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Optimization of an Adsorbed Natural Gas System with Phase Change Material using the Topology Optimization Method

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Abstract. *Natural Gas has been drawing industrial sectors attention as a promising alternative fuel. This solutions attractiveness depends on the quality and efficiency of the storage and transport methods employed. Porous media are known to be an efficient manner to store natural gas by the adsorption mechanism, also known as Adsorbed Natural Gas (ANG). Temperature exerts significant influence on adsorption efficiency. Studies applying Phase Change Materials (PCM) as heat exchanger in ANG systems suggests the combination improves the vessel capacity and adsorption and desorption rates behavior. In addition, the PCM bodies shape and position inside adsorption systems greatly affects the benefits they bring. For this reason, the Topology Optimization Method (TOM) is indicated for this problem. The topology optimization method is a versatile tool for material distribution inside a domain and in the last few decades its capabilities of exploring manufacturing process characteristics as well as its implementation have been improved. This study aims to increase the capacity and performance of Adsorbed Natural Gas (ANG) Vessels using TOM to distribute PCM material in the vessel interior. The physical model consider a coupled heat and mass transfer trough an ANG vessel with PCM in its interior, the boundary conditions are dictated by a pressure input in the vessels extremity and the natural convection on the vessels walls. FEniCS Project libraries are employed in the governing equations implementation and to work the solution for the differential equations and dolphin-adjoint libraries are applied to perform the sensitivities calculus. The project variable* *for the optimization is defined as the PCM distribution inside the vessel. Thermal properties corrections are performed according to an analytical solution for the phase change problem. Phase change enthalpy corrections are performed in the level of the variational problem to model the phase change phenomena. The amount of heat transferred to the phase change enthalpy dictates the phase composition in the domain. The implementation benefits the topology optimization approach as it maintains the duality between the adsorbent volume to adsorb gas and the PCM volume to store heat. An experimental work from the literature is modelled and compared to the numerical results for software validation and model properties calibration. As results a 2D ANG vessel optimization is performed, the final topologies are presented and their total adsorption volume and charging/discharging time are compared.*

Keywords: *Adsorption, Optimization, PCM, ANG, Desorption*

1 INTRODUCTION

Adsorption consists in the adhesion of molecules to surfaces, attracted by disrupted bonds. The modelling of the adsorption phenomena can be found in the literature such as in (Freni et al., 2009; Sahoo et al., 2014). The Adsorbed Natural Gas (ANG) technology employs the adsorption phenomena to store and transport gas in a porous solid matrix. This method of storage offers a similar volume capacity (164 V/V) to the Compressed Natural Gas (CNG) wich can provide 245 V/V. However ANG operates in pressures one magnitude order lower than CNG, being a safer option.

In the last few decades the Phase Change Materials (PCM) drawn scientific community's attention for its ability to increase the capacity of thermal storage systems for various applications (Padovan et al., 2014).

Phase change materials are substances which have a high phase change hentalphy and, therefore, are considered latent thermal storage materials (Sharma et al.,2009). Taking an example of a solid-liquid PCM material outside its phase change temperature, it behaves as a conventional material storing heat as it is heated and elevating its temperature, but when the phase change occurs, large amount of heat is stored due to the change of state of the material. Different from materials used for sensible heat storage systems, PCM absorbs and releases large amounts of heat at practically constant temperature during its phase change, for the same volume, a PCM stores 5 to 14 times more heat than water (Sharma et al.,2009). Yet, such materials generally have high thermal conductivity, allowing for high charge rates and discharge thermal energy.

There is a huge range of PCMs and to better organize them, they were conventionally grouped in organic, inorganic and eutectic (Sharma et al.,2009). The material proposed here, HS34, belongs to the group of inorganic, with a salt hydrate. This type of MMF is the most studied group and most used in latent heat storage systems (Sharma et al.,2009). The solid-liquid transformations of salt hydrates are, in fact, hydration and dehydration processes. Thus, a salt hydrate, in general, melt to a state with less moles of water in their chemical composition or their anhydrous form (without the presence of water). The phase change hentalphy of the substance is the energy needed to make this break in its structure. The most attractive attributes of salt hydrates are its high heat of fusion per unit volume, relatively high thermal conductivity (almost double the paraffin) and minimum variations in the volume during phase change (Sharma et al.,2009). For correct selection of an MMF material for a given application, the operating temperature of both the heating and the cooling must match the transition temperature of the material MMF (Sharma et al.,2009).

