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Design of Adsorption Systems by Topology Optimisation

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Design of Adsorption Systems by Topology Optimisation

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Resumo

Adsorção é um mecanismo de retenção de moléculas de um fluido em superfícies sólidas e apresenta um vasto campo de aplicações, como em refrigeração, processos de separação e armazenamento de combustível. Este trabalho descreve o modelo de adsorção de gás em meios porosos e define uma abordagem de otimização de sistemas de adsorção baseada no Método de Otimização Topológica (MOT). Uma formulação abrangente para os fenômenos de adsorção e dessorção é apresentada, detalhando a dedução de seus formas fracas e montagem das matrizes para a implementação do Método dos Elementos Finitos (MEF). As sensibilidades das funções-objetivo em relação às variáveis de projeto são obtidas pelo método adjunto, que também é apresentado em detalhe. A implementação numérica é auxiliada pelos pacotes FEniCS e Dolfin Adjoint, originando uma ferramenta genérica para a otimização de sistemas de adsorção. Este método é aplicado ao projeto de tanques de Gas Natural Adsorvido (GNA) visando transporte, armazenamento e consumo. Tanques otimizados são propostos e comparados com tanques tradicionais, apresentando melhora dos objetivos de projeto.

Palavras-Chave – Topologia (Otimização), Método dos Elementos Finitos, Adsorção.

Abstract

Adsorption is a retention mechanism of fluid molecules on solid surfaces and presents a wide range of applications, such as refrigeration, separation processes and fuel storage. This work describes the modelling of gas adsorption on porous media and presents an optimisation approach for the design of adsorption systems based on topology optimisation. A comprehensive formulation for the adsorption and desorption phenomena is presented, detailing the derivation of their weak forms and assembling the matrices for the implementation of the Finite Element Method (FEM). The sensitivities of objective functions to topology optimisation design variables are obtained by the adjoint method, which is presented in detail. The numerical implementation is aided by FEniCS and Dolfin Adjoint packages, resulting in a generic software for the optimisation of adsorption systems. The method is applied for the design of Adsorbed Natural Gas (ANG) tanks for on-demand consumption. Optimised tank layouts are proposed and compared with standard tanks, presenting improvement of the design objectives.

Keywords – Topology Optimisation, Finite Elements Method, Adsorption.

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Acronyms

ANG	Adsorbed Natural Gas
CCS	CO_2 Capture and Storage
CNG	Compressed Natural Gas
DA	Dubinin-Astakhov
DR	Dubinin-Radushevich
ECP	Element Connectivity Parametrisation
ESO	Evolutionary Structural Optimisation
ETM	Electro-Thermo-Mechanical Actuator
FEM	Finite Element Method
FFC	FEniCS Form Compiler
FFD	Free-Form Deformation
FIAT	FEniCS Finite Element Automatic Tabulator
FVM	Finite Volume Method
GITT	Generalised Integral Transform Technique
GWP	Global Warming Potential
L-BFGS-B	Limited Memory Broyden-Fletcher-Goldfarb-Shanno with Box Constraints
LDF	Linear Driving Force Model
LNG	Liquefied Natural Gas
MOF	Metal-Organic Framework
ODE	Ordinary Differential Equation
OHT	Offset Hyperbolic Tangents Material Model
PCM	Phase Change Material
PDE	Partial Differential Equation
PLIC	Piecewise Linear Interface Calculation
PSA	Pressure Swing Adsorption
RBF	Radial Basis Function
REV	Representative Elementary Volume
SIMP	Solid Isotropic Material with Penalisation
TSA	Temperature Swing Adsorption
UFC	FEniCS Unified Form-Assembly Code
VoF	Volume of Fluid

Notation

A	Polanyi's adsorption potential
C	Solute concentration
Cp_g	Specific heat capacity of gaseous phase
Cp_s	Specific heat capacity of solid phase
D	Intra-particle diffusional time constant
$\mathbb{D}$	Adsorption kinetics weak form
D_0	Diffusivity of gaseous phase
e	Pseudo-porosity
ϕ	Non-filtered pseudo-porosity
$\mathbb{E}$	Energy balance weak form
E_0	Characteristic energy of adsorption
E_a	Activation energy of adsorption
E_d	Activation energy of desorption
G	Kinetic coefficient of adsorption and desorption reactions
h_W	Heat convection coefficient on external walls
it_{max}	Maximum iterations per continuation step
ΔH	Isosteric heat of adsorption
J	Functional of interest
k_a	Kinetic coefficient of adsorption
k_d	Kinetic coefficient of desorption
k_f	Thermal conductivity of phases combined
k_g	Thermal conductivity of gaseous phase
k_{intra}	Intra-particle diffusion rate constant
k_s	Thermal conductivity of solid phase
K_s	Permeability of the solid phase
$\mathbb{M}$	Continuity weak form
$\dot{m}_{let}$	Mass flow
M_g	Molecular mass of gaseous phase
n_s	Micro-pores dispersion
p	Material model penalisation
P	Pressure
$\mathbb{P}$	Generic material property
P_{atm}	Atmospheric pressure
P_{cr}	Critical pressure
P_{let}	Pressure at inlet/outlet regions
P_{sat}	Saturated pressure
q	Concentration of adsorbed phase
Q	Density of adsorbed phase
q_{eq}	Equilibrium concentration of adsorbed phase
Q_{eq}	Equilibrium density of adsorbed phase
r	Radial coordinate in axisymmetric domains
R_g	Universal gas constant
T	Temperature

T_{atm}	Atmospheric temperature
T_{let}	Temperature at inlet/outlet regions
T_{boil}	Temperature of gaseous phase at boiling point
T_{cr}	Critical temperature
u_g	Specific internal energy of gaseous phase
u_q	Specific internal energy of adsorbed phase
u_s	Specific internal energy of solid phase
$\mathbf{v}_g$	Velocity of gaseous phase
V	Volume
$\mathbf{w}$	State variable
w_s	Specific volume of micro-pores
W_s	Volume ratio of micro-pores
z	Design variable filtering radius
ϕ_s	Characteristic particle diameter of the solid phase
α_e	Mean value of the thermal expansion of liquefied gases
β	Affinity coefficient of adsorbent-adsorbate pair
Γ_D	Domain regions subjected to Dirichlet boundary conditions
Γ_F	Domain regions subjected to fixed temperature
Γ_L	Domain regions subjected to inlet/outlet of gases
Γ_N	Domain regions subjected to Robin boundary conditions
Γ_W	Domain walls
ε_m	Micro-porosity
ε_M	Macro-porosity
ε_t	Total porosity
λ	Adjoint variable
μ_g	Viscosity of the gaseous phase
ξ	Continuous shape function for adsorbed gas and pseudo-porosity fields
Ξ	Shape function matrix for adsorbed gas and pseudo-porosity fields
ρ_{adg}	Local density of adsorbed phase
ρ_{boil}	Density of gaseous phase at boiling point
ρ_f	Density of phases combined
ρ_g	Density of gaseous phase
ρ_s	Density of bulk solid phase
σ	Smoothness factor
$\boldsymbol{\tau}_g$	Viscous stress tensor
τ_s	Pores tortuosity
ϕ	Continuous shape function for pressure field
Φ	Shape function matrix for pressure field
ψ	Continuous shape function for temperature field
Ψ	Shape function matrix for temperature field
ω_{min}	Optimisation tolerance

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1 Introduction

In this Chapter, basic concepts of the adsorption phenomenon are introduced along with some applications, emphasizing Adsorbed Natural Gas (ANG) tanks. Thereafter, a brief review on optimisation methods applied to fluids and heat transfer problems is presented. Finally, the motivation, objectives and expected scientific contributions are stated, based on the lack of previous works approaching the design of adsorption systems by topology optimisation.

