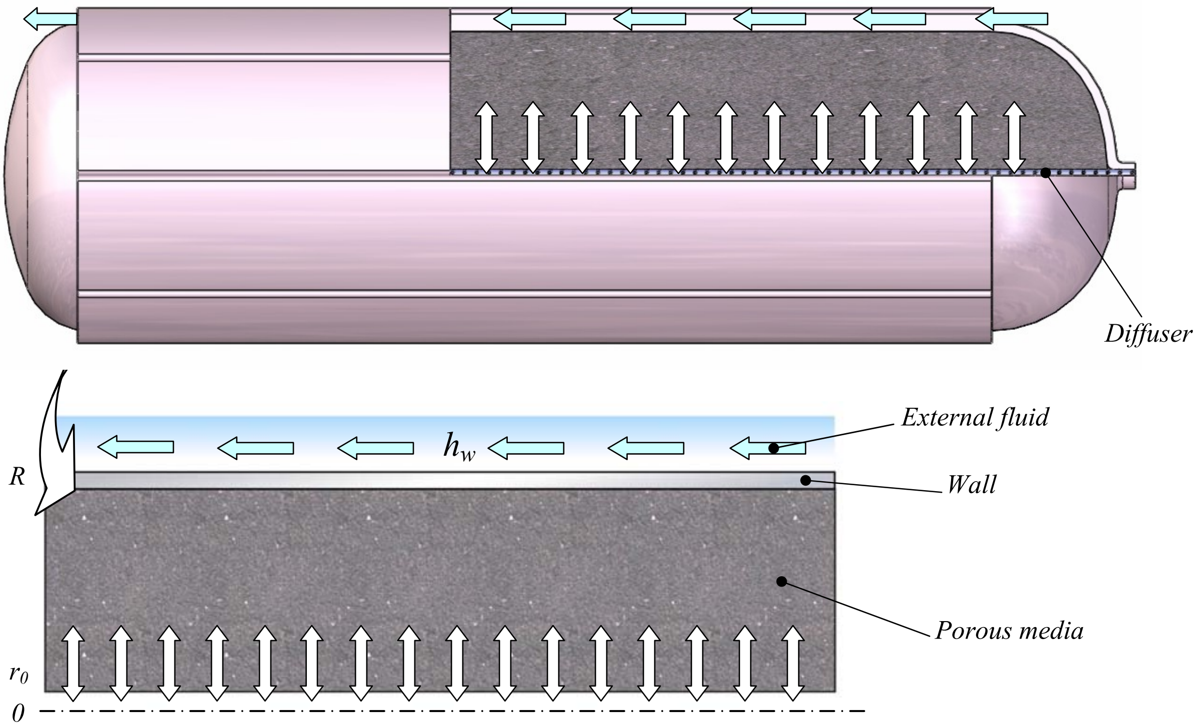

Figure 1. Work scheme of the cylinder analyzed and its numerical representation with one-dimensional domain.

This tank is submitted to four different discharge processes: in the first and second analysis, the discharge process is simulated considering rate flow constant (literature proposition) with 50 *l/min* e 25 *l/min*, respectively, according with Schlosser *et al.* (2004), which relate the cited value to gas consumption type (engine solicitation). In those circumstances the reservoir to be charges with work pressure (3,5 *MPa*), when begins to empty until its internal pressure reach the absolute atmospheric pressure (0,101 *MPa*). In this moment the rate flow is to cease. That is, the thermal effect is constant and creasing for two first processes. In the second situation, the two rate flow is considered yet, however the discharge process occurs according a routine established such as viewed in Tab. 1.

Table 1. Routine of the rate flow variable (2nd situation), corresponding to analysis of the third and fourth process

Rate flow (Q_0)	Time event										
	First day				Second day				Third day		
	1	2	3	4	5	6	7	8	9	10	11
50 (*l/min*)	0,5 *h* moving; 4 *h* stopped	0,5 *h* moving; 1 *h* stopped	0,5 *h* moving; 4 *h* stopped	0,5 *h* moving; 12 *h* stopped	0,5 *h* moving; 4 *h* stopped	Tank emptying	Tank empty	Tank empty	Tank empty	Tank empty	Tank empty
25 (*l/min*)	0,5 *h* moving; 4 *h* stopped	0,5 *h* moving; 1 *h* stopped	0,5 *h* moving; 4 *h* stopped	0,5 *h* moving; 12 *h* stopped	0,5 *h* moving; 4 *h* stopped	0,5 *h* moving; 1 *h* stopped	0,5 *h* moving; 4 *h* stopped	0,5 *h* moving; 12 *h* stopped	0,5 *h* moving; 4 *h* stopped	0,5 *h* moving; 1 *h* stopped	Tank emptying

The numerical tool consists in the solution of the mass and energy equation which govern the discharge process (Biloé *et al.*, 2001) with the suitable boundary conditions. This solution is obtained solving the coupled one-dimensional problem, wise with base in finite volume methods (Patankar, 1980).

