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NUMERICAL SIMULATION OF ADSORBED CARBON DIOXIDE STORAGE SYSTEMS FOR CCS APPLICATIONS

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Abstract. Countries around the world are putting their efforts to reduce the amount of carbon dioxide thrown in the atmosphere. However, it is also necessary to withdraw the gases that have already been emitted. Besides natural processes, like photosynthesis there are some artificial ones that can be used to tackle this global issue. One of these means is the so-called adsorption that already has shown potential to natural gas. The main goal of this work is to show that this technology can be used for Carbon Capture and Storage Applications. This analysis was made using Computational Fluid Dynamics simulations. The results showed that, considering a target pressure of 3.5 MPa and an inflow volume flux of 30 liters per minute, the amount of CO₂ stored is five times greater than the amount of methane under the same conditions. However, the mean temperature inside the CO₂ tank is greater (355 K) than the CH₄ case (350 K). This is an important issue due to the fact that the capacity of adsorption of the activated carbon decreases when its temperature increases. This difference could restrict the adsorption process and eliminate the advantage of the technology if a thermal control of the process is not applied properly.

Keywords: adsorption, carbon capture and storage, computational fluid dynamics

1. INTRODUCTION

Reports of the World Economy Forum showed that, despite the reduction of greenhouse gases in 2020, they are still higher than one decade ago. In response to this scenario, countries have been investing in ways to reduce emissions rates, for example, the generation of electrical energy from renewable sources and direct methods to reduce the amount of gas released into the atmosphere.

Another way to circumvent this issue is to withdraw from the atmosphere the gases that already had been emitted, using CCS processes. One promising technology for increasing the storage tanks capacity is adsorption. This research group previously reported the benefits of using an adsorption bed to store natural gas (methane – CH₄) (Chieriegatti, 2017; Chieriegatti, 2021). The results indicated that adding an adsorbent material inside the tank raised the amount of gas stored compared to a simple compression. The second part of the study demonstrated that thermal control of the process could increase the gas stored even further. These promising results enlightened that carbon dioxide (CO₂) capture and storage systems (CCS) could be implemented using the same technology and a literature review, encouraged the group to pursue this solution.

When taking in consideration the Adsorbed Natural Gas, it is widely known that this technology cannot attain the storage capacity that is achieved in liquefied natural gas. The main advantage of ANG is the possibility to store a good amount of gas without the need of using a cryogenic process that has a high energetical cost (Judd, R.W.; Gladding, R. et. Al, 1998). The same behavior is expected when considering carbon dioxide. Another research group studied the adsorption phenomena and pointed out that there are two issues that must be taken into account: the shape of the adsorption isothermal and the heat of adsorption, the latter is responsible for increasing the mean temperature inside the reservoir during the filling process which decreases the storage capacity (Mota J.; Saadjian E., et Al.,1995).

This work modeled and simulated a carbon dioxide capture system by adsorption using Computational Fluid Dynamics (CFD) based on previous works for natural gas adsorption. Despite the similarity of the problems, there are new challenges, such as the affinity of carbon dioxide with the adsorbent and the quantity of energy released during the process, which demands an appropriate procedure to dissipate the generated heat. Hence, this work's main contribution is to comprehend how the adsorbent material affects the quantity of carbon dioxide stored using numerical simulation. For this purpose, was carried out using a routine programmed in the FreeFem++ platform (Hecht,2012), considering a cylindrical tank and a known curve for the gas inflow mass flux. To model the flow through the adsorbent material, a

porous media, the Navier Stokes's equations with Darcy's law simplifications were adopted. This geometry was adopted to be possible to compare the results between Natural Gas and Carbon Dioxide. The first case was already presented in previous editions of COBEM and it was validated comparing them to experimental results presented in (Sahoo, P.; John, M. et. al, 2011). The second case is the focus of this study. Naturally, the simulations for natural gas were performed again to ensure that the same control parameters were used in both cases.

The simulations were performed by varying one control parameter at a time to evaluate how two objective functionals behaved with these variations. The functionals of interest for this work are: the density of adsorption, that evaluates the amount of gas stored inside the reservoir; and the mean temperature inside the tank. The former is an important functional due to the fact that adsorption is an exothermic process and, the capacity of storage of the adsorbent material inversely proportional to the temperature.

2. MATERIAL AND METHODS

The numerical simulations, as mentioned, were performed in the FreeFem++ platform by means of programming code, developed by the authors. In this code, the system of equations below (Chierigatti, Brasil Lima, et al 2021) was implemented using the Galerkin Method for finite elements. The system is composed by the continuity equation (eq. (1)), momentum equations (eq.(2)), energy equation (eq.(4)) and the adsorption model (eq.(4)) (Sahoo, P.; John, M, 2011)

$$\epsilon_t \frac{\partial \rho_g}{\partial t} + \rho_b \frac{\partial q}{\partial t} + \nabla \cdot \vec{G} = 0 \quad (1)$$

$$\rho_g \nabla p + \frac{\mu}{K} \vec{G} = 0 \quad (2)$$

$$C_{eff} \frac{\partial T}{\partial t} - \epsilon_t \frac{\partial p}{\partial t} + \nabla \cdot (C_{pg} \vec{G} T) - \lambda_{eff} \nabla^2 T - \frac{\Delta H}{M_g} \rho_b \frac{\partial q}{\partial t} = 0 \quad (3)$$

$$q = \rho_{ads} \cdot W_0 \cdot \exp \left[- \left(\frac{A}{\beta E_0} \right)^n \right] \quad (4)$$