1.1 Concept and Applications of the Adsorption Phenomenon

The flow of gases or liquids in porous media are subjected to the retention and release of molecules on the solid phase. One of the retention mechanisms is the sorption phenomenon, which is a general term adopted for both adsorption and absorption reactions. The former is a surface reaction in which gas molecules accumulate on the surface of solid particles attracted by disrupted bonds (MOTA et al., 2004), while the latter is a bulk phenomenon, in which gas molecules diffuse through another phase, accumulating at the grain boundaries and often forming a new phase (BLANCO et al., 2014).

Adsorption is divided into two categories: (i) physical adsorption, based on weak van der Waals forces, which is also known as physisorption, and (ii) chemical adsorption, based on covalent bondings, also known as chemisorption. While the former is easily reversible and leaves the adsorbent intact, the latter involves a chemical reaction that affects the surfaces, as is the case of corrosion phenomenon. Figure 1.1 illustrates the mechanism of adsorption, where molecules concentrate on micro-pores walls.

The capacity of adsorption of porous media is dependent on characteristics such as the distribution and characteristic of micro-pores on the adsorbent, the affinity of adsorbent

Figure 1.1: Distribution of molecules in gaseous (○) and adsorbed (●) phases.

and adsorbate, gas pressure and temperature (BILOE et al., 2002). Considering a given pair adsorbent-adsorbate, the capacity of adsorption increases as pressure increases and temperature decreases.

Several engineering applications are based on the adsorption process. For instance, it is widely employed for fluid separation, both for removing trace contaminants, which is known as purification processes, and for recovering components from a mixture, which is known as a bulk separation processes. Examples of purification are the separation of sulphurous compounds from natural gas, solvents from air and SO_2 from vent streams (CAVALCANTE, 2000). Among bulk separations, the following pairs can be encountered: N_2 - O_2 , Water-Ethanol and Fructose-Glucose (CAVALCANTE, 2000).

The operation of adsorption separation processes can be undertaken as a batch process, by percolating fluid through the adsorbent until saturation and then purging it. The purge, also known as adsorbent regeneration, is usually undertaken by varying the temperature, which is termed Temperature Swing Adsorption (TSA), or by controlling the pressure, in a method called Pressure Swing Adsorption (PSA), or by purging the adsorbent with an inert desorbate, which could be easily separated by later processes, such as distillation. It is possible to have an adsorption separation in a continuous counter-current approach, by submitting adsorbents to adsorption and desorption at the same time, and also in a chromatographic way, which is based on the moving bed concept where the fluid flows in the opposite direction to the solid phase (CHARTON; NICOUD, 1995).

Adsorption can also be used for refrigeration, by using use solid adsorbents such as silica-gel and zeolite, to produce the cooling effect (WANG; VINEYARD, 2011). In this class of refrigerators, an adsorbent is dried out by applying heat, which increases its pressure and temperature and causes the desorption of refrigerant vapour. This step is equivalent to the compression step in compressor refrigerators. The vapour is then

liquefied in the condenser, while heat is rejected to a cooling tower. When the adsorbent is sufficiently dried out, the heat intake stops and heat dissipation takes place. Next, the adsorbent connection switches from the condenser to the evaporator, where the saturated liquid boils, vapour is adsorbed and chilled water is generated, which is used for air-conditioning. Given that this cycle is intermittent, continuous cooling output is achieved by associating two adsorbents driven anti-cyclically, as illustrated by Figure 1.2.

Figure 1.2: Adsorption cooling process (SOLARNEXT, 2009).

Adsorption systems present low electrical energy consumption in comparison to other refrigeration methods and can be activated by temperatures as low as 323 K, while absorption systems require at least 363 K (WANG; VINEYARD, 2011). This opens up the possibility of using low-grade heat such that derived from solar energy. The refrigerants used in adsorption cycles have zero ozone depletion potential and low Global Warming Potential (GWP), which is an index dependent on the strength with which certain greenhouse gas absorbs infrared radiation, on the spectral location of its absorbing wavelengths and on its atmospheric lifetime (ELROD, 1999). They can also operate in environments with significant vibrations, since the adsorbent is solid (in contrast with the liquid used in absorbent refrigerators) and the systems have fewer mechanical parts. The main drawbacks of adsorbent refrigerators are their low coefficient of performance (quantity of achieved cooling effect per unit of heat delivered), intermittent operation (when not associated in two or more generators) and their large size and weight (WOLAK; KRASZEWSKI, 2016).

Adsorption is also promising in CO_2 Capture and Storage (CCS). The greenhouse

effect is drawing more and more attention from researchers worldwide. Although carbon dioxide naturally exists in the atmosphere, it is one of the greenhouse gases and its concentrations have increased due to human actions, such as burning fuels. In fact, according to Toledo et al. (2013), by the year 2100, CCS will be responsible for 15% to 55% of greenhouse gases reduction. One of the proposed methods for CCS consists in the capture of CO_2 in installations where it can be placed for long-term storage in the earth crust. However, the pressure rise due to CO_2 injection is a major concern regarding this technology. Finding a safe and effective method that can be feasible in industrial scale at competitive costs is the challenge regarding this topic. When it comes to CO_2 capture, several solid adsorbents such as alumina, silicates, silica, silica-alumina, activated carbon, zeolites and also MOFs (Metal-Organic Frameworks) are known to be capable of adsorbing CO_2 . Aspects such as gas impurity (CO_2 mixed with other gases) (WETENHALL et al., 2014) and thermal behaviour hinders the operation of such systems and must be addressed during design process. These studies show not only adsorption systems can handle CCS but also they can be enhanced by adjusting characteristics of their geometry and composition. Optimizing such systems may bring more possibilities and capabilities for the CCS via adsorption.