In (Toledo et al., 2013) the behavior of a carbon dioxide adsorbent tank (CO_2) aided by a set of fixed PCM balls in its interior was studied. The study carried out computer simulations and the results obtained were confronted with an experimental test. The experiment shows that the maximum temperature inside the tank with the MMF spheres is lower than that measured on the tank with PCM. Also, for different pressures of adsorption, the storage capacity of the tank with PCM was higher than that for the tank with no PCM. Furthermore, the study of (Toledo et al., 2013) shows the existing influence between the volume of the spheres and the effect they have on the system performance. In (Li et al., 2015), an methane adsorption vessel employing petroleum coke as adsorbent and a mixture of lauric acid and dodecanoic acid as phase change material is studied. An experimental vessel is built and the adsorption cycle and desorption cycle are performed aiming to compare an ANG vessel with PCM and an ANG vessel without PCM. (Li et al., 2015) verifies an increase of adsorbed and desorbed gas in the vessel with PCM. Hence both studies, (Toledo et al., 2013; Li et al., 2015), indicate PCM as an effective alternative for a passive thermal control in an adsorption tank.

In this work, the topology optimization method is employed to performer a material distribution inside an adsorption vessel in order to extremize the amount of adsorbed gas. Once (Toledo et al., 2013) stated that the geometry and position of PCM bodies affect the behaviour of the tank, TOM is a promising method to handle the proposed problem.

2 Physical Problem Formulation

In this study, the fluid velocity is given by the pressure gradient as stated by the Darcy Law. The local thermal equilibrium is considered so that for a certain region on the domain, a single temperature value can determine the temperate for the gas and for the solid (their temperature is the same). The methane thermal capacity is considered constant for all the temperature range in the analysis. All PCM properties are considered isotropic, the adsorption enthalpy is assumed to be invariable throughout the whole process. Finally, the equilibrium pressure is given as a function of temperature (Chung et al., 2009):

$$P_{eq}(T) = P_{ref} \cdot e^{\left(A - \frac{B}{T}\right)} \tag{1}$$

where A and B are constants and P_{ref} is the reference pressure.

For the adsorption physical problem it is necessary to express the mass and energy balance in terms of temperature and pressure as described in (Freni et al., 2009):

$$\varepsilon \frac{\partial}{\partial t}\left(\frac{P}{T}\right) - \nabla \cdot \left(\frac{K_s}{\mu_g} \cdot \frac{P}{T} \cdot \nabla P\right) = -(1-\varepsilon)\frac{\partial \rho_s}{\partial t}\frac{K_s}{\mu_g} \tag{2}$$

$$\begin{aligned} \varepsilon C_{ps}\frac{M_g P}{R_g T}\frac{\partial T}{\partial t} - \frac{M_g}{R_g}\nabla \cdot \left(\frac{C_{pg}K_s}{\mu_g} \cdot \nabla P \cdot P\right) + (1-\varepsilon)\rho_s C_{ps}\frac{\partial T}{\partial t} \\ -\nabla \cdot (k_s \cdot \nabla T) = (1-\varepsilon)|\nabla H|\frac{\partial \rho_s}{\partial t} + H_{pcm} \end{aligned} \tag{3}$$

where ε is the porosity, μ_g is the fluid viscosity,R_g is the ideal gas constant, M_g is the molecular mass of the gas, K_s is the medium permeability, C_{ps} is the solid phase specific heat, C_{pg} is the gas phase specific heat, k_s is the medium thermal conductivity and H_{pcm} is the heat absorbed or released due the the phase change process.