2.1. Mass and energy equations

The conception of that model is proposed according with supposition that simplify the physics of the analyzed problem. This way, the following premises is adopted:

In first place, the diameter e length rate of the cylinder associated to gas diffuser presence allows us to consider a one-dimensional problem according to radial direction. That is, all axial effects are neglected as referred early (Biloé *et al.*, 2001); The natural gas is though to be integrally methane and its behaves as an ideal gas. Besides, the gas, porous media and tank properties are though to be constant in the range of temperature and pressure boarded; Fourier's and Darcy's laws determine the heat and mass flow in the composite, respectively (Biloé *et al.*, 2001); following Mota (1995) and Lamari *et al.* (2000), the natural convection inside the reservoir is neglected.

According to simplifications imposed to model in analysis, the mass balance is obtained by the following relation:

$$\frac{\partial}{\partial t}\left(\varepsilon_t \rho_g + \rho_s q\right) + \vec{\nabla}\cdot\left(\rho_g \vec{u}_g\right) = 0 \tag{1}$$

where

$$\rho_g = \frac{P}{R_g T} \tag{2}$$

$$q = W_0 \rho_a \exp\left[-\left(\frac{R_g T \ln\left(\frac{P_s}{P}\right)}{E_0 \beta}\right)^n\right] \tag{3}$$

$$u_g = -\frac{K}{\mu}\vec{\nabla} P \tag{4}$$

The terms varying in time $\varepsilon_t.\rho_g$ and $\rho_s.q$ corresponds to gaseous phase accumulation and adsorbed phase accumulation, respectively. The term $\vec{\nabla}.(\rho_g \vec{u}_g)$ represents the gas flow in radial direction. In conformity with Biloé *et al.* (2002), the accessible porosity (ε_t) is a function of the amount of adsorbed gas $q(P,T)$, represented by well-known Dubinin-Astakhov equation (Eq. 3), whose parameter is casting in a Tab. 2. According to premises above, the density of the no-adsorbed gas phase (ρ_g) is obtained by perfect gases equation (Eq. 2).

Table 2. Isothermal parameters of the Dubinin-Astakhov equation

Parameter	Value	Reference
W_0 (Maximum adsorbed gas volume - m^3/kg)	*1,17x10⁻³*	*Biloe et al., 2001*
R_g (Methane gas constant - $J/kg.K$)	*518,35*	*Mota et al., 1995*
E_0 (Characteristic energy of adsorption - J/mol)	*15884*	*Biloe et al., 2001*
ρ_a (Adsorbed gas density - kg/m^3)	-	*Ozawa et al., 1976*
P_s (Saturated vapor pressure - MPa)	-	*Ozawa et al., 1976*
β (Affinity coefficient)	*0,35*	*Stoekli et al., 2000*
n (Shape factor)	*1,39*	*Biloe et al., 2001*

The energy balance in porous media (Eq. 5) is obtained by the relation proposed in Mota *et al.* (1995):

$$C_{pa}\frac{\partial}{\partial t}\left(\left(\varepsilon_t \rho_g + \rho_s q\right)T\right) + \rho_s \frac{\Delta h}{M_g}\frac{\partial q}{\partial t} - \varepsilon_t \frac{\partial P}{\partial t} + \rho_s C_{ps}\frac{\partial T}{\partial t} + C_{pg}\vec{\nabla}.\left(T\rho_g \vec{u}_g\right) - \vec{\nabla}\cdot\left(\lambda\vec{\nabla}T\right) = 0 \tag{5}$$

where C_{ps} and C_{pa} are the heat capacity of adsorbent and adsorbed gas phase, respectively. As for heat capacity of adsorbed phase, Biloe *et al.* (2001) consider that the attributed value to this variable corresponds to characteristics value of the liquid phase as viewed on Tab. 2. That approach is considered for the authors due physics proximity which the adsorption phenomenon presents in relation to gas condenses process (Ozawa *et al.*, 1976). Finality, Δh corresponds to isosteric heat of adsorption.

Table 2. General properties of the porous media, gas adsorbed phase and cylinder, utilized in simulation proceeding

Parameter	Value	Reference
ρ_s (Adsorbent density - kg/m^3)	*450*	*Biloe et al., 2001*
ρ_c (Steel density - kg/m^3)	*8238*	*Biloe et al., 2001*
C_{ps} (Adsorbent heat capacity - *J/kg.K*)	*1241,25*	*Biloe et al., 2001*
C_{pa} (Adsorbed gas heat capacity - *J/kg.K*)	*2316*	*Biloe et al., 2001*
C_{pc} (Steel hat capacity - *J/kg.K*)	*468*	*Biloe et al., 2001*
λ_s (Adsorbent conductivity - *W/m.K*)	*7,3*	*Biloe et al., 2001*
λ_c (Steel conductivity - *W/m.K*)	*13,5*	*Incropera and DeWitt, 2003*
Δh (Heat of adsorption - *J/mol*)	*-16000*	*Biloe et al., 2001*
μ (Gas viscosity - *kg/m.s*)	$1,25x10^{-5}$	*Mota et al., 1995*
K (Adsorbent permeability - m^2)	$1x10^{-14}$	*Biloe et al., 2001*

