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A NUMERICAL ANALYSIS OF CO_2 STORAGE BY ADSORPTION USING ZIF-8.

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Abstract: In 21st century, the reduction of CO_2 concentration in the atmosphere is one of the most challenges of the humanity, specifically in the engineering. To start a possibility solution proposal, this work consisted in an analysis of carbon dioxide storage, using adsorption by ZIF-8, a material that belongs to a class called Zeolitic Imidazolate Frameworks, which have high porosity, high thermal resistance and chemical stability. The main contribution of this work is to verify which parameters are relevant in the CO2 storage capacity by adsorption. To archive this goal, the study was made through computational simulations using the open source FreeFem++ software, inputting a specified quantity of pure CO_2, entering in an 1,82 liter tank filled by the adsorbent until its internal pressure reached 1,0 MPa. First, the isothermal curve was validated with the literature, and after adjusting the parameters of adsorption model, called Dubinin Astakov (D-A). The simulations were performed, varying CO_2 inlet flow, the tank's aspect ratio with the values of 1; 1,9; 3; 5 and 7, and the external wall's heat transfer coefficient with values of 5, 700 and 1000 W/m²K. Each simulation generated at each step the tank's average and maximum temperatures, internal pressure, and the carbon dioxide adsorption density. All the simulations started with a standard temperature of 300 K and pressure of 100 kPa. Temperature and adsorption density distributions were generated to analyze in which part of the tank the adsorption is higher. The results showed that the regions where the temperatures are higher, the adsorption is lower, and in the end of the simulation, the simulations with the lower average temperatures had the higher adsorption density. The highest values of adsorption density were obtained with higher surface areas under the influence of forced convection, rather than natural convection, and with lower CO_2 inlet flow. The highest adsorption density reached was 15,67 %, in a simulation with 50% of the tank's volume per minute as CO_2 inlet flow rate, aspect ratio of 7,0; and 700 W/m²K heat transfer coefficient. The average temperature obtained in the end of this simulation was 326,20 K and it took 3644 seconds for the tank to achieve the internal pressure of 1,0 MPa.

1 INTRODUCTION

Since the First Industrial Revolution, the rhythm of the human progress, both technological and economical, has been unprecedented. This development happened mostly due to fossil fuels, whose burn release carbon to the atmosphere. Then, the increase of carbon dioxide concentration in the atmosphere causes climatic and health problems. To tackle this problem, the concept of "Carbon Capture and Storage" (CCS) has become an attractive alternative. Particularly in the storage, there are two consolidated methods: Simple Compression (increase the density based on the pressure growing) and Liquified Gas, decreasing the specific volume of the gas with the liquid phase changing.

Alternatively of these methods, the gas storage using an adsorbed material gains relevance in the last years. To a reasonable extent, the method provides a means of storing gas at substantially higher concentration than can be achieved with simple compression at the same pressure. Although it does not attain the density that is typically found with Liquified Gas, it is potentially much simpler, since it does not require the energy-demanding of liquefaction process [1].

Considering the carbon dioxide, the Zeolitic Imidazole Framework (ZIF) has been standing out as an adsorbent material due the great adsorption affinity with CO_2. Nonetheless, the carbon dioxide adsorption releases a relevant amount of energy and due the low adsorbents thermal conductivity, the filling process causes a fast growing of the temperature inside the tank, which is harmful to adsorption phenomena, reducing the quantity of gas stored. Then, the proposals of the active heat management during this process are crucial to make it viable and economically attractive.

1.1 Objective

This work had an objective to make numerical analysis of some setups of the carbon dioxide filling process in ZIF adsorbed tanks, Comparations are done varying some parameters, such as the value of the inlet flow, geometry of the tank and the properties of the external convection. The numerical solver algorithm was previously developed by the researchers, in a work where the study is focused in the Natural Gas (CH_4) adsorption in the active carbon storage tanks[1]. Now, the gas was changed to carbon dioxide and the adsorbent changed to ZIF, particularly, to the ZIF-8, described in the section 2.2

2 LITERATURE SURVEY AND METHODOLOGY

2.1 Adsorption

According to Chieregatti [1], "The Adsorption is defined as the adhesion of molecules in an extremely thin layer (as of gases, solutes or liquids) to the surfaces of solid bodies or liquids with which they are in contact. (…) The adsorption is a surface phenomenon and large specific surface area is preferable for providing large adsorption capacity, but the creation of a large internal surface area in a limited volume inevitably gives rise to large numbers of small sized pores between adsorption surfaces".