Fuel storage also present a prolific area of application for adsorption. Given the low density of gas fuel, it is usual to store them in high-pressure or low-temperature vessels. In the case of natural gas storage, Compressed Natural Gas (CNG) is ordinarily stored at 200 atm, offering a capacity of 245 V/V, which means a density 245 higher than at atmospheric temperature and pressure. In turn, Liquefied Natural Gas (LNG) requires cryogenic temperatures to force gas condensation, which happens, for methane, at around 113 K and provides a storage capacity of 600 V/V (HIRATA et al., 2009). On the other hand, Adsorbed Natural Gas (ANG) tanks consist of natural gas adsorbed in a solid matrix of coal, accumulated in its pores. Due to the relatively high density of the adsorbed phase, an overall storage capacity around 164 V/V can be achieved at room temperature with pressure ranging from 35 atm to 50 atm (HIRATA et al., 2009). These characteristics place ANG vessels as a promising method to maintain gas confinement, as it works at atmospheric temperature and much lower pressure than CNG.

1.2 Adsorbed Natural Gas Tanks

The ease of storing gas by the ANG method allows the expansion of the current applications of natural gas, both for just-in-time consumption and for long-term storage.

The possibility of storing gas at lower pressure enables the adoption of wrappers made of lighter materials and with complex shapes, which would be prohibitive in high-pressure tanks due to stress concentration. The concept of box-shaped vessel for LNG storage (KAIST, 2014) can also be adopted in the ANG method, improving the efficiency in the use of space in comparison to cylindrical and spherical alternatives.

Supplying natural gas to consumption sites often present challenging logistics when the construction of a pipeline is not economically feasible. Gas supply is then guaranteed via virtual pipelines, which currently consist of trucks carrying CNG tanks to deliver natural gas to customers. ANG tanks demand less energy on gas compression, save transport costs for being lighter than CNG and reduce gas flare losses (INGEVITY, 2017).

Several companies have been designing ANG tanks for vehicular use. It is claimed that it can reduce in 50% the costs of refuelling stations and improve safety due to its controlled release of gas at low pressure (ANGP, 2017).

1.2.1 Design Approaches

The major drawback of ANG tanks is that their internal temperature variation prevents them from reaching their full capacity of gas adsorption in fast filling and emptying cycles. Since the adsorption reaction is exothermic, when a molecule of gas is adsorbed by the surface, heat is released. This behaviour is detrimental to the storage of gas by means of adsorption because the saturation of adsorbed gas decreases with the increase of temperature. Conversely, when filling an adsorbent bed, the probability of a molecule being adsorbed is increasingly lower, because of the heat generated by previous adsorption reactions. In turn, the desorption reaction is endothermic, consuming heat when molecules detach from the surface. This behaviour is also disadvantageous, since it makes the desorption of molecules harder due to the fall in temperature, hindering the gas recovery from the adsorbent.

Therefore, effective ANG tanks can not rely on materials presenting high capacity of adsorption only. It is necessary to ensure appropriate thermal management in order to allow reasonable short filling and emptying cycles. Given the poor conductivity typically presented by adsorbent materials, thermal management is essential to the feasibility of ANG tanks.

Shorter cycles can be achieved by varying the tank shape and boundary conditions. Sahoo et al. (2011) analysed different inlet flow rates, aspect ratios and convection co-

efficients. Naturally, the achieved storage density has shown to be higher for slim tanks subjected to high heat convection with the surroundings.

Cooling elements can also be added to the tank. Mota et al. (2004) relies on a cooling jacket traversed by hot exhaust gases, imposing forced convection to the tank during a desorption cycle. Subjected to exhaust gases at 80 °C, the jacketed tank has presented a final average temperature 30 °C hotter than the conventional reference tank in a 3-hour cycle, which results in an important increase of the net deliverable capacity. It is also reported that the inclusion of radially-extruded fins, arbitrary distributed throughout the adsorbed bed, has improved the deliverable capacity in 5% more. Based on such results, Mota et al. (2004) recommends future optimisation of fins distribution.

The distribution of fins across the adsorbent bed is also recommended by Vasiliev et al. (2014) on the adsorption of hydrogen on Busofit activated carbon. In this case, fins are connected to a double-pipe heat exchanger traversed by a cooling fluid at 233 K, which is built in the centre of the adsorbent bed. Similar to Mota et al. (2004), fins have allowed 25% more gas to be adsorbed, despite being arbitrarily distributed.

It is important to remark, however, that the models presented by Mota et al. (2004) and Vasiliev et al. (2014) are dependent on intense active cooling, based on cooling fluids at 80 °C and −40 °C, respectively, flowing across the whole adsorbent bed length. The gains achievable with such methods are naturally high, although the energy required to run such systems can make them less efficient per unit of gas stored. Therefore, an exergy assessment would be necessary in order to determine the feasibility of such ANG tanks.

When active cooling is inefficient or infeasible, some alternative methods based on passive thermal management are interesting. Toledo et al. (2013) studies the adsorption and desorption of CO_2 on systems containing spheres of Phase Change Materials (PCM). These materials behave as heat sinks, due to their high latent heat, and can be distributed across the adsorbent bed in order to control temperature variations.

1.2.2 Numerical Modelling

Several numerical methods have been applied to model adsorption systems. Hirata et al. (2009) adopts an hybrid numerical-analytical method based on the Generalised Integral Transform Technique (GITT) for modelling a simple one-dimensional problem considering the energy balance only, which is overly simplified for the scope of this work.

In Thacker et al. (2014) and Mota et al. (1996), the Partial Differential Equations

(PDE) are reduced to a set of Ordinary Differential Equations (ODE) by interior orthogonal collocation, in which the non-symmetry of the collocation matrix is disadvantageous (SUN et al., 1996).

The Finite Volume Method (FVM) is adopted in Santos et al. (2009), Mota et al. (2004) and Vasiliev et al. (2014) and the Finite Element Method (FEM) in Yonge (1992) and Sahoo et al. (2011). FVM and FEM are the most popular techniques for solving problems with coupled heat transfer and fluid flow, sharing the same fundamental idea of satisfying a weak form, differing on the choice of the weighting function (CHAO et al., 2002). Given the vast literature of latter methods, the FEM method is adopted in this work.

1.3 Optimisation Methods applied to Fluids and Heat Transfer Problems

Optimisation methods are suitable to the design of devices subjected to thermofluidic interaction, such as in adsorption systems. A key aspect when designing such systems is the way trial geometries are represented through the design variables. According to Hall et al. (2017), there are five main groups of parametrisation, based on (i) surface points, (ii) control points, (iii) level sets, (iv) descriptive functions or (v) volumetric representation.