In eq. (1), ϵ_t is the porosity of the adsorbent material; ρ_g is the free gas specific mass; ρ_b is the specific mass of the adsorbent; q is the density of adsorption and \vec{G} is the vector of mass flux. In eq. (2), ∇p is the pressure gradient; μ is the viscosity of the gas and K is the permeability of the adsorbent bed. In eq. (3), $C_{eff} = (\epsilon_t \rho_g + \rho_b q) C_{pg} + \rho_b C_{ps}$, which C_{pg} and C_{ps} represents the specific heat of gas and adsorbent respectively; T is the temperature inside the reservoir; $\lambda_{eff} = \epsilon_t \lambda_g + (1 - \epsilon_t) \lambda_s$ is the effective thermal conductivity in terms of porosity and thermal conductivity of gas (λ_g) and adsorbent (λ_s); ΔH is the heat of adsorption and M_g is the molar mass of the gas.

The eq. (4) is the Dubinin-Astakov (D-A) adsorption model where ρ_{ads} is specific mass of the adsorbed gas; defined by: $\rho_{ads} = \frac{\bar{\rho}_{ads}}{\exp[\alpha_e(T-T_b)]}$, where $(\bar{\rho}_{ads})$ is the specific mass of liquid phase of the adsorbed fluid in the saturation region (T_b); α_e is the thermal expansion of liquefied gas; W_0 is the microporous volume per unit mass of adsorbent; β is the affinity coefficient related to the adsorbate-adsorbent interaction; E_0 is energy of adsorption; n is the DA exponent (Sahoo, P.; John, M, 2011) and the parameter A is the adsorption potential and it is defined by: $A = RT \ln \left(\frac{P_s}{P} \right)$, where $P_s = P_{cr} \left(\frac{T}{T_{cr}} \right)^2$.

The term $\partial q / \partial t$ in equations (1) and (3) is evaluated based on the model called linear driving force (Xiao, J; Peng, R et al.,2012):

$$\frac{\partial q}{\partial t} = k \cdot (q^* - q) \quad (5)$$

In eq.(5), q^* is the density of adsorption of the adsorbed gas in the equilibrium with saturated gas phase and it is calculated by means of the eq. (4). The coefficient k is the mass transfer coefficient at an aggregated level.

3. RESULTS AND DISCUSSION

3.1 Carbon dioxide adsorption in activated carbon

The simulations were performed in the FreeFem++ platform. The geometry adopted to model the reservoir was an axisymmetric cylinder, as used in previous works once it is desired to compare the amount of gas stored between carbon dioxide and methane. The geometry and the computational mesh are show in Figure 1

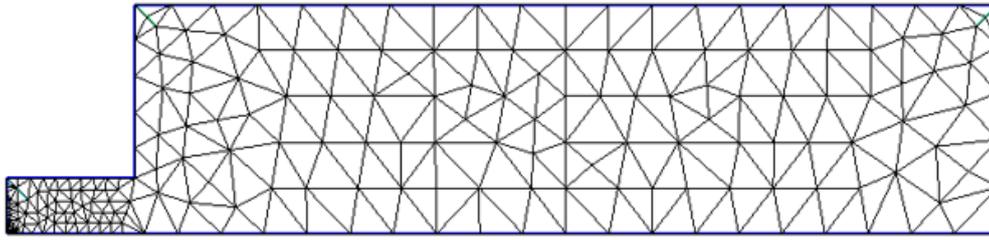


Figure 1. 2D-axisymmetric mesh geometries

The parameters used in all the simulations are presented in the Table 1

Table 1 – Data and Initial Conditions – Same of presented in previous work (Chierigatti, B.G; Brasil Lima, J.S. et al, 2017)

	Value		Value		Value
ρ_0	0.7049 kg/m ³	T_∞	300 K	α	$2.5 \cdot 10^{-3} K^{-1}$
C_{pg}	1680 J/kg.K	C_{ps}	650 J/kg.K	E_0	$25.04 \cdot 10^3 J/mol$
μ_g	$1.48 \cdot 10^{-5} Pa.s$	λ_g	0,01663/m.K	P_{cr}	$7,38 \cdot 10^6 Pa$
ϵ_t	0.65	ϵ_b	0.30	$\overline{\rho_{ads}}$	$1,56 \cdot 10^3 kg/m^3$
λ_s	0.54 W/m.K	ρ_b	500 kg/m ³	n	1.8
ΔH	12000 J/mol	h	5 W/m ² K (natural)	β	0.35
M_g	0.044 kg/mol		700 W/m ² K (forced)	W_0	$5,6 \cdot 10^{-4} m^3/kg$
* STP Conditions		K	$3.7 \cdot 10^{-10} m^2$	T_{cr}	304 K
		P_i	20000 Pa	T_b	195 K
		T_i	303 K	k	$3.2 s^{-1}$
		q_i	$q(P_i, T_i)$		

The boundary conditions considered are shown in Table 2:

Table 2: Boundary Conditions (Chierigatti, B.G; Brasil Lima, J.S. et al, 2021).