The solution of the adsorption phenomenon physical model, whose equations must be applied on a computational model for the interests variables calculations, depending on the considerations about the flow. The program developed by Chieregatti [1] was modelled for the

same type of flow of this work, differing on the gas and the porous environment in analysis.

2.2 Zeolitic Imidazole Framework 8 (ZIF-8)

According to Binling Chen [2], "A number of MOFs with zeolitic architectures have been successfully synthesized as hybrid frameworks. Among them, the advent of zeolitic imidazole frameworks (ZIFs) has recently gained considerable attention. ZIFs are a sub-family of MOFs which consist of M–Im–M (where M stands for Zn, Co cation and Im stands for the imidazolate linker) formed by a self-assembly approach".

One of the ZIFs is the ZIF-8 ($[Zn(C_4H_5N_2)_2]_n$), which has been studied for gas storage and separation, catalysis, sensor, drug delivery, electrical energy storage, among others applications. The reason the ZIF-8 is receiving much attention from researchers of the CO_2 adsorption area is because of its large pore diameter (11.6 Å), becoming a strong candidate for catalysis, CCS and separation processes.

2.3 Past publications

The researchers group initiated the studies in the adsorption of natural gas, known Adsorbed Natural Gas, or ANG. After the numerical solver developed [5], some solutions were proposed to increase the amount of gas stored. Then, to perform an active thermal control of the filling process in different ways such as using heat exchange's devices inside the tank, the group did numerical simulations with different device configuration, where one of the results is presented in the Figure 1:

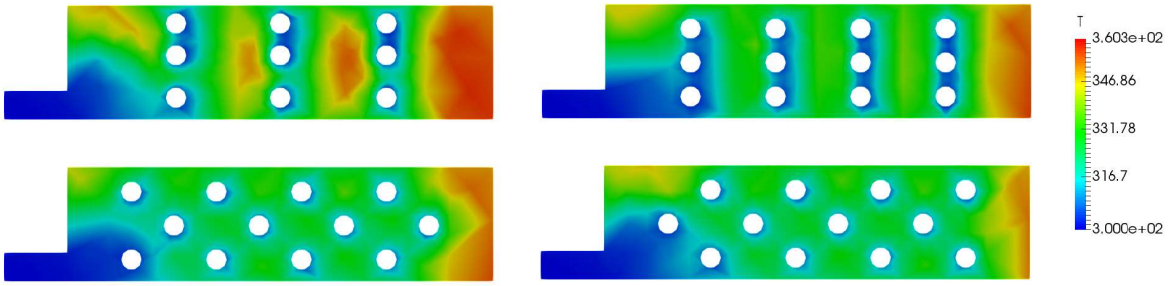

Figure 1. Temperature distributions of numerical 2D-axisymetrical simulations using different internal heat exchangers disposals [3].

The work showed that the tubes that are arranged in tandem showed best results of quantity of gas stored in comparison to aligned tubes, where the capacity of the tank increased more than 20% as compared to baseline test, without the heat exchangers. Although the results were satisfactory, the trade-off between the quantity of tubes and the available volume inside the tank is an important parameter to find the best configurations.

Advancing in the research, the group focused on to study the sensitivities of the parameters that influence the capacity of stored gas. Using the solver developed in the previous work [5], a sensitivity analysis using the so-called Adjoint Method was developed, where the influence of the forced convection, inlet gas temperature and filling flow curves were evaluated, considering as objective functions the volume average pressure and volume average temperature and the quantity of adsorbed gas stored.