Methods in the first group considers the mobility of every node on the surface mesh, such that their coordinates are the design variables of the optimisation problem (REUTHER et al., 1999). This method requires that the gradient of the objective function must be smoothed to avoid noisy surface shapes. It is widely adopted for aerodynamic optimisation, although presenting high computational cost and slow convergence rates. In the second group, control points are defined in order to reduce the problem size. Splines, Bezier curves or B-Splines are some of the possibilities for interpolating smooth surfaces based on fewer points. Free-Form Deformation (FFD) (SEDERBERG; PARRY, 1986) and Radial Basis Function (RBF) (MORRIS et al., 2008) are methods in which control points are used to deform the mesh through a relationship between the position of these points and the mesh nodes. In the third group, surface boundaries are defined by level sets of a function related to the sensitivity of each region to the objective function. The level set function is evolved according to a time step analogy, in which at every step a new geometry is defined at the chosen level (usually zero) (DIJK et al., 2013). In the fourth group, shape functions are associated with class functions, which represent basic types of bodies. In methods belonging to this group, the design variables can scale shape func-

tions, which will define the body constrained to class functions, or be used as coefficients to multiply perturbation functions (HALL et al., 2017).

In the last group, free boundaries are represented by the concept of fractional Volume of Fluid (VoF), where the fraction of material stored in grid cells defines solid and fluid regions. The Piecewise Linear Interface Calculation (PLIC) method (ANISZEWSKI et al., 2014) uses the fluxes of the fraction function to determine a well-defined solid-fluid interface. Other methods ignore the notion of surfaces by only controlling the extent to which a given point is solid, as is the case of the density approach in topology optimisation. Volume-based methods present the advantage of handling any topology change, allowing the creation and disappearance of surfaces across the domain.

Topology optimisation seeks optimised distributions of different materials inside a fixed design domain in order to maximise or minimise an objective function. Topology optimisation is usually implemented in association with FEM, considering a design variable in each finite element or node in the domain. The design variables are generally called pseudo-densities and range from 0 to 1, in order to represent the presence of material and absence of material (void) or two different materials. It is considered one of the most generic methods of optimisation as it is able to represent any material contour inside the design domain.

In structural problems, 0 and 1 often denotes the absence and presence of material, respectively. In thermal problems, a common optimisation problem is to distribute materials with different conductivities along the design domain, being one material represented by 0 and the other by 1. The optimisation of fluidic problems is addressed based on the governing equation of porous media flow to represent solid regions. Solid materials are represented by pseudo-densities equal to 0 and are considered to be a porous medium with a very low permeability, while fluid regions are denoted by 1 and governed by Navier-Stokes equations.

The implementation of topology optimisation methods to heat transfer problems was introduced by Xie et al. (1999), which adopt an Evolutionary Structural Optimisation (ESO) approach by removing under-utilised elements from the domain mesh. In the ESO method, elements are removed according to a rejection criterion until reaching a steady state. Such criterion is then iteratively updated following an evolution rate, culminating in the final topology. In Turteltaub (2001), the optimisation of transient heat conduction problems is studied by varying the material properties inside a fixed design domain by following the SIMP scheme and including a regularisation term on the objective function.

However, the results presented did not cover the solid-void optimisation case, which is later addressed by Sigmund (2001) by designing thermal and electro-thermal micro-actuators subjected to top heat convection only.

In order to take the side convection into account in the design of electro-thermal actuators, the work of Yoon & Kim (2005) is based on the Element Connectivity Parametrisation (ECP) method, where the design variables are the links between elements instead of their densities. Bruns (2007) gives special attention to convection-dominated problems, by discussing their susceptibility to numerical instabilities inherent to the density dependent interpolation schemes commonly used in topology optimisation. Such instabilities are dealt with by ensuring that the convection term contributions are lumped matrices.

Borrvall & Petersson (2003) applied topology optimisation to the design of fluid systems seeking to minimise the power dissipation in fluid flow channels. A well-posed optimisation problem is introduced, presenting solution convergence to a binary function space as the mesh is refined. It is based on a material model with a different penalisation scheme, which will be detailed further in Section 3.4.1. Gersborg-Hansen et al. (2005) initially extended this approach to incompressible laminar viscous flow at moderate Reynolds numbers, thus solving a non-linear problem. Then, Guest & Prevost (2006) proposed a new generalized method, by combining and scaling the Stokes and Darcy equations.

Yoon (2010) coupled heat transfer to the fluid problem, optimising heat dissipating structures with forced convection. This multiphysics optimisation is also approached by Koga et al. (2013) and Matsumori et al. (2013) with similar purposes. Kontoleon et al. (2012) widened the set of problems tested, including three-dimensional manifolds. Yoon (2012) optimised Electro-Thermo-Mechanical (ETM) actuators by considering their interaction with the surrounding fluid.

Despite the theory of topology optimisation applied to fluid mechanics being based on the variation of porosity, where media presenting very low porosity emulate impermeable solid regions, few works applied the method to the optimisation of actual porous media. The concept of impermeability adopted in Guest & Prevost (2006) and in Borrvall & Petersson (2003) considers that a material presenting permeability $K = 1.00 \times 10^{-8} \text{ m}^2$ behaves like a wall, while in typical ANG tanks the fluid flow permeates an activated carbon presenting $K = 3.70 \times 10^{-10} \text{ m}^2$ (SAHOO et al., 2011).

On structural design, Andreasen & Sigmund (2013) presents an implementation of topology optimisation for saturated poroelastic media, with respect to the macroscopic material distribution based on the homogenisation theory. The method is applied to the

design of shock absorbers, where the energy dissipation is due to the flow resistance.

The use of topology optimisation for the design of adsorbed systems is not yet reported in literature. Figure 1.3 presents the topology optimisation procedure for designing ANG tanks. A fixed initial domain with given boundary conditions is discretised in finite elements. Pseudo-porosities are associated with each element and their values are optimised aiming to maximise or minimise a given objective function, resulting in a final topology. A post-processing step is then necessary, in order to recover the discrete nature of the problem and to smoothen the contours of the material distribution. Finally, the post-processed topology can be verified numerically through other software before proceeding to manufacturing.

Figure 1.3: Topology optimisation procedure.

1.4 Motivation

Adsorption systems play an important role in a wide range of applications, with a vast range of commercial products reliant on the process. Aiming to improve the performance of adsorption devices, past research has been limited to the improvement of adsorbent characteristics, such as the pores geometry and distribution (BILOE et al., 2002). The

design of adsorption systems by stating and solving an actual optimisation problem has not been reported in literature. Topology optimisation is suitable to address the design of such systems and expand their current applications.

1.5 Objectives

This work proposes a method for the design of adsorption systems based on topology optimisation by seeking the following objectives:

- To formulate a comprehensive numerical model of gas adsorption on porous media;
- To formulate topology optimisation problems regarding the maximisation of the mass of gas adsorbed in Adsorbed Natural Gas (ANG) tanks;
- To obtain optimised ANG tank layouts able to adsorb gas more efficiently.

1.6 Scientific Contributions

This research addresses some previously unexplored topics, presenting the following scientific contributions:

- Statement of weak and discrete formulations of the adsorption problem and its adjoint system;
- Development of an optimisation method for adsorption systems;
- Definition of a novel material model based on offset hyperbolic tangents;
- Presentation of optimised Adsorbed Natural Gas (ANG) tanks based on the distribution of cooling materials;

1.7 Thesis Outline

This document is organized as follows. In Chapter 2, the governing equations of the adsorption phenomenon are presented. In Chapter 3, topology optimisation problems regarding ANG tanks are defined. Chapter 4 details the numerical implementation of the proposed model. In Chapter 5, layouts of ANG tanks obtained by topology optimisation are presented. Chapter 6 reports overall conclusions on the optimisation of adsorption systems.