Boundary Type	Conditions
Inflow	$\vec{G} \cdot \vec{n} = G_{ref}$ $-\lambda_{ref} \cdot (\vec{n} \cdot \nabla T) = G_{ref} \cdot C_{pg} \cdot (T_{in} - T)$
Wall	$\vec{G} \cdot \vec{n} = 0$ $-\lambda_{ref} \cdot (\vec{n} \cdot \nabla T) = h \cdot (T - T_\infty)$
Symmetry	$\vec{G} \cdot \vec{n} = 0$ $(\vec{n} \cdot \nabla T) = 0$

The first set of simulations were carried out considering a target pressure inside 3.5 MPa and varying the inflow volume flow from 5 up to 30 liters per minute (LPM). In all cases two functionals were evaluated: density of adsorption and mean temperature inside the reservoir. The first results, shown below, in Figures 2 and 3:

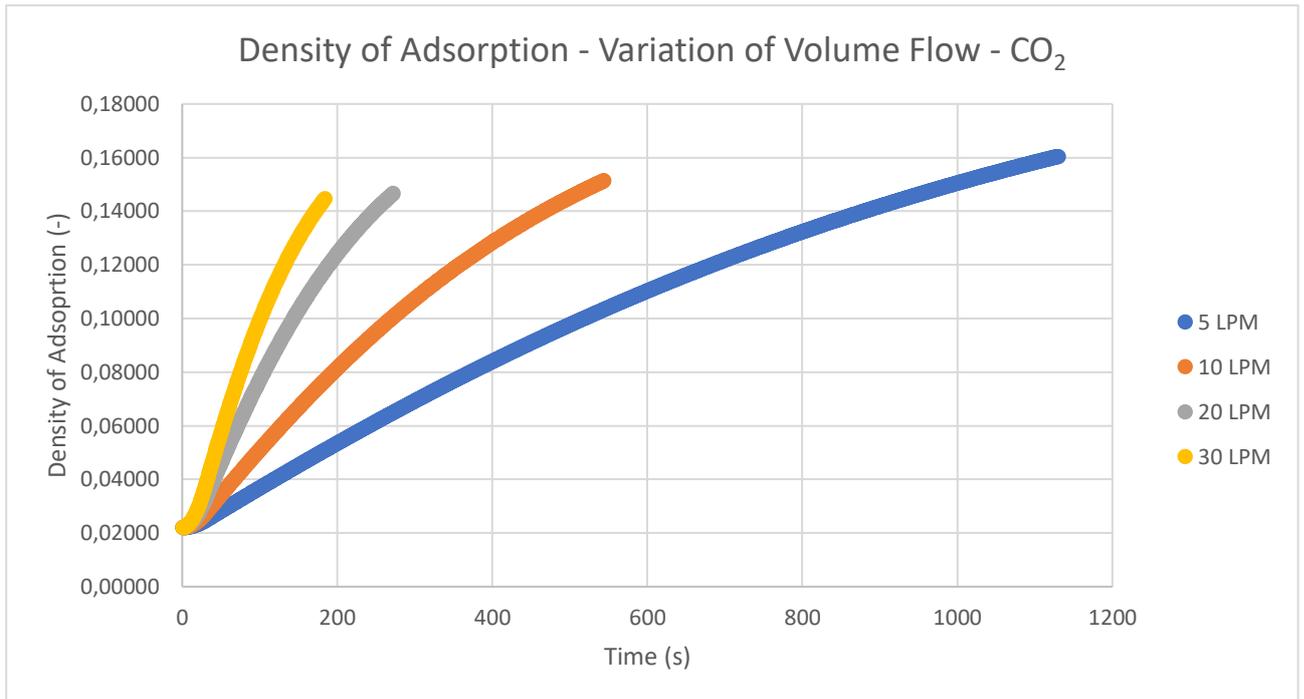


Figure 2. Density of adsorption along the time with respect to the inflow volume flow with target pressure of 3.5 MPa. The blue curve represents the flow of 5 LPM and the yellow one, the flow of 30 LPM.