The adsorbent bed density variation in adsorption and in desorption is determined by finite differences as follows (Mayer et al., 1987):

$$\frac{\partial \rho_s}{\partial t} = G_a(\rho_{ss} - \rho_s) \tag{4}$$

where ρ_{ss} is the saturation density for the adsorbent bed and G_a is given by:

$$G_a = D_a \exp\left(\frac{-E_a}{R_g T}\right) \ln\left(\frac{P}{P_{eq}}\right) \tag{5}$$

where D_a is the kinetic constant for adsorption, E_a is the adsorption activation energy and P_eq is the equilibrium pressure. For the dessorption phase:

$$\frac{\partial \rho_s}{\partial t} = G_d(\rho_s - \rho_{s0}) \tag{6}$$

where ρ_{s0} is the initial density (density of the adsorbent with no gas) and G_d is given by:

$$G_d = D_d \exp\left(\frac{-E_d}{R_g T}\right)\left(\frac{P - P_{eq}}{P_{eq}}\right) \tag{7}$$

where D_d is the kinetic constant for dessorption, E_d is the dessorption activation energy.

For the adsorption equilibrium state the following relation can be written (Sahoo et al., 2010):

$$q_{ss} = \rho_{s0} + \rho_{ads} W_s \exp\left(-\left(\frac{A}{E_a}\right)^{n_s}\right) \tag{8}$$

where ρ_{ads} is the adsorbed gas density, W_s is the specific pore volume, n_s is the affinity coefficient and A is the Polanyi adsorption potential given by:

$$A = R_g T \ln\left(\frac{P_{sat}}{P}\right) \tag{9}$$

where P_{sat} is given by:

$$P_{sat} = P_{cr}\left(\frac{T}{T_{cr}}\right)^2 \tag{10}$$

where P_{cr} is the critical pressure and T_{cr} is the critical temperature of the gas.

3 Phase Change Material Model

The phase change material formulation follows the one dimensional analytical model from the Stevan Phase Change Problem. The phase change barrier position is given by:

$$\delta(t_{mel}) = 2 \cdot \beta \cdot \sqrt{\alpha_l \cdot t_{mel}} \tag{11}$$

where α_l is the thermal difusivity of the liquid phase, t_{mel} is the amount of time that the solid phase spent melting, β is given as the solution for the non-linear equation:

$$\beta e^{\beta^2} erf(\beta) = \frac{C_{p,l}(T_w - T_m)}{L\sqrt{\pi}} \tag{12}$$

where $C_{p,l}$ is the specific heat of the liquid phase, T_m is the phase change temperature and T_w is the node temperature. The heat stored in the phase change phenomena can be directly related to the phase change barrier. Hence the heat consumed or released by the PCM body is written as:

$$H_{pcm} = \varepsilon_{pcm} \cdot \rho_{pcm} \cdot L \cdot \frac{\partial \delta(t_{mel})}{\partial t} \tag{13}$$

This approach aims to apply the 1D analytical model in the element nodes in order to represent the PCM phase change enthalpy inside the studied domain.

4 Finite Element Formulation

The weak forms of the equations from section 2 and section 3 are discretized over a 3-node element with order 1 for temperature and order 2 for pressure and density. In order to solve the adsorption physical problem the following non-linear system is solved via the finite elements method.

$$\begin{Bmatrix} \mathrm{W(T)} & \mathrm{Z(P,T)} \\ 0 & \mathrm{N} + \mathrm{L}_c(T) + L_r(P,T) \end{Bmatrix} \begin{Bmatrix} \mathrm{P} \\ \mathrm{T} \end{Bmatrix} + \begin{Bmatrix} \mathrm{Q}_c(T) + Q_r(P,T) & 0 \\ \mathrm{J}_c + J_r(P) & \mathrm{K} + \mathrm{D}_r \end{Bmatrix} \begin{Bmatrix} \mathrm{P} \\ \mathrm{T} \end{Bmatrix} = \begin{Bmatrix} \mathrm{G} \\ \mathrm{H} + \mathrm{D}_c \end{Bmatrix} \tag{14}$$

where the matrices coefficients are the result of the approximation of the governing equations on a finite element inside the domain.