Assembling all works developed, a complete optimization loop algorithm was developed [5] and systematic studies of the filling flow curve were performed and published. The results

showed a non-intuitive curve that proposes a rapid increase of the flow during the first 25% of the process time and a smooth decrease of the flow in the remaining time. The figure 2 shows one of the cases published [6]:

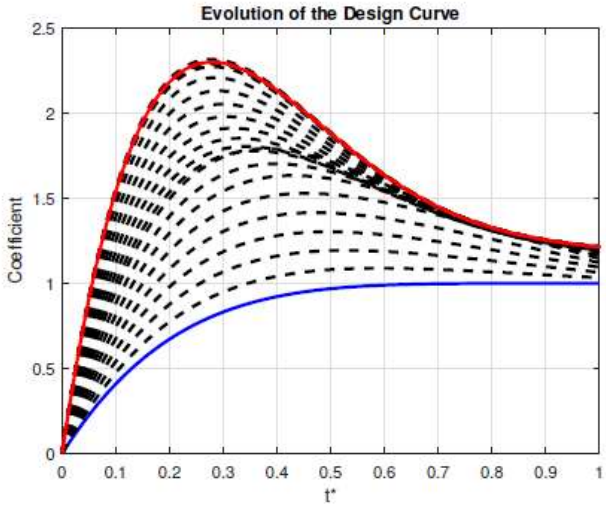

Figure 2. Filling flow design optimization [1]

Now, with the changing of the gas and the adsorbed material, the group proposes a complete analysis of the CO_2 filling by adsorption, starting with this work, when the main sensitive parameters were studied to guide the future works using optimization methods.

2.4 Mathematical Model

Using similar considerations, presented in [1], the initial considerations assumed in this work were:

- Carbon Dioxide (CO_2) 100% pure.
- Carbon Dioxide considered an ideal gas.
- All the thermophysics properties are constant during the intervals of temperature and pressure of the process.
- The gas and liquid solid of the adsorbed gas are locally in thermal equilibrium.
- The adsorption surface is considered isotropic and all its particles as spheres with homogeneous porous distribution.
- Resistance inside the particle and in its layer for mass and heat transferences are not considered.
- Natural convection inside the adsorption surface is not considered.
- Adsorbed heat is constant.
- Thermal effects of the cylinder are not considered.

After applying the conditions above and some manipulations in the generic Navier Stokes equations, three general equations were obtained defining continuity (eq. 1), momentum (eq. 2) and energy (eq. 3):

$$\partial_o\left(\epsilon_t \rho_g + \rho_b q\right) + \nabla \cdot \vec{G} = 0 \tag{1}$$

Where the symbol ∂_o represents the time derivative, ϵ_t is the total porosity of the adsorption bed, ρ_b is its density and $\vec{G} = \rho_g \cdot \vec{v}$ is the mass flux vector, where $\vec{v}$ is the velocity vector. The literature reports distinct approaches to the momentum equation in porous media. Among them, the volume averaged Navier Stokes equation is well consolidated[1]. An analysis of the order of magnitude shows that the inertial, convective and diffusive terms are negligible in comparation with the pressure gradient and the source term, called Darcy term which is in terms of the adsorption bed properties. Then, the momentum equation was simplified by:

$$\frac{\mu}{K}\vec{G} + \rho\nabla P = 0 \tag{2}$$

The energy equation must consider the thermodynamic effects of adsorption, which is accomplished by adding a source term, on the RHS:

$$C_{eff}\partial_o T - \epsilon_t \partial_o P + C_{pg}\vec{G}\nabla T - \lambda_{eff}.\nabla^2 T = \rho_b \frac{\Delta H}{M_g}.\partial_o q \tag{3}$$

Where $C_{eff} = \left(\epsilon_t \rho_g + \rho_b q\right)C_{pg} + \rho_b \cdot C_{ps}$ is the effective heat capacity, C_{pg} and C_{ps} are the specific heats at constant pressure of the gas and the adsorbent, respectively. The parameter $\lambda_{eff} = \epsilon_t \lambda_g + (1 - \epsilon_t)\lambda_s$ is the thermal conductivity, in terms of the gas (λ_g) and the bed (λ_s) conductivities. On the RHS, ΔH is the isosteric heat of adsorption, M_g is the molar mass and q is the same adsorption density that happens in the eq.(1).

The adsorption model used was Dubinin-Astakhov to evaluate, with distinct temperatures and pressures, the adsorbed quantity by a mass-based description.