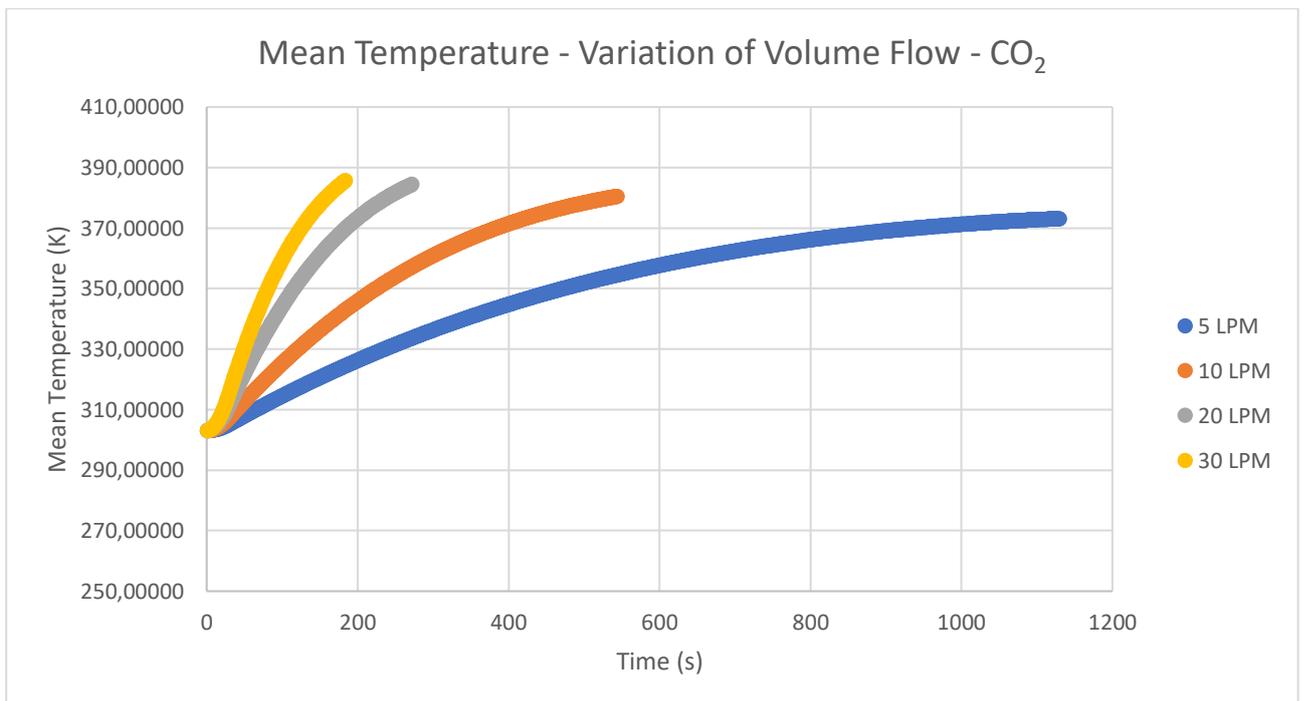


Figure 3. Mean temperature inside the reservoir along the time with respect to the inflow volume flow with target pressure of 3.5 MPa. The blue curve represents the flow of 5 LPM and the yellow one, the flow of 30 LPM.

The results above show that with a lower volume flow, it is possible to store more gas but, the inflow process will take more time. For example, to achieve a density of adsorption of 14%, it will take nine times more with a flux of 5 LPM than with 30 LPM. This shows an important tradeoff in the phenomenon between time and density of adsorption, that means it is possible to store more gas by lowering the volume flow, but it will take longer, and, in some applications, this is undesirable. The second result corroborates the first one as it shows that the temperature inside the tank increases quickly when the volume flow is higher, and, hence, the amount of gas stored will be limited due to the fact of the adsorption is exothermic. In Figures 4 and 5, it is possible to visualize the field of temperature inside the reservoir to some of the cases whose results were presented before.



Figure 4. Distribution of temperature inside the reservoir for volume flow of 5 LPM and after 1420 s for target pressure of 3.5 MPa



Figure 5. Distribution of temperature inside the reservoir for volume flow of 5 LPM at the end of the inflow process for target pressure of 3.5 MPa

The hottest regions are located far from the inflow region, which was expected to occur. In previous works, the importance of the thermal control of the process was mentioned but it is not focus of this study. Here, one presents the difference on using the same technology to different gases. The final paper will present the comparisons between the results already presented and the ones with methane.

3.2 Natural gas adsorption in activated carbon

The main goal of this work is to study whether the adsorption technology can be used successfully to store carbon dioxide, as it is for natural gas, or not. To accomplish this objective, it is necessary to compare the same results using natural gas that is, analyze the same objective functionals with respect to the same control parameters. In Figures 6 and 7, one can see the results of the simulations for natural gas with the exact same conditions that were used to carbon dioxide