5 Topology Optimization Method for Adsorption Systems

The TOM has been employed to design optimized adsorption vessels with PCM by distributing the PCM material inside the domain. In this work TOM aims to extremize an objective function for a vessel exposed to a transient pressure input and natural convection. The optimization problem is stated bellow:

$$\begin{aligned} \text{Maximize :} \quad & J_a = \int_{\Omega_s} \rho_s(T_f)dx \\ \text{s.t. :} \quad & 0 \leq \varepsilon_{pcm} \leq 1 \end{aligned} \tag{15}$$

where T_f is the final time for the transient analysis.

5.1 Material Model for Topology Optimization

In this work, it is assumed that the elements represent regions in the domain space. The ε_{pcm} is the project variable which defines the portion of PCM inside an element inside the domain, it can vary from 0, no PCM, to 1, 100% of PCM. Hence an element is a mixture of PCM and adsorbent and gray scales (intermediate values between 0 and 1) are allowed. For the properties related to the PCM portion inside an element, the material model is as follows:

For the barrier position ans, thus, the amount of heat in the phase change, it can be written as:

$$\delta(\varepsilon_{pcm}) = 2 \cdot \varepsilon_{pcm} \cdot \beta \cdot \sqrt{\alpha_l \cdot t_{mel}} \tag{16}$$

The specific heat can be stated as:

$$C_p(\varepsilon_{pcm}) = C_{ppcm} \cdot \varepsilon_{pcm} + C_{pads} \cdot (1 - \varepsilon_{pcm}) \tag{17}$$

The thermal conductivity can be stated as:

$$k(\varepsilon_{pcm}) = k_{pcm} \cdot \varepsilon_{pcm} + k_{ads} \cdot (1 - \varepsilon_{pcm}) \tag{18}$$

The initial density can be stated as:

$$\rho_{s0}(\varepsilon_{pcm}) = \rho_{pcm} \cdot \varepsilon_{pcm} + \rho_{s0ads} \cdot (1 - \varepsilon_{pcm}) \tag{19}$$

The saturation density can be stated as:

$$\rho_{ss}(\varepsilon_{pcm}) = \rho_{pcm} \cdot \varepsilon_{pcm} + \rho_{ssads} \cdot (1 - \varepsilon_{pcm}) \tag{20}$$

6 Results

Given the initial domain, exhibited in fig 1b. A 3200 element mesh with a initial PCM distribution is studied. A topology optimization analysis is run assuming this initial conditions and a transient pressure input in the left corner of the domain. The heat is assumed to leave the domain only by natural convection and the right corner of the domain is considered to be insulated. The boundary conditions are presented in fig 2.

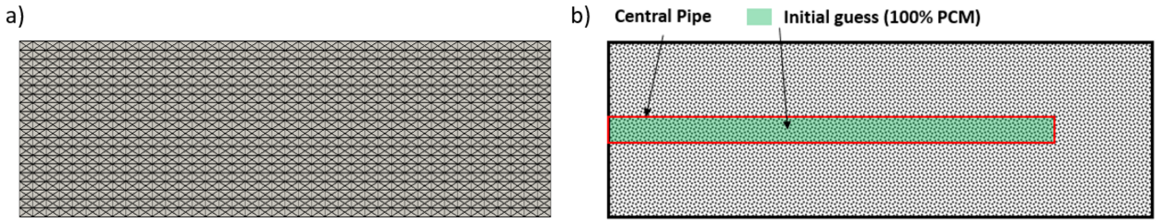

Figure 1: a) The mesh employed in the analysis. A 3200 mesh composed by triangular elements. b) The initial domain for the topology optimization. The gray region is 100% adsorbent and the green region is the PCM region

For the analysis, the properties values were assumed as for Maxsorb III and methane for adsorption and lauric acid for PCM. Assuming $P_{atm} = 101350.0Pa$, $T_{atm} = 293.0K$, $h_{room} = 16.0\frac{W}{m^2 \cdot K}$, $E_a = 10626.0\frac{kg}{m^3}$, $R_g = 8.31\frac{J}{molK}$, $R_{s0} = 318.00\frac{kg}{m^3}$, $R_{ag} = 422.36\frac{kg}{m^3}$, $W_f = 1.01 \cdot 10^{-3}\frac{kg}{m^3}$, $P_{cr} = 4.6MPa$, $T_{cr} = 190.0K$ and $n_p = 2.0$.