The initial conditions are:

$$T(r,0) = T_0 \;\; ; \;\; P(r,0) = P_c \tag{6}$$

where T_0 and P_c are the room temperature (25 *ºC*) and the charge pressure (3,5 *MPa*), respectively. In the case where the rate flow is variable (2nd situation), the initial conditions in each time event are the results of the anterior event. The boundary conditions are posed to diffuser and wall on the mass (Eq. 7) and energy (Eq. 8) equations, respectively. The mass rate flow is prescript on the diffuser, bettering the boundary condition proposed by Biloé *et al.* (2001).

$$\dot{m}_{r-r_0} = Q_0 \rho\left(P_{diffuser}, T_{diffuser}\right) \;\; ; \;\; \left.\frac{\partial P}{\partial r}\right|_R = 0 \tag{7}$$

$$\lambda_s \left.\frac{\partial T}{\partial r}\right|_{r-r_0} = \frac{\rho_a Q_0 C_{Pa}}{A_{diffuser}}\left(T_{diffuser} - T_{ext}\right) \;\; ; \;\; e_w C_{pw} \rho_w \frac{\partial T}{\partial t} = h_w \left(T_{fluid} - T_R\right) - \lambda_c \left.\frac{\partial T}{\partial r}\right|_R \tag{8}$$

2.1. Numerical resolution method

The equations 1 and 5 are solved coupled utilizing a numerical routine developed by Souza and Lima (2005). A good agreement with experimental data available by reference paper (Biloé *et al.,* 2001) as can be viewed on the Fig. 2.

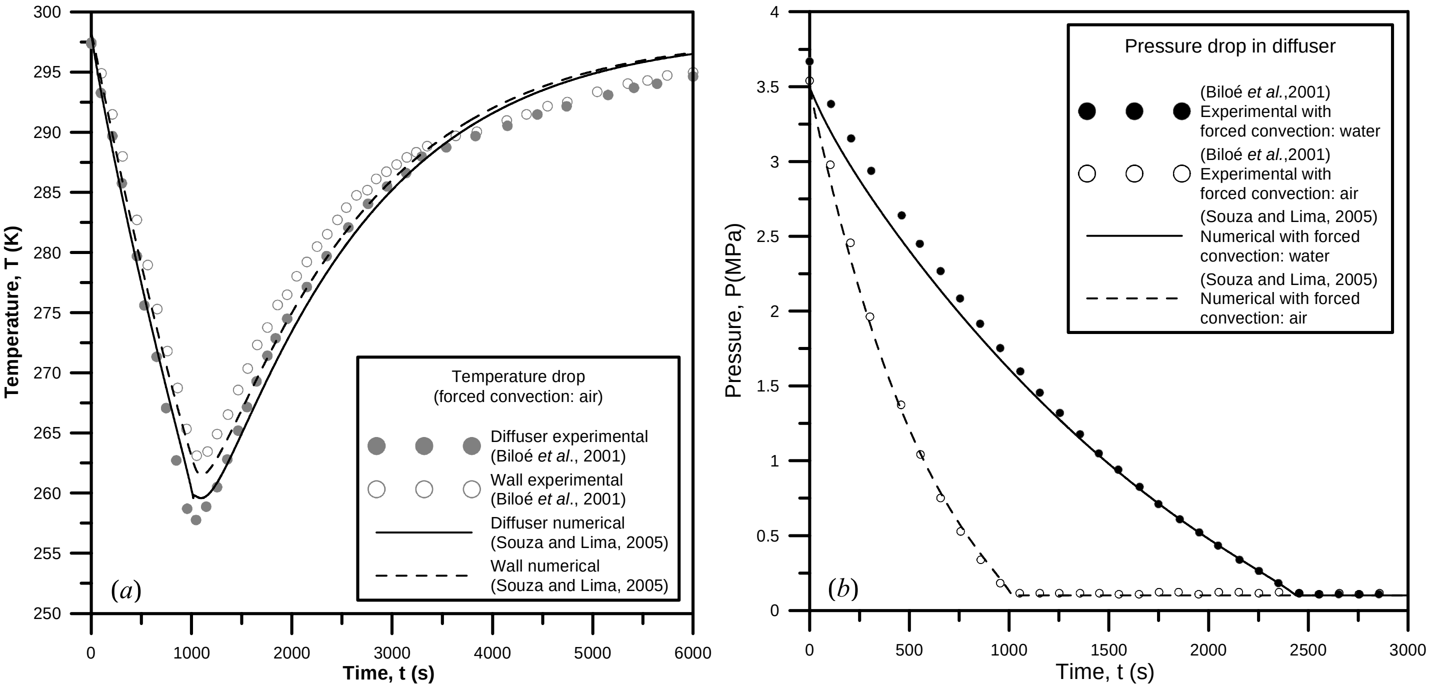

Figure 2. Experimental (Biloé *et al.*, 2001) and simulated temperature (*a*) and pressure (*b*) profiles (numeric validation)

The methodology of solution utilized on the numerical routines consists in an iterative procedure at each time level "t", where the fields of pressure and temperature estimated at iteration "$k+1$" are corrected comparing it with the field of anterior iteration "k", repeating that process until reach the convergence criteria (10^{-4}). From this moment on, the numerical code can put forward to time level "$t + \Delta t$". The iterative procedure is fundamental to solve the nonlinearity problems characteristics of the Eq. 1 and 5.