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

Where $\boldsymbol{\rho_{ads}}$ is the adsorbed gas density, $\boldsymbol{W_0}$ is the micropore volume per unit of adsorbent mass, $\boldsymbol{\beta}$ is the affinity Coefficient, $\boldsymbol{E_0}$ is the characteristic adsorption energy, $\boldsymbol{n}$ is D-A model exponent and A is the Polany's potential of adsorption, defined as follows:

$$A = R.T.\ln\left(\frac{P_s}{p}\right) \tag{5}$$

The saturation pressure (Ps) and the adsorbed gas density are defined as:

$$P_s = P_{cr}\left(\frac{T}{T_{cr}}\right)^2 \tag{6}$$

$$\rho_{ads} = \frac{\bar{\rho}_{ads}}{\exp[\alpha_e(T - T_b)]} \tag{7}$$

Where P_S is the gas saturation vapor pressure, T_{cr} and P_{cr} the critical temperature and pressure of the gas and ρ_{ads} the adsorbed gas density in the liquid phase at the saturation region (T_b), and α_e is the average thermal expansion of the liquefied gas.

Chieregatti[1] also changed the term $\partial q/\partial t$ that appears in the Continuity and Energy equations with the approach of the Linear Driving Force (LDF) model, presented in the eq.(8):

$$\frac{\partial q}{\partial t} = k.(q^* - q) \tag{8}$$

Where $q^*$is the adsorbed gas in equilibrium with its saturated phase and k is the mass transference coefficient.

2.5 Numerical Solver

The equations (1) – (8) was previously implemented in the FREEFEM++ platform [7]. This platform is a high-level integrated development environment (IDE) for numerically solving partial differential equations (PDE) in 2 and 3 dimensions. It is an ideal tool for studying the finite element method, but it is also very useful for research, to quickly test new ideas or multi-physics and complex applications [7]. The advantages of FREEFEM++ was described by Chieregatti [1] and the main points are described below:

- Problem description (real or complex valued) by their variational formulations, with access to the internal vectors and matrices,if needed . This is very important for modified equations implementations.
- It allows one to program multi-variables, multi-equations, bi and three dimensional steady or time dependent, linear or nonlinear coupled systems
- It has an automatic mesh generator, based on the Delaunay-Voronoi algorithm. The inner point density is proportional to the density of points on the boundaries. As the NG tanks have simple geometries, we circumvent the need for comercial mesh generator software packages.
- It has a large variety of linear direct and iterative solvers (LU, Cholesky, Crout, CG, GMRES, UMFPACK, MUMPS, SuperLU, ...) and eigenvalue and eigenvector solvers (ARPARK).

2.6 Post processing

The results obtained by the processing of the FREEFEM++ algorithm could be processed in tables and graphs, using Microsoft Excel® or MATLAB®. The images of the properties field were processing in the free software PARAVIEW.

3 DEVELOPMENT

3.1 CO_2 and Adsobent data

The first step taken to validate the ZIF-8 and CO_2 parameters was to obtain as istothermal adsorption curve, and in order to do so, the result was compared with Bose (2019) with the equations (4)-(7). The required CO_2 parameters were obtained using the Toolbox website [11], as shown below:

Table 1 - CO2 parameters

Description	Parameter	Value	Unit
CO_2 density at boiling point	$\overline{\rho}_{ads}$	1562	Kg/m³
CO_2 temperature at boiling point	T_b	194,686	K
CO_2 critical pressure	P_{cr}	$7{,}38 * 10^6$	Pa
CO_2 critical temperature	T_{cr}	304,13	K

Afterwards, the ZIF-8 parameters were obtained using Bose [8] :

Table 2 - CO2 Adsorption parameters

Description	Parameter	Value	Unit
Characteristic Energy of adsorption	$\boldsymbol{E_0}$	26,65	KJ/mol
Microporous volume per unit of adsorbent	$\boldsymbol{W_0}$	$5{,}9 * 10^{-4}$	m³/kg

The β coefficient represents the affinity coefficient between the ZIF-8 and the CO_2, and it was adjusted to the Energy of Adsorption used in this work, resulting on 0,21. The value of α was calculated extrapolating the graphs made by Teymourtash [12] reaching the value of $5{,}55.\,10^{-3}K^{-1}$. Finally, the $n_{ads}$is the adsorption coefficient of the adsorption model used, and its final value was 1,8. Varying the pressure P from 0 to 4 MPa, the isothermal curve could be achieved and validated.