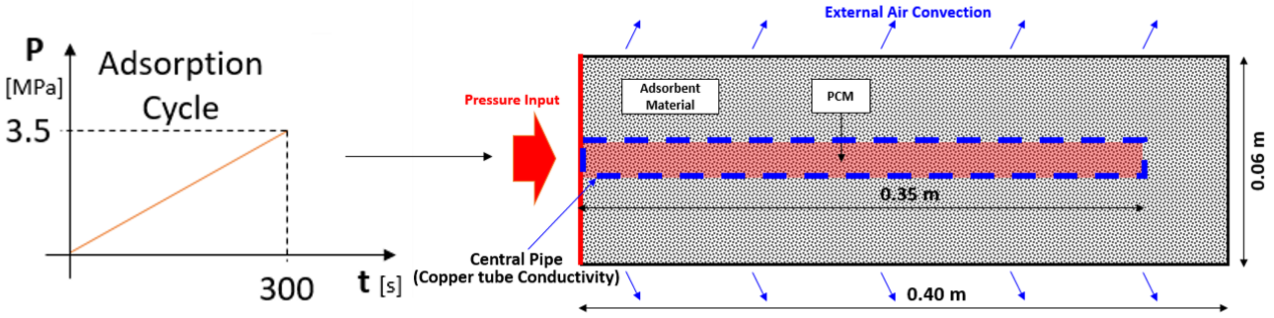

Figure 2: Boundary Conditions for topology optimization. The pressure profile as a function of time and the natural convection in the upper and lower boundaries o the vessel.

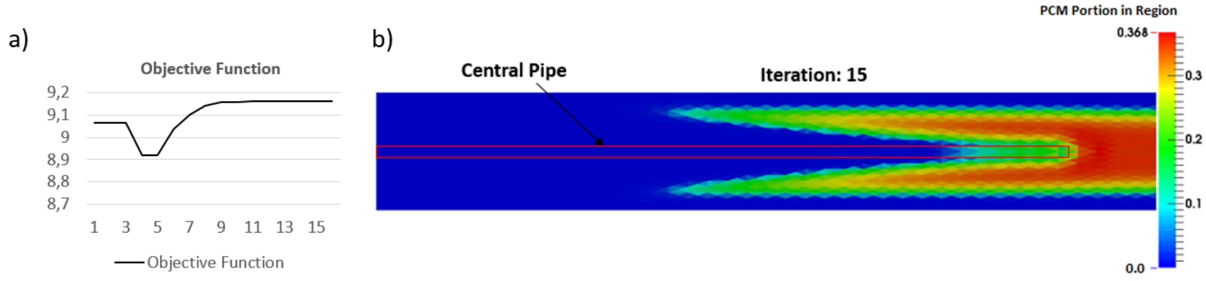

Figure 3: a) The objective function values throughout the iterations. b) The material distribution inside the domain. The blue regions have less PCM in the composition and the red regions have higher amounts of PCm in the composition.

The optimization run results are show in fig 3. In fig 3a, the objective function behaviour is shown. After 10 iterations it becomes stable and in fig 3b, the material distribution for the 15^{th} iteration is presented as the optimized result.

The topology optimization method is able to distribute the PCM material inside the studied domain. The optimized solution contains 7.9 liters more gas than the initial design considering the same time for the adsorption cycle.

The PCM distribution is highly affected by the conductivity of the materials in the domain. It can be seen in fig 3b that the copper tube in the center of the domain impacts in the material distribution, showing that PCM is mostly placed in regions with lower conductivity. However, in the right extremity of the tube, a PCM composition can be verified. This suggests that high conductivity doesn't nullifies the benefits of PCM in adsorption vessels and they must be placed and quantified in a manner to operate with synergy inside the system.

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