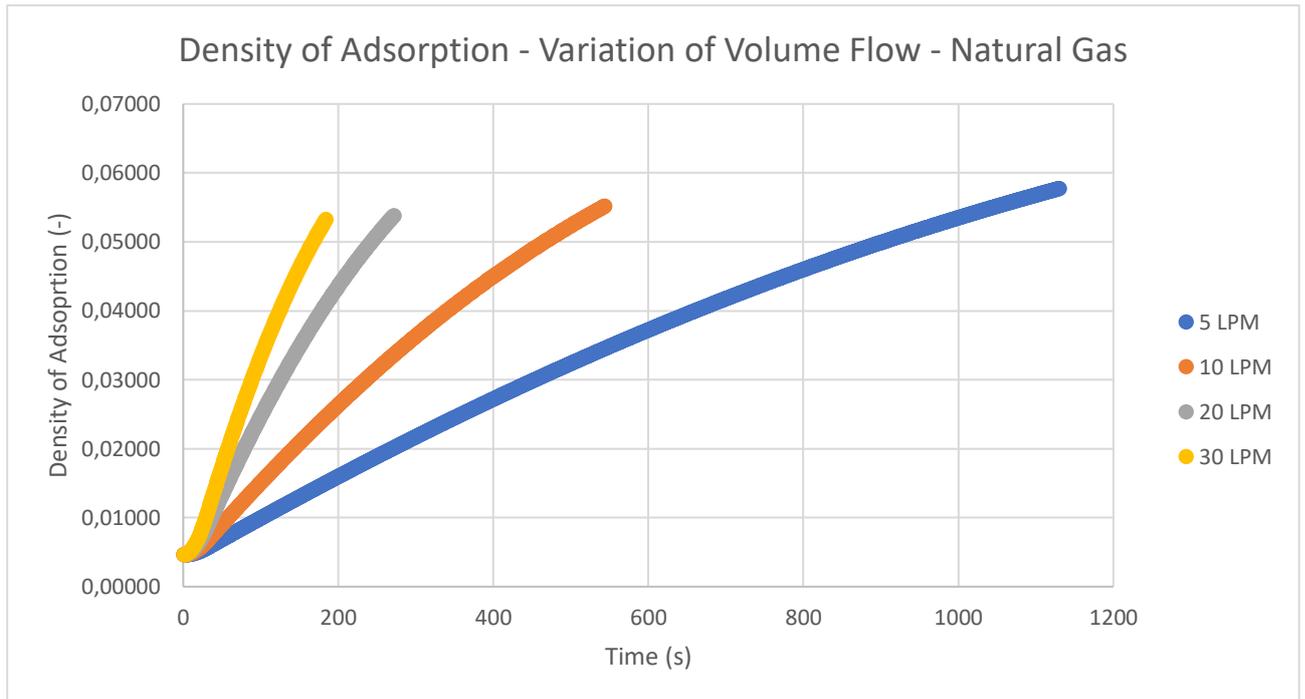


Figure 6. Density of adsorption along the time with respect to the inflow volume flow with target pressure of 3.5 MPa. The blue curve represents the flow of 5 LPM and the yellow one, the flow of 30 LPM.

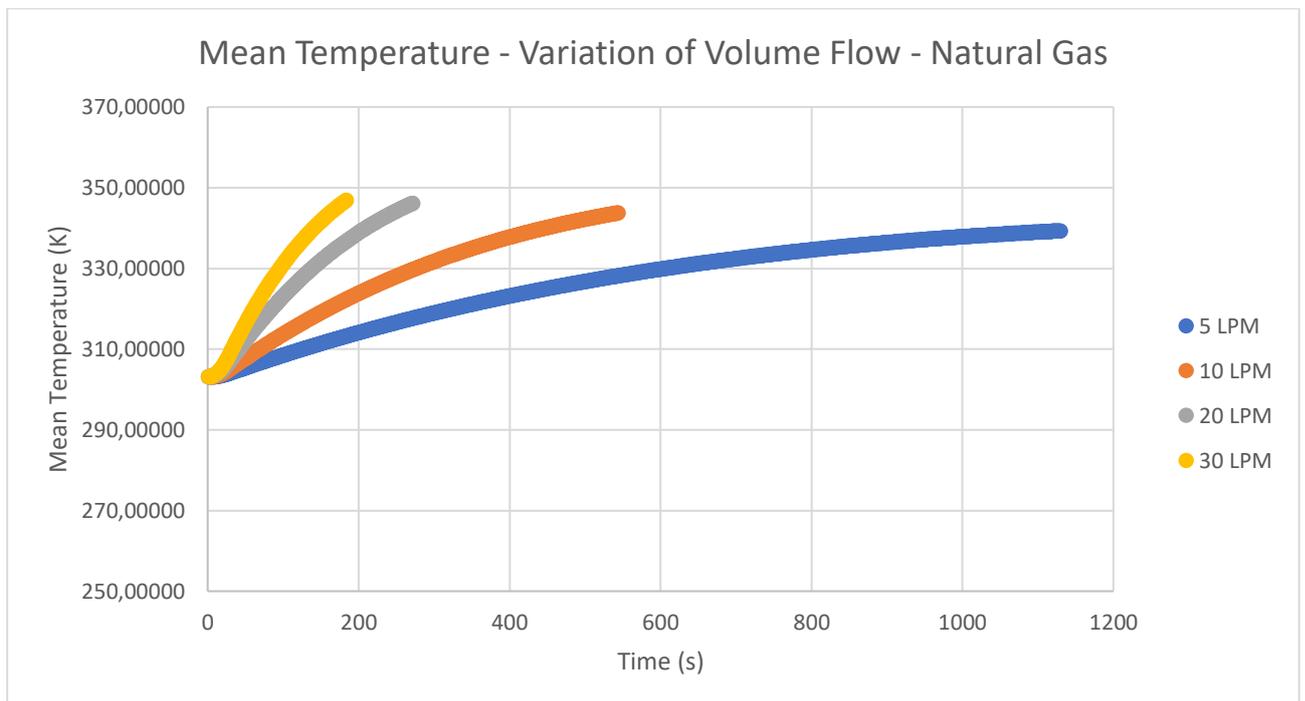


Figure 7. Mean temperature inside the reservoir along the time with respect to the inflow volume flow with target pressure of 3.5 MPa. The blue curve represents the flow of 5 LPM and the yellow one, the flow of 30 LPM.

The results above show that the behavior of the density of adsorption and the mean temperature inside the reservoir is the same observed in the carbon dioxide case although the objective functionals have different values. The same tradeoff between amount of gas stored and filling time, noticed before, is present here once again.

3.3 Comparison between natural gas and carbon dioxide adsorption in activated carbon

In order to conclude if the adsorption technology is suitable for carbon dioxide as it is for natural gas, it is important to compare both cases in the same basis. In Figures 8 and 9, one can see the results for density of adsorption of both gases for volume flow of 5 and 30 LPM, respectively.