2 Modelling of Adsorption Systems

The adsorption problem is governed by typical fluidic and thermal equations applied to porous media coupled with equations defining the interactions between adsorbent and adsorbate. This Chapter presents the general assumptions and the governing equations considered when modelling the adsorption problem. The weak formulation of the governing equations is also derived.

2.1 Modelling Flow in Porous Media

The modelling of the actual flow in porous media is very challenging, given the complex network of channels presented by such materials. By regarding the porous media as a continuum, it is possible to approximate the macroscopic fluid motion through its channels by taking an average of the microscopic flow within a Representative Elementary Volume (REV) (WHITAKER, 1986). Figure 2.1 shows on the right the continuum interpretation of the porous medium presented on the left. The averaged velocity of the flow inside each REV is represented by the arrows.

The Darcy's law is an approximation which describes the fluid flow in porous media that is valid for a limited range of low velocities. Deviations presented by experimental results motivated the consideration of microscopic inertial effects, as in the Forchheimer equation (MULJADI et al., 2016), in which

$$-\nabla p = \frac{\mu_f}{K} \mathbf{v}_g + \beta \rho_g |\mathbf{u}_g|^2 \mathbf{n}, \quad (2.1)$$

where ρ_g denotes the fluid density, β is the non-Darcy coefficient and $\mathbf{n}$ is a unit vector in the direction of ∇P .

Figure 2.1: Continuum modelling of porous media based on Representative Elementary Volume (REV).

In order to determine the cases when non-Darcy effects are meaningful, the Reynolds number was the first criterion to be used. It is based on the assumption that non-Darcy effects in porous media are similar to turbulence in conduits, in which Reynolds number is given by (ZENG; GRIGG, 2006)

$$Re = \frac{\rho_g \phi_p \mathbf{V}_g}{\mu}, \quad (2.2)$$

where the conduit diameter is considered to be in the same magnitude of the average particle diameter ϕ_p in the porous medium.

Previous research present a wide range for the transition region between Darcy and non-Darcy porous media flow. Different authors report discrepant transition regions, with Reynolds number ranging from 0.1 to 1000 (MULJADI et al., 2016). Due to the lack of a precise delimitation of this region, criteria based on Reynolds number are not widely adopted (ZENG; GRIGG, 2006).

A second criterion is based on the Forchheimer number, which is given by (ZENG; GRIGG, 2006)

$$Fo = \frac{\rho_g K \beta \mathbf{V}_g}{\mu}, \quad (2.3)$$

where β denotes the non-Darcy coefficient.

While the measurement of the particle diameter ϕ_p in the Reynolds number is not trivial, the permeability K and the coefficient β involved in the Forchheimer number are easily obtained experimentally by measuring the pressure drop in a specimen for a range of different flow rates (ZENG; GRIGG, 2006). It has been found that a Forchheimer number equal to 0.11 is a good reference for the acceptance of Darcy's law approximation in porous media. The meaning of a flow presenting $Fo = 0.11$ is that non-Darcy effects represent 10% of the forces involved.

In modelling ANG tanks, Mota et al. (2004) and Sahoo et al. (2011) consider all inertial and viscous effects negligible and adopt pure Darcy's law. Mota et al. (1996), Rahman et al. (2011) and Vasiliev et al. (2014) consider additional terms for accounting the inertial effects by following Ergun or Forchheimer equations. In general, models neglecting non-Darcy effects have presented good agreement with experimental validation, being preferred in order to reduce computational cost.

2.2 Modelling Adsorption Equilibrium and Kinetics

Adsorption is modelled as the retention of molecules from a solute with concentration C_0 (relative to the fluid phase volume) on solid particles at a concentration q (relative to the solid phase mass). Such retention reduces the number of molecules on the mobile phase, resulting in a new solute concentration C . Given a fixed temperature, a relationship $q = f(C)$ is observed, which is named the sorption isotherm. This process is expressed by (LIMOUSIN et al., 2007)

$$q = \frac{V}{M} (C_0 - C) + q_0, \quad (2.4)$$

where V is fluid phase volume, M is the solid phase mass and q_0 is the initial concentration of adsorbed molecules on solid particles.

The desorption process is the release of solute molecules from the solid particles, increasing the concentration of the liquid phase. It can be noted that the same equation is valid for modelling both adsorption and desorption processes, given that for adsorption $C_0 > C$ and $q_0 < q$ while for desorption $C_0 < C$ and $q_0 > q$. Figure 2.2 illustrates these processes.

Figure 2.2: Adsorption and desorption processes.

Adsorption process requires an energy of activation, E_a , and is exothermic, presenting an isosteric heat of adsorption ΔH . In turn, the desorption reaction is endothermic and requires an energy of activation, E_d . Figure 2.3 the variation of energy in an exothermic reaction along the reaction pathway.

Figure 2.3: Adsorption energetics (MCBRIDE, 1994).

Giles (1974) divides the isotherms into four classes according to their initial slope termed as S, L (Langmuir), H (high affinity), and C (constant partition), which are depicted in Figure 2.4. C-isotherm considers a simple linear function for expressing $q = f(C)$, which means that the sorbate has infinite adsorption sites. L-isotherm assumes steady decrease on the concentrations ratio, presenting a well defined plateau in some cases. H-isotherm is suitable when the affinity between adsorbate and adsorbent is very high and the available sites are occupied promptly. S-isotherm presents an inflection point which is the result of the opposition of two mechanisms: the low rate observed for low concentrations reproduces the difficulty that some adsorbates have to attach to the adsorbent and after the adsorption of the first molecules the adsorption of others is favoured through a phenomenon named cooperative adsorption.

L-isotherm and H-isotherm are also known as concave isotherms and several different models are based on them, such as Freundlich, Langmuir, Dubinin, Polanyi, Kisarlov and Vacancy Solution Model (WOOD, 2002).

According to the Freundlich models, a plateau is never reached, even for very high concentrations. It is given by (LIMOUSIN et al., 2007)

$$q = FC^n, \quad (2.5)$$

where F and n are constants obtained experimentally, being $n < 1$.

Langmuir models are based on the assumption that the adsorbate presents a limited capacity of adsorption q_{max} . It is derived from the kinetics of adsorption and desorption.

Figure 2.4: Classes of isotherms (GILES, 1974).

Given that the rate of adsorption is proportional to the vacant sites for adsorption, it can be expressed as (PATIHA et al., 2016)

$$\frac{\partial q}{\partial t} = k_a(q_{max} - q)C, \quad (2.6)$$

where k_a is the kinetic coefficient of adsorption obtained experimentally for each adsorbent-adsorbate pair.