3. RESULTS OBTAINEDS

In the first situation analyzed were obtained the temperature (Fig.3*a*) and pressure drop (Fig.3*b*), besides the efficiency curves (Fig.3*d*) for constant rate flow of 50 *l/min* and 25 *l/min* as can be viewed on the Fig. 3*c*. In the simulation of both process, is verified which the time necessary to the reservoir to empty is approximately 2,5 *h* and 5,4 *h*, respectively (clear vertical lines).

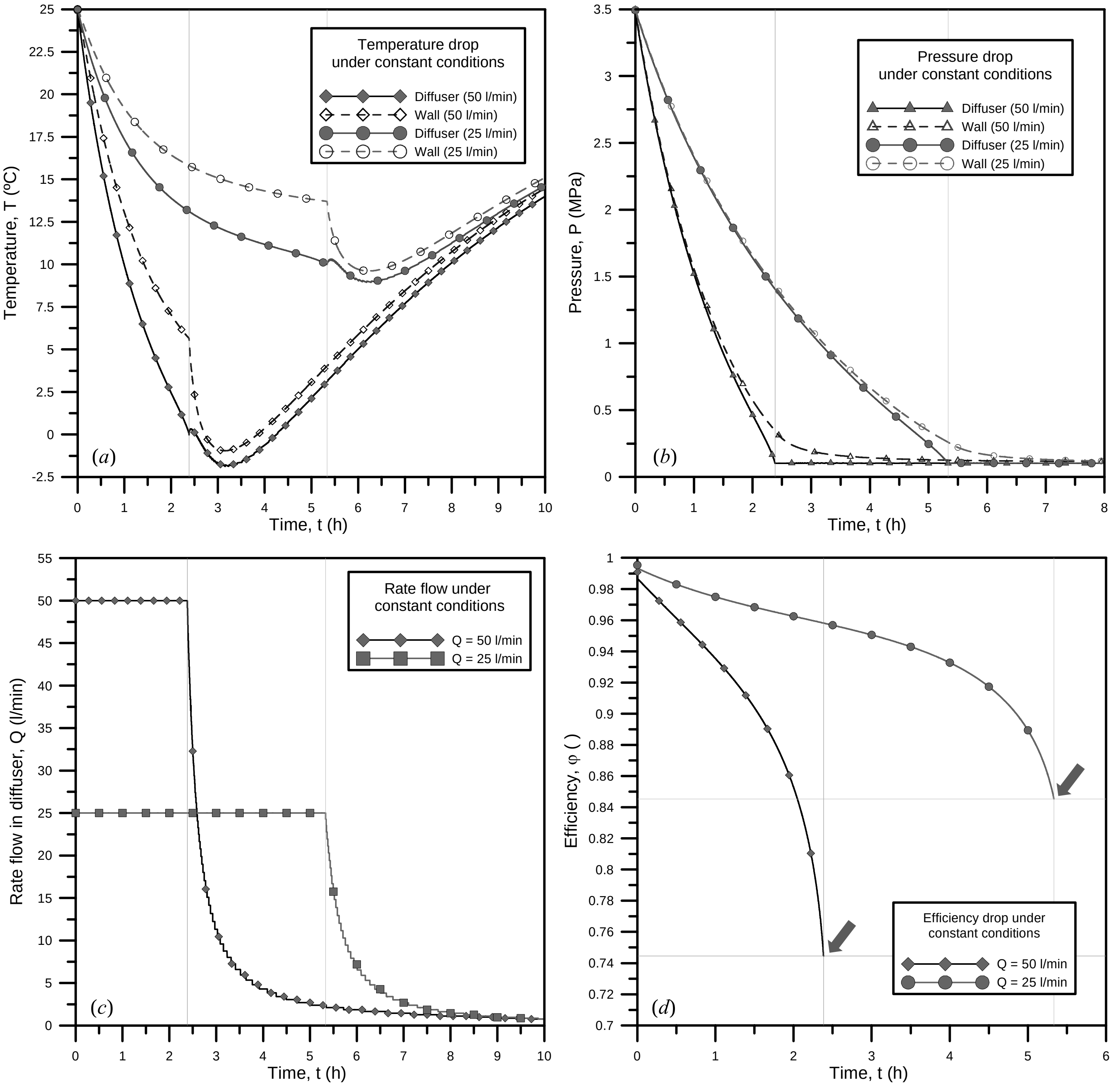

Figure 3. Profiles of temperature (*a*), pressure (*b*), rate flow (*c*) and efficiency (*d*) for two values of rate flow constants