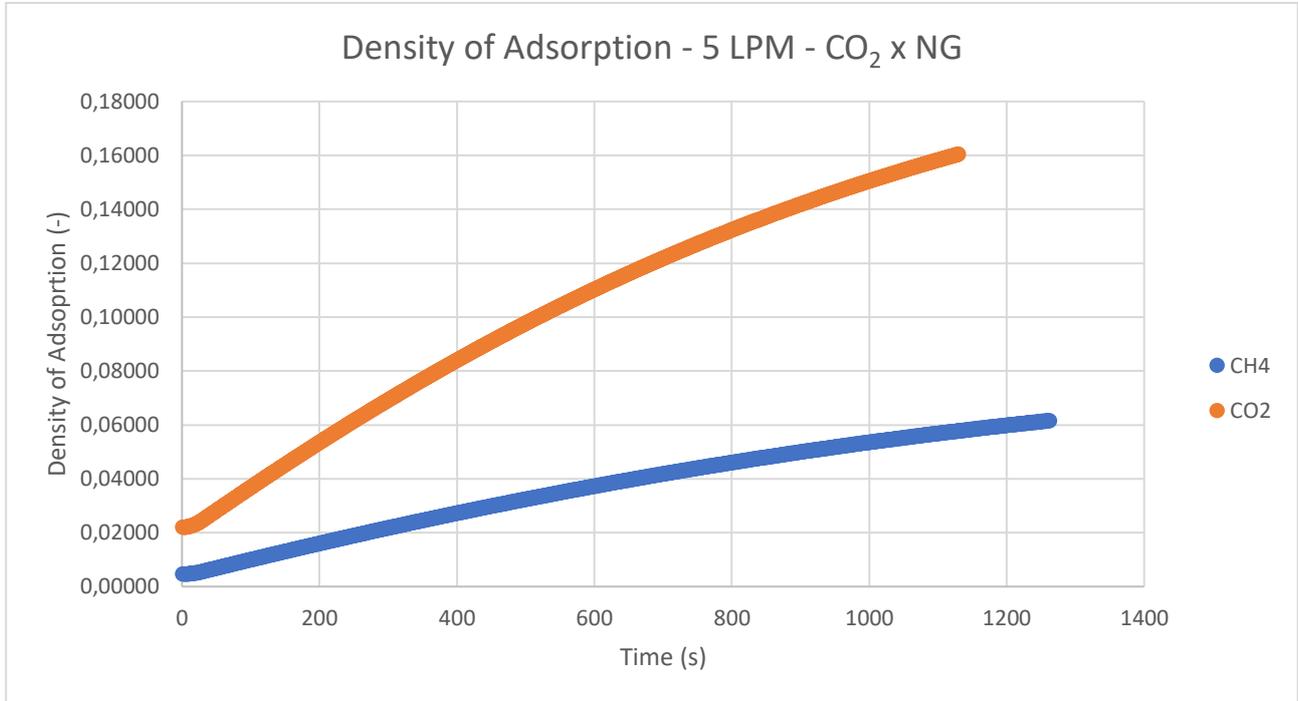


Figure 8. Density of adsorption along the time with target pressure of 3.5 MPa and 5 LPM. The blue curve represents the density of adsorption for natural gas and the orange one, for carbon dioxide.