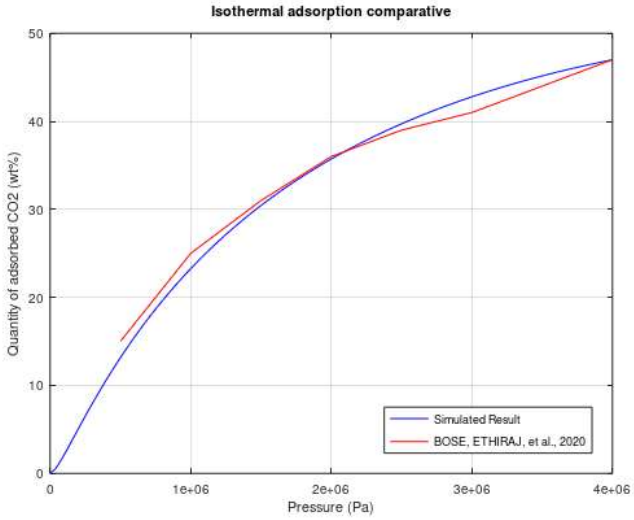

Figure 3 - Isothermal Curve graph validation

3.2 Tank Geometry

The initial tank's dimensions were also the same as used by Chieregatti [1], as shown below, considering a 2D-axisymetric simulation:

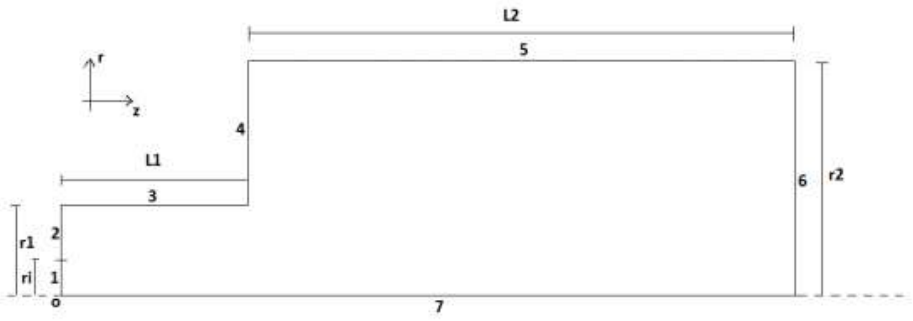

Figure 4 - Dimensions of the tank

Where the section 1 is the inlet section, 2,3,4,5 and 6 are the tank walls and 7 is the symmetry line. The dimensions of the reference tank are $r_i = 3{,}175\ mm, r_1 = 13{,}00\ mm, r_2 = 53{,}3\ mm$, $L_1 = 30{,}00mm$, $L_2 = 202{,}00\ mm$. The simulations varying the L/D ratio, keeping constant the same internal volume.

3.3 Mesh Description

The mesh of the geometry used had the same parameters used in the previous works that have already been cited, considering the best results of the mesh sensitivity. The geometry has 1851 triangular elements and a refining at the entry of the gas, as shown below:

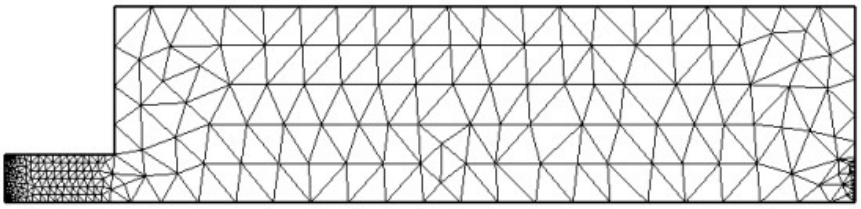

Figure 5 - Representation of the tank's mesh

3.4 Boundary Conditions

The table 2 presents the boundary conditions using in the simulations:

Table 2. Boundary Conditions

Boundary Type	Conditions
Inlet	$\vec{G} \cdot \vec{n} = G_{in}$ $T = T_{in}$
Wall	$\vec{G} = \vec{0}$ $\vec{n} \cdot \nabla T + h(T - T_{ext}) = 0$
Symmetry	$\vec{G} \cdot \vec{n} = 0$ $\vec{n} \cdot \nabla T = 0$

The first of the inlet conditions imposes a known profile (parabolic) on the specific mass flow rate [1]. The function G_{in} specifies a filling curve that may depend on space, time and finite set of parameters. Analogously the second inlet condition imposes a known temperature profile T_{in}, which may also be a function of time, space and a set of parameters. No-slip is imposed on tank walls, along with convective heat transfer conditions. There, T_{ext} represents the external air temperature in the tank surroundings, and h is the average convective heat transfer coefficient.