Is verified also which ther is a considerable difference between pressure values obtained in diffuser and wall during the end of the discharge (Fig. 3*b*). That is, the endothermic adsorption process derived from discharge restrings the flow of gas forthcoming the wall, hence the storage efficiency is denied and that one problem is creasing when the rate flow has a major value (Biloé *et al.*, 2002), as viewed on the Fig. 3*d* (arrows). For a rate flow of 50 *l/min*, were obtained a efficiency (φ) of approximately 74,5 *%*. For other side, into 25 *l/min*, is verified a efficiency of approximately 84,6 *%*. The cylinder efficiency, submeted to adsorption system, is obtained through relation among the maximum delivered capacity of methane under dynamics conditions (Γ_{dd}) and the same capacity under isothermal conditions (Γ_{di}) such as viwed on the Eq. 9. The details correspondents to parameters Γ_{dd} e Γ_{di} are viwed at Biloé *et al.* (2001*b*) and Biloé *et al.* (2002).

$$\varphi = \frac{\Gamma_{dd}}{\Gamma_{di}} \tag{9}$$

Without the thermal effects, the pressure field tends to return at equanimity to long of radial coordinate, as can viewed in the Fig. 4. Another effect perceived associated to reservoir empty is a thermal equilibrium at porous media, with the rate flow ceasing, once the source term and the boundary condition on the diffuser entrance is annul. This is the principle of the efficiency improvement when variables discharge processes are considered. On time which the engine does not work, there is not descharge, hence there is not thermal effects (freezing of the porous media), thus the porous media tends to thermal equilibrium depending of sttoped time (4 *h*, 1 *h* or 12 *h*).

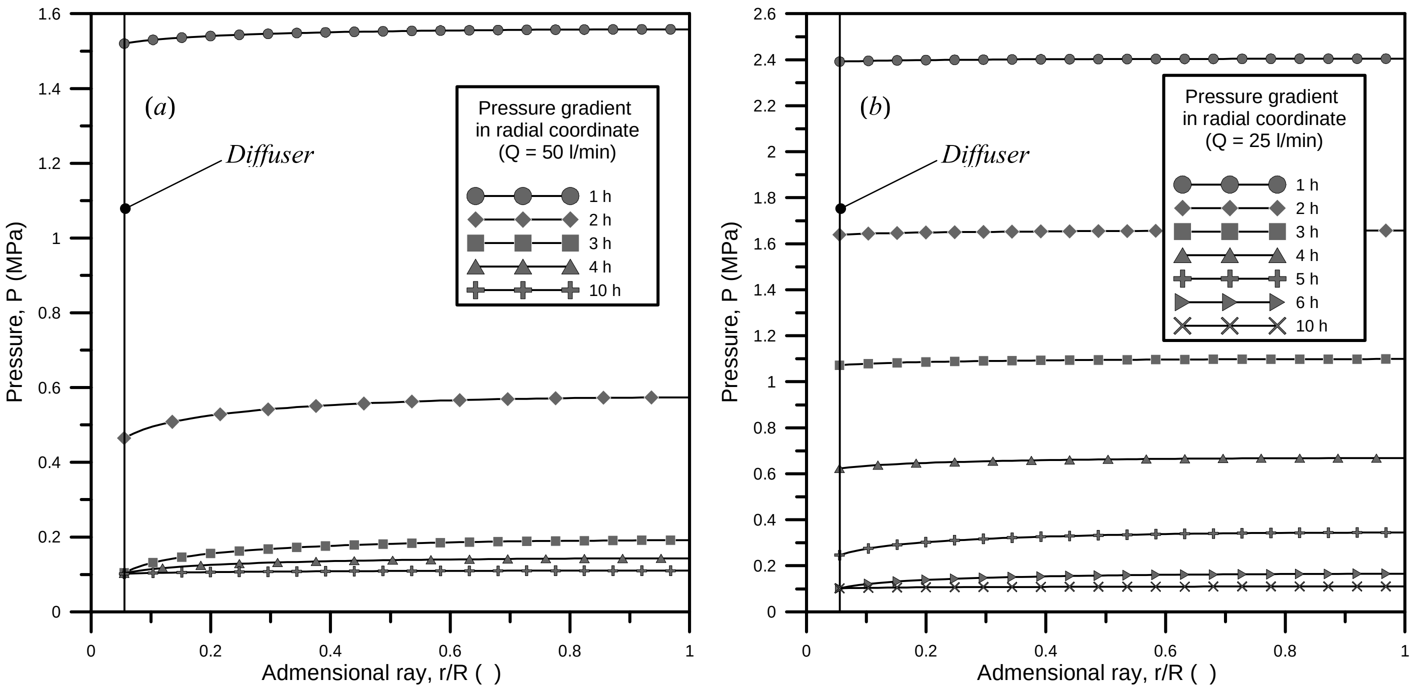

Figure 4. Profile of pressure to long of the radial coordinate for a rate flow of 50 *l/min* (*a*) and 25 *l/min* (*b*)

For the case of variable rate flow (2nd situation), the discharge period interspaced by no-discharge periods are governed by the data listed on the Tab. 1. There is verified which for the rate flow discharge of 50 *l/min*, the duration of the gas stock is few more than 1 day, already for the rate flow of 25 *l/min*, there is gas during approximately 2,5 days. That evidence two manner of gas consumption. On that sequence, each case (0,5 *h* of gas consumption, followed by a time period stopped), except the first one, had initial conditions (pressure and temperature fields) coming of the anterior case. The first case to both rate flow values receive the initial condition represented through Eq. 6.