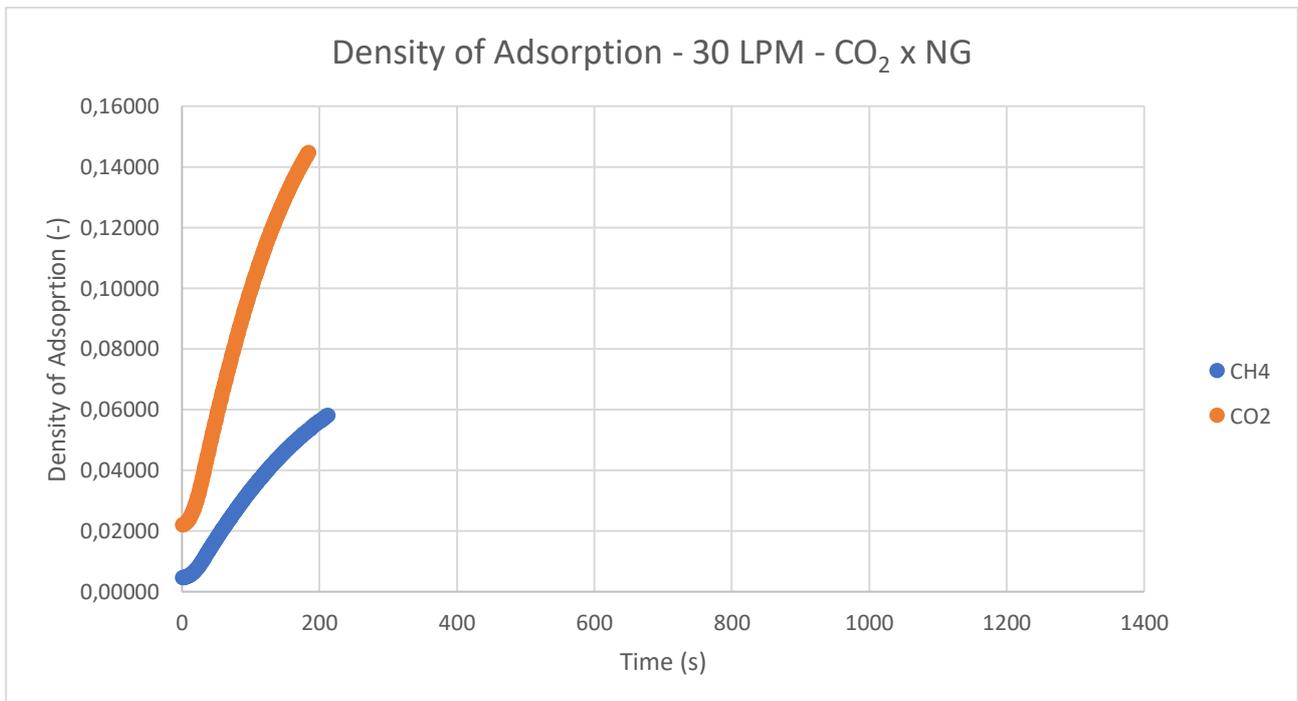


Figure 9. Density of adsorption along the time with target pressure of 3.5 MPa and 30 LPM. The blue curve represents the density of adsorption for natural gas and the orange one, for carbon dioxide.

The results above prove that, with the same conditions, it is possible to store more carbon dioxide than natural gas which shows that this technology is suitable for carbon dioxide. For example, with inflow of 5 LPM, it is possible to store three times more gas when using CO₂ while with 30 LPM, it is possible to store 2.5 times more gas. However, using carbon dioxide brings another problem because the mean temperature inside the tank is higher than with natural gas and, as already mentioned, when the temperature of the adsorbent material increases, its capacity of adsorption decreases. In Figures 10 and 11 it is possible to notice this fact.

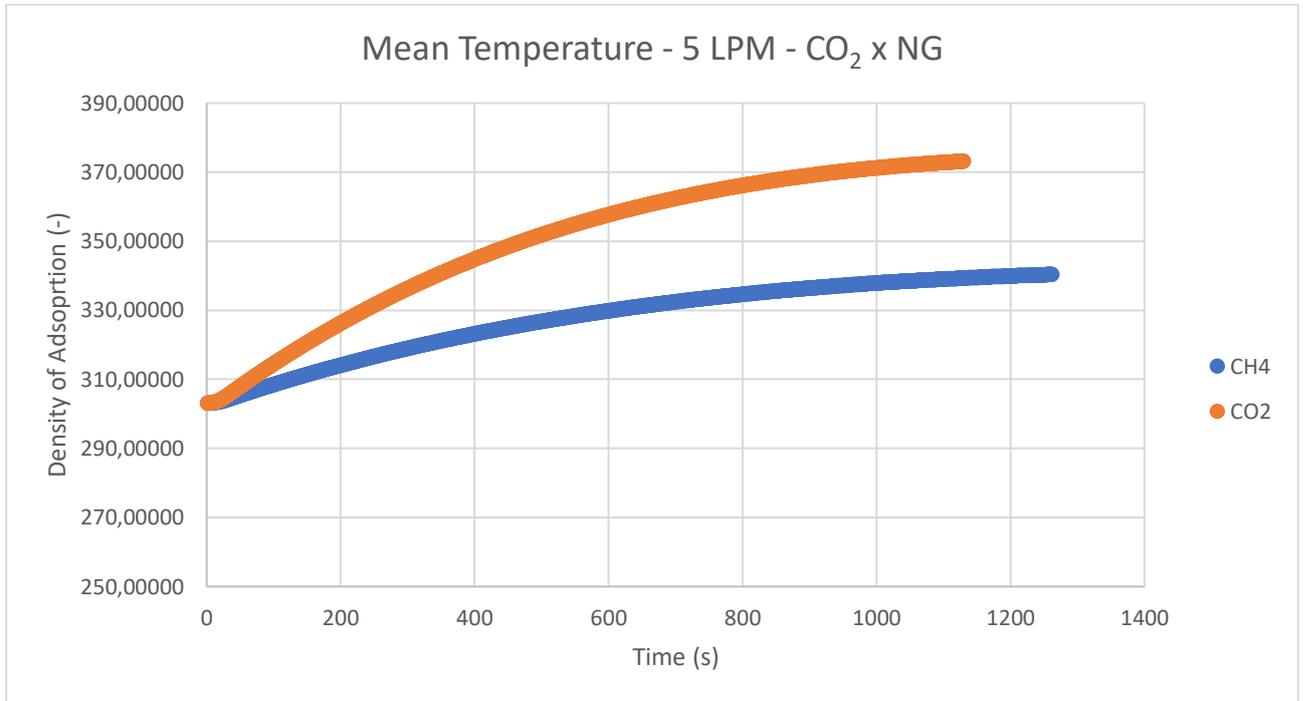


Figure 10. Mean temperature along the time with target pressure of 3.5 MPa and 5 LPM. The blue curve represents the density of adsorption for natural gas and the orange one, for carbon dioxide.