The desorption rate is proportional to the occupied sites (PATIHA et al., 2016), which is expressed as

$$\frac{\partial q}{\partial t} = k_d q, \quad (2.7)$$

where k_d is the kinetic coefficient of desorption.

At equilibrium, the rates of adsorption and desorption are equal and q is given by (PATIHA et al., 2016)

$$q = \frac{q_{max}C}{\frac{k_d}{k_a} + C}. \quad (2.8)$$

The Dubinin models are the most versatile methods of expressing adsorption equilibrium, being expressed by means of adsorbate and adsorbent properties and temperature (WOOD, 2002). It relies on the Polanyi's adsorption potential theory, which defines a potential equal to the change in free energy from the bulk liquid to the adsorbed state, taking the vapour saturation pressure p_{sat} as reference (WOOD, 2001). It is expressed as

$$A = RT \left(\frac{P_{sat}}{P} \right). \quad (2.9)$$

The Dubinin isotherm is then defined in terms of volume of micro-pores W occupied by adsorbate (WOOD, 2001), given by

$$W = W_0 \exp \left(- \left(\frac{A}{\beta E_0} \right)^n \right), \quad (2.10)$$

where W_0 is the total volume of micro-pores and the exponent n can assume different values depending on the specific model, being equal to 2 for Dubinin-Radushkevich isotherms. E_0 and β denote, respectively, the characteristic adsorption energy for the reference vapour and the affinity of the adsorbate to the adsorbent, usually taking benzene as reference ($\beta_{benzene} = 1$).

The kinetics of adsorption consists of a sequence of three steps: (i) mass transfer of the adsorbate from the solution to the external surface of the adsorbent, (ii) diffusion through the adsorbent and (iii) adsorption itself (LARGITTE; PASQUIER, 2016). When modelling adsorption kinetics, it is usual to assume that either the diffusion or the actual adsorption is the rate limiting and dictates the rate of the process as a whole.

Two main models are reported for adsorption kinetics taking the intra-particle diffusion as the limiting step: Crank and Weber-Morris. Crank model considers homogeneous diffusion across an adsorbate consisting of spheres, which is defined as (LARGITTE; PASQUIER, 2016)

$$\frac{\partial q}{\partial t} = \frac{D_S}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial q}{\partial r} \right), \quad (2.11)$$

where D_S is the surface diffusivity and r denotes the radial distance.

Weber-Morris model is based on the empirical observation that the uptake varies nearly proportionally with $\sqrt{t}$ (ALKAN et al., 2007). It is expressed by (QIU et al., 2009)

$$q = k_{intra} \sqrt{t}, \quad (2.12)$$

where k_{intra} is the intra-particle diffusion rate constant.

When the adsorption itself is the rate limiting step, Elovich or Lagergren equations are often used to model the phenomenon. Elovich models are expressed by (LARGITTE; PASQUIER, 2016)

$$\frac{\partial q}{\partial t} = a \exp \left(- b q \right), \quad (2.13)$$

where a is the initial rate of adsorption and b is a constant obtained experimentally related to the variation of the energy of adsorption.

Lagergren models present an asymptotic approach to the equilibrium of the adsorbed

phase q_{eq} through a pseudo first order equation given by (LARGITTE; PASQUIER, 2016)

$$\frac{\partial q}{\partial t} = k_a(q_{eq} - q), \quad (2.14)$$

where k_a is the adsorption rate constant.

Some other models are derived from the original Lagergren model. One variation consists of the extension of the pseudo first-order form to the pseudo n -order laws given by (LARGITTE; PASQUIER, 2016)

$$\frac{\partial q}{\partial t} = k_a(q_{eq} - q)^n, \quad (2.15)$$

where n defines the pseudo order of the equation.

Another Lagergren derived model, know as Langmuir, includes the consideration of the reversibility of the adsorption reaction by adding the desorption kinetics as (LARGITTE; PASQUIER, 2016)

$$\frac{\partial q}{\partial t} = k_a(q_{eq} - q) - k_d q, \quad (2.16)$$

where k_d is the desorption rate constant.

In ANG tanks, the equation of Dubinin-Astakhov (DA), or its variation Dubinin-Radushevich (DR), is adopted by most authors for predict the amount of gas adsorbed at the equilibrium and the kinetics of adsorption is approximated by the Lagergren model (RAHMAN et al., 2011; SAHOO et al., 2011; VASILIEV et al., 2014). Alternatively, Mota et al. (1996) adopts a Langmuir-type prediction for the equilibrium and suggests that the kinetics of adsorption can be neglected for the typical intraparticle diffusional time constants of adsorbent beds. This assumption is generally valid, but also depends on other factors, such as the energy of activation, and it will be studied further in this work.

2.3 Governing Equations

A typical sorption domain Ω is illustrated in Figure 2.5, where Γ_W and Γ_L denote sub-regions of $\partial\Omega$ where boundary conditions of wall and inlet/outlet are imposed, respectively.

In this work, the following assumptions are made:

Ideal gases: in the systems considered, gases are considered to present ideal thermo-

Figure 2.5: Adsorption domain.

dynamic behaviour (SAHOO et al., 2011), therefore, their densities are described by

$$\rho_g = \frac{M_g P}{R_g T}, \quad (2.17)$$

where M_g is the molecular gas mass, R_g is the universal gas constant, P is the gas pressure and T is the gas temperature.

Darcy's Porous Media: non-Darcy effects are neglected in the fluid flow, according to Eq. (2.1) with $\beta = 0$.

Local thermal equilibrium: the sorbent bed is locally in thermal equilibrium with the gas (MOTA et al., 2004). All intra-particle and film resistances in heat and mass transfer are neglected.

Negligible viscous forces: the viscous forces are neglected due to the low gas viscosity and the relatively large bed-particle diameter ratio (MOTA et al., 2004).

Constant specific heat capacity: the specific heat capacity is considered to be constant within the typical range of temperatures observed in sorption systems. Its variation is neglected since it usually varies around only 8% (MOTA et al., 2004) in a range of 100 K.

Constant adsorption enthalpy: this work considers an approximation in which ΔH assumes a constant mean value within the range of pressures and temperatures studied (SAHOO et al., 2011).

Lagergren adsorption model: For the studied cases, it is considered that the film diffusion is dominant and the rate of sorption is governed by Lagergren model (VASILIEV et al., 2014).