On the Fig. 5 and 6*a* are verified, for the cases 1 to 5 (common between both rate flow), a temperature drop to long of the gas consumption, followed of temperature increase immediately after the engine stop (clear vertical line). That occur due the cease of rate flow associated to change of convection coefficient value (h_w), changing of 30 W/m^2K to 5 W/m^2K. The temperature increase in the porous media is very significant to efficiency improvement. That is, if in each new discharge process a temperature field were equal to environment temperature, the efficiency reaches values near of the unity (100 *%*).

The case where is verified rate flow cease due the tank emptying (case 6 to 50 *l/min* and case 11 to 25 *l/min*), as viewed on the Fig. 6*b*, has a different behavior. There the recovery of the temperature field does not immediate. That occurs due the already low rate flow at final of the process. Hence, the source term does not contribute significantly to the process. On the efficiency curves (Fig. 6*d* and 7*b*) is possible view the more significant performance drop just during the emptying cylinder, once in this case the pressure difference is not sufficient to draw back the residual gas inside the reservoir. Such pressure difference can be viewed to case 6 and 11 on the Fig. 6*c* and 7*a*, respectively. Especifically, in those cases, the end of the discharge are provocateds by ausency of the pressure difference among the diffuser and environment on the contrary of the other cases boardeds, which had its discharges ceaseds due turn engine off after 0,5 *h* using it.

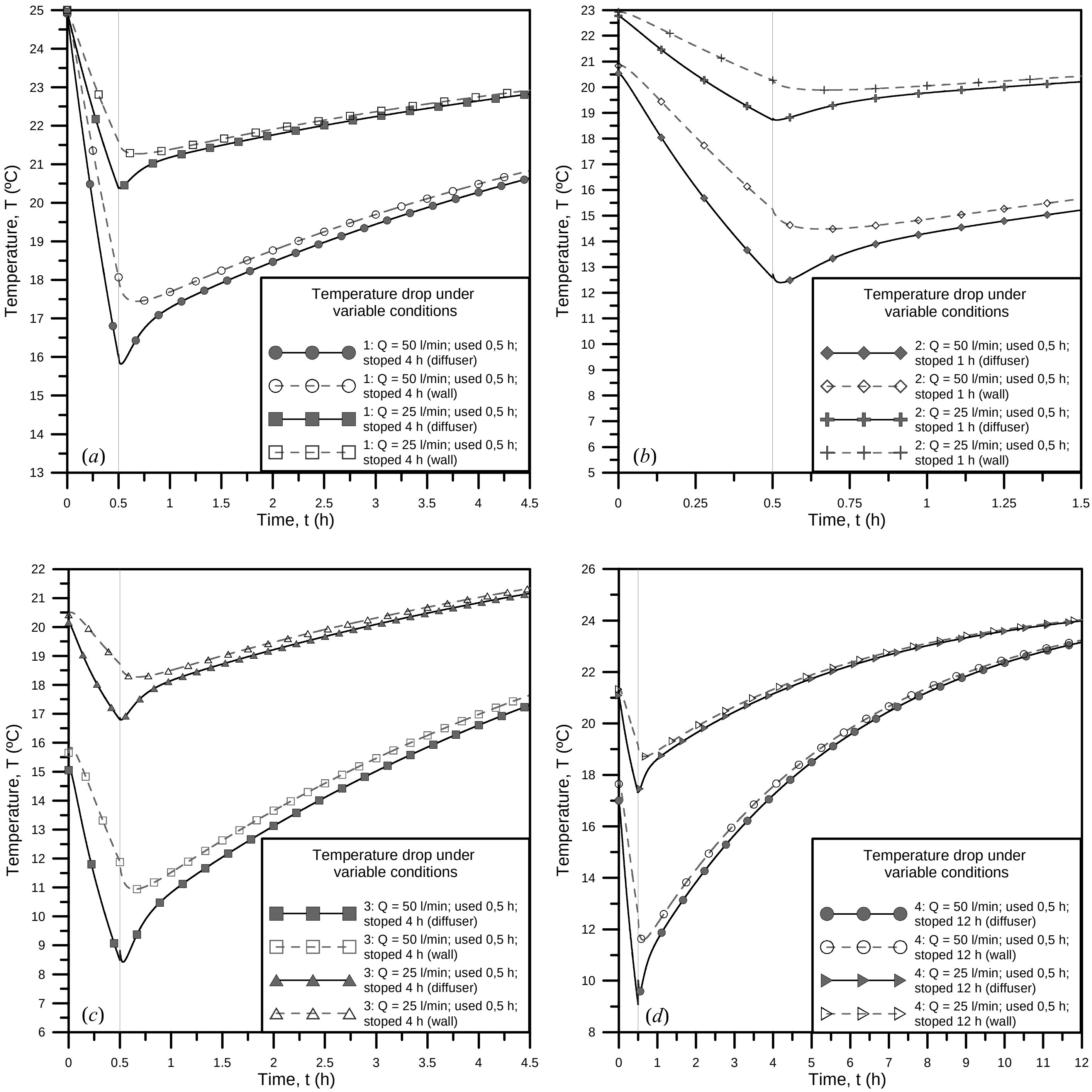

Figure 5. Temperature drop to equivalence of the cases into rate flow of 50 *l/min* and 25 *l/min*. Case 1 (*a*), Case 2 (*b*), Case 3 (*c*) and Case 4 (*d*)