3.5 Setup of the simulations

The simulations had three variations: the heat transfer coefficient, the inlet flow of CO_2 and the aspect ratio of the tank. The first one had the values of 5 W/m²K (natural convection), 700 and 1000 W/m²K (forced convection). The aspect ratio (the tank's length divided by its diameter) used in [1] was 1,9 (reference tank), and in this work it had the values of 1,0, 1,9, 3,0,

5,0 and 7,0. The CO_2 inlet flow was based on the number of the tank's volume, which is 0,00181876 m³, so it was adopted that the flow was 0,00181876 m³/min or equivalent to it, having the variation of 100%, 75% and 50%.

The results processed by FREEFEM++ were shown using the Paraview software, totalizing 18 simulations with the outputs of temperature (maximum and medium) and the medium adsorption for each step until the pressure achieved 1,0 MPa.

All the simulations had a similar behavior in terms of spots where the adsorption was higher, which was where the temperature was lower. In all of them, the temperature started at 300 K, and increased along with the quantity of CO_2.

4 RESULTS

The table below shows the results of all the 18 simulations, with the respective parameters considered in the first six columns, and the data obtained one-step before the pressure achieved 1,0 MPa.

Table 3. Results of developed simulations

Simulation	h (W/m²K)	Flow Capacity	Radius (m)	Length (m)	Aspect Ratio	Time (s)	Med. Temp (K)	Max. Temp (K)	Med. Adsorption
1	5	100%	0,0533	0,202	1,9	512	396,61	424,92	0,041679
2	5	75%	0,0533	0,202	1,9	836	387,02	421,76	0,051881
3	5	50%	0,0533	0,202	1,9	1725	370,22	408,99	0,072604
4	700	100%	0,0533	0,202	1,9	1034	365,03	416,11	0,087157
5	700	75%	0,0533	0,202	1,9	1576	356,02	406,90	0,100393
6	700	50%	0,0533	0,202	1,9	2834	343,48	389,51	0,121306
7	700	100%	0,0660	0,132	1,0	1497	359,90	416,08	0,095049
8	700	100%	0,0457	0,274	3,0	1710	350,16	395,33	0,109482
9	700	100%	0,0386	0,386	5,0	1963	341,93	376,72	0,125626
10	700	100%	0,0345	0,483	7,0	2110	336,38	368,47	0,135330
11	700	50%	0,0660	0,132	1,0	2695	347,42	400,91	0,115000
12	700	50%	0,0457	0,274	3,0	3052	337,974	376,631	0,131253
13	700	50%	0,0386	0,386	5,0	3422	330,78	360,14	0,146895
14	700	50%	0,0345	0,483	7,0	3644	326,20	351,78	0,156727
15	1000	100%	0,0660	0,132	1,00	984	368,569	422,395	0,0826441
16	1000	100%	0,0457	0,274	3,00	1128	359,167	406,652	0,0956272
17	1000	100%	0,0386	0,386	5,00	1315	350,756	388,084	0,111603
18	1000	100%	0,0345	0,483	7,00	1418	344,746	380,184	0,120599

The analysis of the results considered two parameters as the most relevant: the medium adsorption (the higher, the better) and the required time (the lower, the better), having in mind that all the simulations ended when the internal pressure reached 1 MPa.

To analyze the effect of the change of heat transfer coefficient, cases with the same aspect ratio and inlet flow were compared. The biggest increase on adsorption was between simulations 1 and 4, where it went from 0,041679 to 0,087157, as shown below:

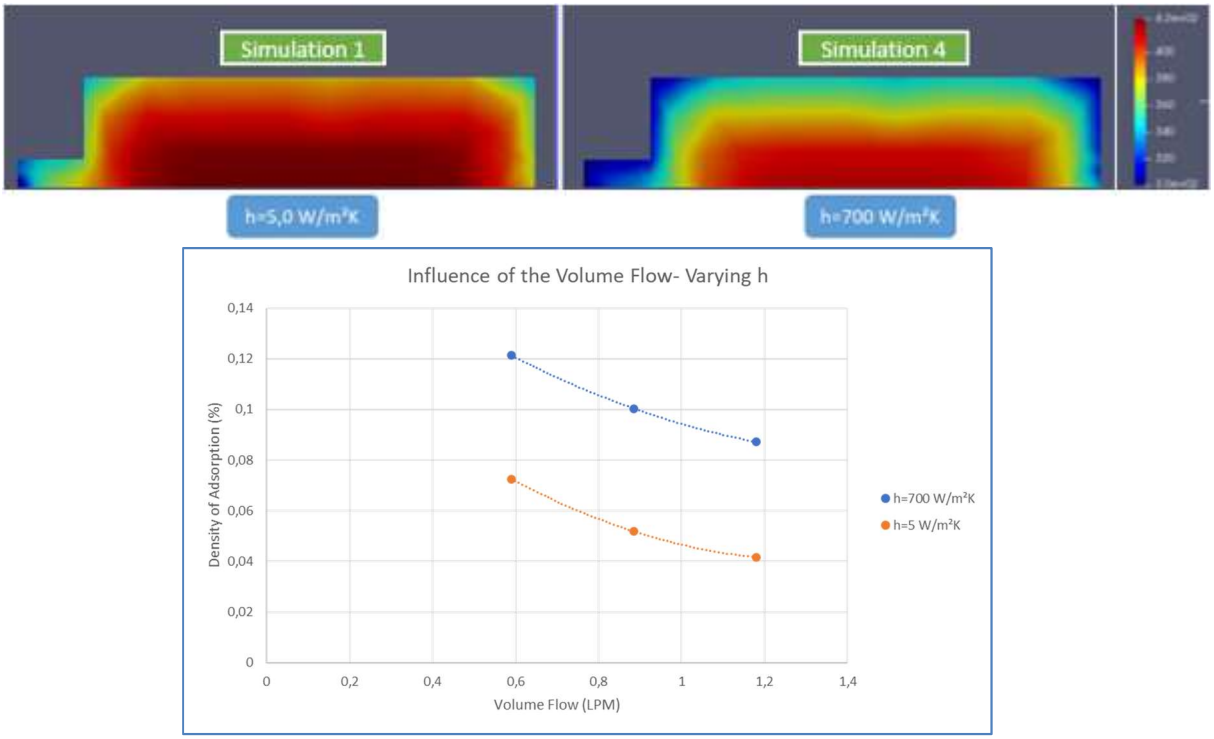

Figure 6 – Comparison between different external heat transfer coefficient.

To analyze the effect of the change of inlet CO_2 flow, cases with the same aspect ratio and heat transfer coefficient were compared. The biggest increase on adsorption was between simulations 1, 2 and 3, where it went from 0,041679 to 0,051881 to 0,072604, as shown below:

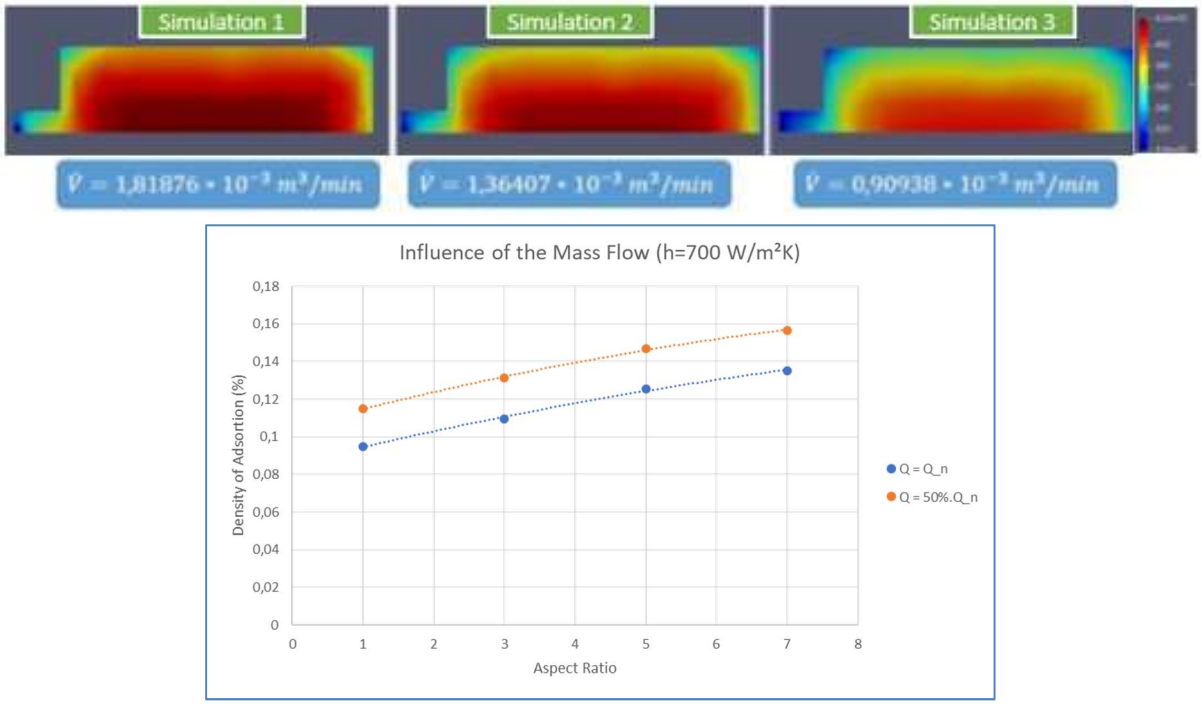

Figure 7 – Comparison between different filling flow values

To analyze the effect of the change aspect ratio, cases with the same inlet flow and heat transfer coefficient were compared. The biggest increase on adsorption was between simulations 15, 16, 17 and 18, where it went from 0,0826441 to 0,0956272 to 0,111603 to 0,120599, as shown below:

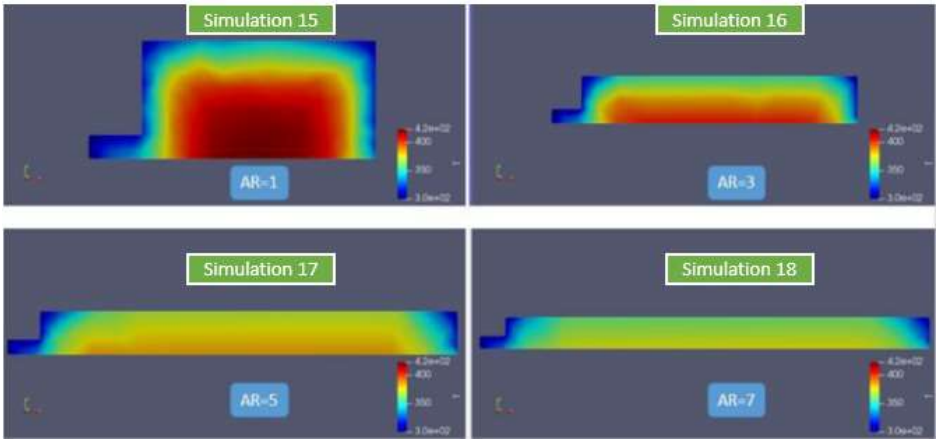

Figure 8 – Comparison between different tank aspect raio dimensions

The figure above shows that, regardless of the aspect ratio, the smaller inlet flow promotes a higher adsorption than the bigger. This can be explained due to the heating the adsorption process causes inside the tank, once where there is more gas to be adsorbed, more heat is released. In general, the forced heat transfer convection requires more time to achieve 1 MPa, however, the internal temperature increases considerably. By increasing the aspect ratio, the simulation time and the adsorption increased, but the temperature was lower in each case.

5 CONCLUSIONS

The main focus of this work was to analyze the adsorption of carbon dioxide using ZIF-8 as adsorbent material and to determine which parameters have more influence in the efficiency of this process. All the simulations that were carried out showed that the amount of gas stored can be increased by varying the aspect ratio of the tank, the inflow flux and the external heat transfer coefficient.

However, there is an important tradeoff in the adsorption process between the amount of gas stored and the filling time. This occurs because in order to store more gas, it is necessary to fill the tank with lower inflow fluxes. Hence, it would be necessary more time to complete the process.

Furthermore, it was observed that the temperature inside the tank increases in a higher rate than the temperature in the same process when activated carbon was used as adsorbent material. This fact reassure that the thermal control of this process is extremely important to increase its efficiency.

A natural sequel of this research is to optimize the filling process of carbon dioxide in a tank with ZIF-8. To achieve this goal an optimization method will be necessary. It is planned to use the so-called Adjoint Method to estimate the sensitivity derivative of a given objective function and to use this information in an optimization loop algorithm.

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