2.3.1 Natural Material Models

Effective properties of porous media are determined by material models based on macro-porosity (ε_M) and micro-porosity (ε_m). Given these two classes of porosity, the total porosity (ε_t) is defined as

$$\varepsilon_t = \varepsilon_M + (1 - \varepsilon_M)\varepsilon_m. \quad (2.18)$$

Density: the density of the system is given by the sum of gaseous and solid phase weighted by the total porosity, ε_t , with the addition of the density of the adsorbed phase, based on its concentration, q , as

$$\rho_f(\varepsilon_t) = \varepsilon_t \rho_g + (1 - \varepsilon_t) \rho_s + (1 - \varepsilon_t) \rho_s q. \quad (2.19)$$

Permeability: dependent on the macro-porosity, following the Kozeny-Carman's model for spherical particles (CARMAN, 1937), given by

$$K_s(\varepsilon_M) = \frac{\phi_s^2 \varepsilon_M^3}{72 \tau_s (1 - \varepsilon_M)^2}, \quad (2.20)$$

where ϕ_s is the effective characteristic particle diameter and τ_s denotes the pores tortuosity.

Thermal Conductivity: it can be given by both Maxwell-Eucken's or Russel's relations (SMITH et al., 2013). The former considers the effect of large spherical pores with thin walls and the latter the effect of a cubic pore inclusion in the material matrix by considering a parallel/series resistor. Here, the conductivity of the thin film of gas adsorbed, k_q , is neglected and the Maxwell-Eucken relation is adopted to interpolate the gaseous and solid conductivities (SMITH et al., 2013), given by

$$k_f(\varepsilon_t) = k_s \frac{k_g + 2k_s + 2\varepsilon_t(k_g - k_s)}{k_g + 2k_s - \varepsilon_t(k_g - k_s)}, \quad (2.21)$$

where k_s and k_g are the thermal conductivities for the solid and gas, respectively.

2.3.2 Adsorption and Desorption Kinetics

The concentration q represents the mass of adsorbed phase per mass of adsorbent. Therefore, the density of adsorbed phase in reference to the volume of the adsorbent bed, Q , is given by

$$Q = (1 - \varepsilon_t) \rho_s q. \quad (2.22)$$

The specific volume of micro-pores, w_s , represents the volume of micro-pores per mass of adsorbent. The ratio of micro-pores volume per adsorbent bed volume, W_s , is then given by

$$W_s = (1 - \varepsilon_t)\rho_s w_s. \quad (2.23)$$

From the equilibrium concentration of adsorbed gas, q_{eq} , (SAHOO et al., 2011), the equilibrium density of adsorbed gas is given by

$$Q_{eq} = \rho_{adg} W_s \exp\left(-\left(\frac{A}{\beta E_0}\right)^{n_f}\right), \quad (2.24)$$

where β is the affinity coefficient of the adsorbent-adsorbate pair, E_0 is the characteristic energy of adsorption and n_s stands for the effective micro-pores dispersion.

The local adsorbed gas density, ρ_{adg} , is given by (SAHOO et al., 2011)

$$\rho_{adg} = \frac{\rho_{boil}}{\exp(\alpha_e(T - T_{boil}))}, \quad (2.25)$$

where ρ_{boil} is the gas density at boiling point temperature (T_{boil}) and α_e is the mean value of the thermal expansion of liquefied gases.

Polanyi's adsorption potential, A , is given by

$$A = R_g T \ln\left(\frac{P_{sat}}{P}\right), \quad (2.26)$$

which saturated pressure P_{sat} is given by

$$P_{sat} = P_{cr} \left(\frac{T}{T_{cr}}\right)^2, \quad (2.27)$$

where P_{cr} and T_{cr} are, respectively, the critical pressure and temperature of the gas.

The rate of adsorption decreases as more gas is adsorbed, following the Linear Driving Force (LDF) model given by (MOTA et al., 1996)

$$\begin{aligned} \frac{\partial Q}{\partial t} &= G(Q_{eq} - Q) \quad \text{in } \Omega \times [0, t_f] \\ Q &= Q_{ini} \quad \text{in } \Omega \text{ at } t = 0, \end{aligned} \quad (2.28)$$

where the coefficient G , which dictates the adsorption and desorption kinetics, is given by (VASILIEV et al., 2011)

$$G = D \exp\left(\frac{-E_{[a,d]}}{R_g T}\right), \quad (2.29)$$

where the activation energy of adsorption (E_a) is considered when $Q \leq Q_{eq}$ and the activation energy of desorption (E_d) otherwise. D is the intra-particle diffusional time

constant, given by (SAHOO et al., 2011)

$$D = 4 \frac{D_0}{\phi_s^2}, \quad (2.30)$$

where ϕ_s is the characteristic particle diameter and D_0 is the gas diffusivity.

2.3.3 Continuity

In adsorption systems, the coupled continuity equation of gaseous, solid and adsorbed phases is expressed by

$$\frac{\partial}{\partial t} \left(\varepsilon_t \rho_g + (1 - \varepsilon_t) \rho_s + Q \right) + \nabla \cdot \left(\rho_g \mathbf{v}_g \right) = 0 \quad \text{in } \Omega \times [0, t_f], \quad (2.31)$$

where ρ_s is the bulk adsorbent density, which is constant.

The continuity equation considering ideal gases and Darcy's laws becomes (SAHOO et al., 2011)

$$\frac{\varepsilon_t M_g}{R_g} \frac{\partial}{\partial t} \left(\frac{P}{T} \right) + \frac{\partial Q}{\partial t} - \frac{M_g}{R_g \mu_g} \nabla \cdot \left(K_s \frac{P}{T} \nabla P \right) = 0 \quad \text{in } \Omega \times [0, t_f], \quad (2.32)$$

where the solid density ρ_s is considered constant.

By expanding the transient derivative term, continuity is given by

$$\begin{aligned} \frac{\varepsilon_t M_g}{R_g} \left(\frac{1}{T} \frac{\partial P}{\partial t} - \frac{P}{T^2} \frac{\partial T}{\partial t} \right) + \frac{\partial Q}{\partial t} - \frac{M_g}{R_g \mu_g} \nabla \cdot \left(K_s \frac{P}{T} \nabla P \right) &= 0 \quad \text{in } \Omega \times [0, t_f], \\ P &= P_{ini} \quad \text{in } \Omega \text{ at } t = 0, \\ T &= T_{ini} \quad \text{in } \Omega \text{ at } t = 0, \\ Q &= Q_{ini} \quad \text{in } \Omega \text{ at } t = 0. \end{aligned} \quad (2.33)$$

For determining a fixed mass inflow or outflow, a Robin boundary condition is applied on Γ_L as

$$-\frac{M_g K_s}{R_g \mu_g} \frac{P}{T} \frac{\partial P}{\partial \mathbf{n}} = \rho_g \mathbf{v}_g \cdot \mathbf{n} = \dot{m}_{let} \quad \text{on } \Gamma_L \times [0, t_f], \quad (2.34)$$

where the mass flow is denoted by $\dot{m}_{let}$

Despite the imposition of a fixed mass inlet making sense for adsorption, the depletion of a fixed amount of gas during desorption cycles is not possible as the tank is emptied. Therefore, pressure inlet can be set, which represents the connection of the tank to a infinity reservoir at fixed pressure for adsorption or the opening of the tank outlet to the atmosphere for desorption. In order to model the gradual pressure transition inside the tank, a possible approach is to smoothly vary the pressure on Γ_L according to a sinusoidal

profile given by

$$P_{\Gamma_L}(t) = \begin{cases} P_{ini} + \sin^2\left(\frac{\pi}{2}\frac{t}{\sigma t_f}\right)(P_{let} - P_{ini}) & \text{on } \Gamma_L \times [0, \sigma t_f] \\ P_{let} & \text{on } \Gamma_L \times [\sigma t_f, t_f], \end{cases} \quad (2.35)$$

where P_{ini} and P_{let} denote initial and filling/emptying pressures, t_f is the final time and $0 < \sigma \leq 1.0$ is a smoothness factor. Figure 2.6 illustrates P_{Γ_L} curves for adsorption and desorption cycles.