On Fig. 5*a*, were verifyed a considerable numerical pulses (clear vertical line) on the temperature profiles during the discharge cease for rate flow of 50 *l/min* analysis. That is an effect of the boundary condition change already commented early. That pulse is more meaning when the reservoir is emptying due the thermal inertia.

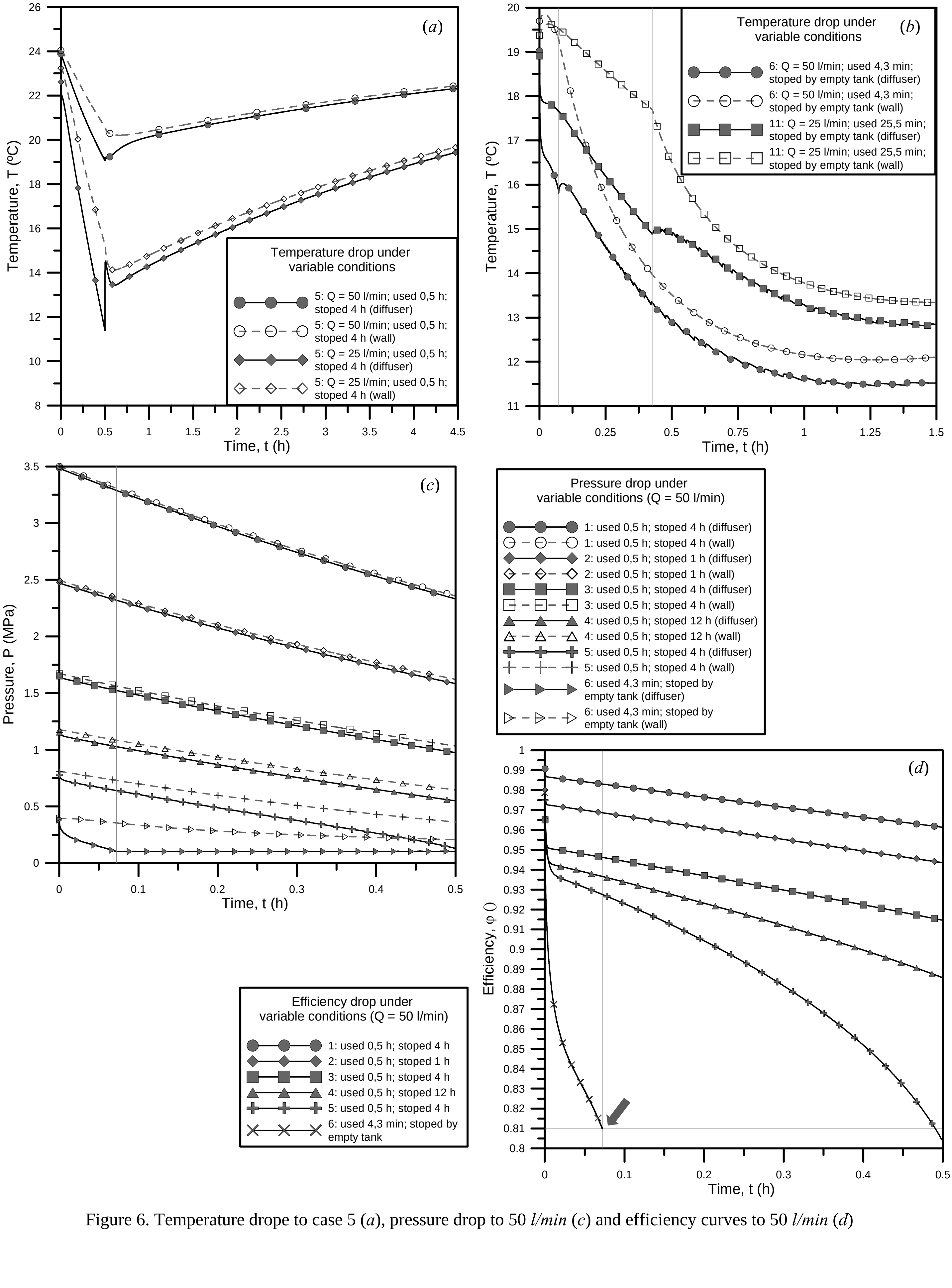

Figure 6. Temperature drope to case 5 (*a*), pressure drop to 50 *l/min* (*c*) and efficiency curves to 50 *l/min* (*d*)