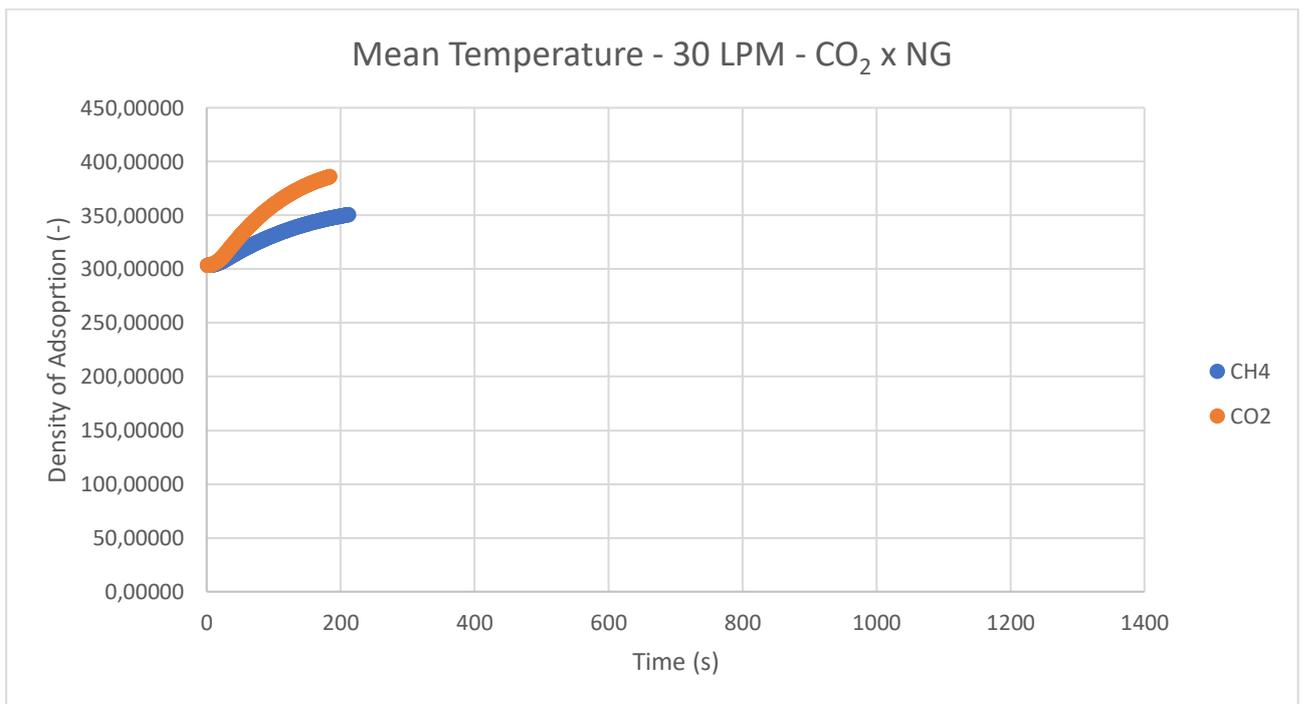


Figure 11. Mean temperature along the time with target pressure of 3.5 MPa and 30 LPM. The blue curve represents the density of adsorption for natural gas and the orange one, for carbon dioxide.

As shown in the graphics above, for 5 LPM the mean temperature for carbon dioxide is approximately 9% higher than the one for natural gas and, for 30 LPM it is 11% higher. This behavior of the temperature lights the importance of a thermal management during the filling process in order to optimize the amount of gas stored.

4. CONCLUSIONS

The results prove that the adsorption technology is suitable for carbon dioxide as it is for natural gas once it is possible to store more gas than the latter case. This can be explained due to the fact of the affinity of CO₂ and the activated carbon is higher than with natural gas, that is mainly methane. The results showed that it is possible to store three times more gas for low volume flow (5 LPM) and that the tradeoff between the amount of gas stored and the filling time is also present to carbon dioxide, that is, one can store more gas if the tank is filled slowly. The main problem found, when using adsorption for carbon dioxide, is the increase of the mean temperature inside the reservoir when comparing with natural gas what can make the filling a self-destructive process as the capacity of the activated carbon to store more gas decreases when the temperature increases. For future studies the concepts of thermal management and gas recirculation will be applied, separately, to optimize the amount of gas stored.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

- Judd, R. W.; Gladding, R. e. al. The use of adsorbed natural gas technology for large scale storage. BG Technology, Gas research and Technology Centre., 1998.
- Hecht, F.; New development in FreeFem++. Journal of Numerical Mathematics, 2012, no 3-4, 251-265
- Mota, J.; Saadjian, E. et. al. A simulation model of high-capacity methane adsorptive storage system. Adsorption 1, 1995.
- Sahoo, P.; John, M. e. al. Filling characteristics for an activated carbon based adsorbed natural gas storage system. I & EC research, 2011.
- Chierigatti, B.G., Brasil Lima, J. S., Volpe, E.V. and Hayashi, M.T., On the use of heat exchange's devices in order to improve adsorption and desorption process of ANG tanks, 24th ABCM International Congress of Mechanical Engineering, 2017.
- Sahoo, P.; John, M. e. al. Filling characteristics for an activated carbon based adsorbed natural gas storage system. I & EC research, 2011.
- Chierigatti, B.G., Brasil Lima, J.S., Volpe, E.V., and Hayashi, M.T. Optimization loop based on Adjoint Sensitivity Analysis for Flows through Porous Media with Adsorption. International Journal for Numerical Methods in Engineering, 2021
- Chierigatti, B.G., Brasil Lima, J. S., Volpe, E.V. and Hayashi, M.T., On the use of gas recirculation to increase the adsorption capacity in the natural gas storage systems, 26th ABCM International Congress of Mechanical Engineering, 2021.
- Xiao, J; Peng, R et al. A CFD model for charge and discharge cycle of cryo-adsorptive hydrogen storage on activated carbon. International Journal of Hydrogen Energy, 2012

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