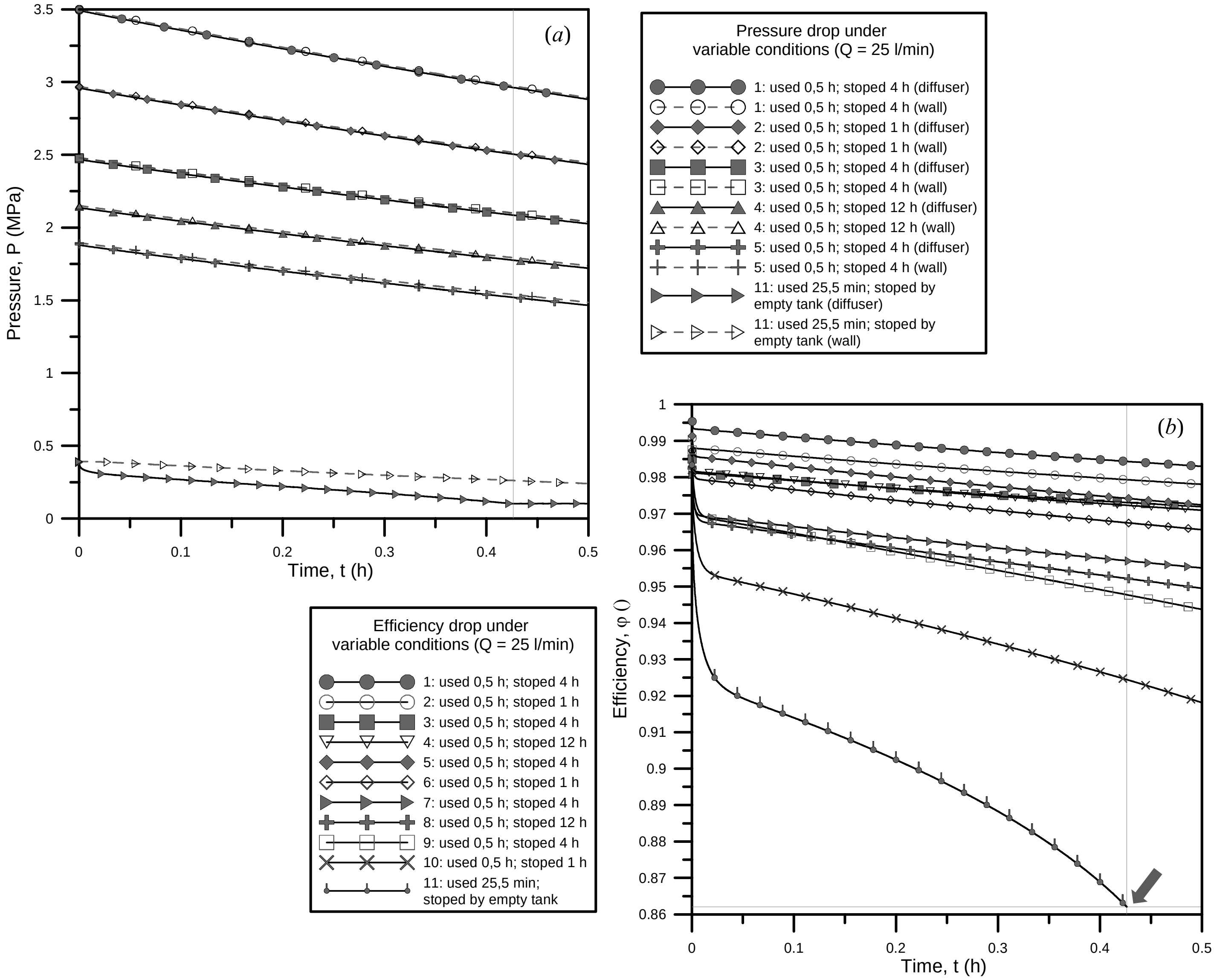

Figure 7. Pressure drop to rete flow of 25 *l/min* (*a*) and efficiency curves also to 25 *l/min* (*b*)

4. CONCLUSION

The contribution offers by passage of the gases in the gallery around is an unquestionable reality as already evidenced by Mota *et al.* (1995), Vasiliev *et al.* (2000) and Biloé *at al.* (2001). For that kind of reservoir (CILBRAS® 69.356.920 V), the improvement at efficiency reach approximately 10 % working with air inside the galleries (Souza and Lima, 2005). Although, for a closer visualization of the real adsorbed natural gas use is necessary to analyze a routine, consider the pauses suffer by system. On the present study there was a improve of approximately 1,7 % (as viewed on the Fig. 7*b* and 3*d*) when is compared the variable discharge with the constant discharge, to rate flow of 25 *l/min*. On the case refers to rate flow of 50 *l/min*, were obtained a improvement of 6,5 % (as viewed on the Fig. 6*d* and 3*d*) for variable discharge use. Such progress on the efficiency values can be changed, where the main parameters are the rate flow value (associated to engine solicitation, consumption, etc), times either use or stopped (associated to refresh and thermal equilibrium time) and, finally, the dimensions of the reservoir. That is, this study is only an indicative of adsorption system use possibility.

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