Figure 2.6: Inlet pressure (P_{Γ_L}) during (a) adsorption and (b) desorption cycles.

2.3.4 Energy Balance

The energy balance of the gaseous phase is given in terms of internal energy, u_g , by (BIRD et al., 2007)

$$\frac{\partial \rho_g u_g}{\partial t} + \nabla \cdot (\rho_g u_g \mathbf{v}_g) - \nabla \cdot (k_g \nabla T) + P \nabla \cdot \mathbf{v}_g + \boldsymbol{\tau}_g : \nabla \mathbf{v}_g = 0, \quad (2.36)$$

where $\boldsymbol{\tau}_g$ is the viscous stress tensor.

Such balance is rewritten in terms of Cp_g and T as (BIRD et al., 2007)

$$\frac{\partial \rho_g Cp_g T}{\partial t} + \nabla \cdot (\rho_g Cp_g T \mathbf{v}_g) - \nabla \cdot (k_g \nabla T) + \boldsymbol{\tau}_g : \nabla \mathbf{v}_g - \frac{\partial \ln V}{\partial \ln T} \bigg|_P \frac{DP}{Dt} - \rho_g T \frac{DCp_g}{Dt} = 0, \quad (2.37)$$

where D denotes the Lagrangian derivative, Cp_g is considered constant and $\frac{\partial \ln V}{\partial \ln T} = 1$ for ideal gases.

Following the assumption that viscous forces are negligible, the energy balance reduces to

$$\frac{\partial \rho_g Cp_g T}{\partial t} + \nabla \cdot (\rho_g Cp_g T \mathbf{v}_g) - \nabla \cdot (k_g \nabla T) - \frac{\partial P}{\partial t} - \mathbf{v}_g \cdot \nabla P = 0, \quad (2.38)$$

which is rearranged as

$$\begin{aligned} \rho_g C p_g \frac{\partial T}{\partial t} + C p_g T \left\{ \frac{\partial \rho_g}{\partial t} + \nabla \cdot (\rho_g \mathbf{v}_g) \right\}_c + \rho_g C p_g \mathbf{v}_g \cdot \nabla T \\ - \nabla \cdot (k_g \nabla T) - \frac{\partial P}{\partial t} - \mathbf{v}_g \cdot \nabla P = 0, \end{aligned} \quad (2.39)$$

where the continuity equation is observed in $\mathcal{C}$, making these terms to vanish.

By substituting the momentum equation based on the Darcy's law, the balance becomes

$$\begin{aligned} \rho_g C p_g \frac{\partial T}{\partial t} - \rho_g C p_g \frac{K_s}{\mu_g} \nabla P \cdot \nabla T \\ - \nabla \cdot (k_g \nabla T) - \frac{\partial P}{\partial t} + \left\{ \frac{K_s}{\mu_g} \nabla P \cdot \nabla P \right\}_{\approx 0} = 0, \end{aligned} \quad (2.40)$$

where the last term is neglected, given the very small pressure gradients observed in the range of permeabilities of interest in this work.

Analogously, the energy balance of the solid phase is given by

$$\rho_s C p_s \frac{\partial T}{\partial t} - \nabla \cdot (k_s \nabla T) = 0. \quad (2.41)$$

The energy balance associated to the adsorbed phase includes a source term due to the exothermic adsorption reaction, being expressed as

$$C p_q Q \frac{\partial T}{\partial t} - \nabla \cdot (k_q \nabla T) = |\Delta H| \frac{\partial Q}{\partial t}, \quad (2.42)$$

where ΔH is the isosteric heat of adsorption.

The energy balance for coupled gaseous, solid and adsorbed phases assuming local thermal equilibrium between phases and ideal gas is then given by (MOTA et al., 2004)

$$\begin{aligned} \varepsilon_t \left(\frac{C p_g M_g}{R_g} \frac{P}{T} \frac{\partial T}{\partial t} - \frac{\partial P}{\partial t} \right) + (1 - \varepsilon_t) \left(\rho_s C p_s \frac{\partial T}{\partial t} \right) + C p_g Q \frac{\partial T}{\partial t} \\ - \frac{C p_g M_g}{R_g \mu_g} K_s \frac{P}{T} \nabla P \cdot \nabla T - \nabla \cdot (k_f \nabla T) = |\Delta H| \frac{\partial Q}{\partial t} \quad \text{in } \Omega \times [0, t_f], \\ P = P_{ini} \quad \text{in } \Omega \text{ at } t = 0, \\ T = T_{ini} \quad \text{in } \Omega \text{ at } t = 0, \\ Q = Q_{ini} \quad \text{in } \Omega \text{ at } t = 0, \end{aligned} \quad (2.43)$$

where the effective thermal conductivity, k_f , is given by Eq. (2.21).

Due to the local thermal equilibrium assumption, the temperature on Γ_L can be considered equal to the inlet gas temperature, which is imposed by a Dirichlet boundary

condition defined as

$$T = T_{let} \quad \text{on } \Gamma_L \times [0, t_f]. \quad (2.44)$$

Alternatively, an inlet heat flux can be considered on Γ_L , which is expressed by a Robin boundary condition (SAHOO et al., 2011) given by

$$-k_f \frac{\partial T}{\partial \mathbf{n}} = -\rho_g C p_g \mathbf{v}_g \cdot \mathbf{n} (T - T_{let}) = \frac{M_g C p_g K_s P}{R_g \mu_g} \frac{P}{T} \nabla P \cdot \mathbf{n} (T - T_{let}) \quad \text{on } \Gamma_L \times [0, t_f]. \quad (2.45)$$

Assuming that heat convection takes place on the walls, a Robin boundary condition is also defined on Γ_W . Such condition is imposed by

$$-k_f \frac{\partial T}{\partial \mathbf{n}} = h_W (T - T_\infty) \quad \text{on } \Gamma_W \times [0, t_f]. \quad (2.46)$$

On the region $\Gamma \setminus (\Gamma_W \cup \Gamma_L)$, since no boundary terms are explicitly defined, the heat flux is null, which represents adiabatic condition.

2.4 Weak Formulation of Adsorption Systems

Weak formulations are used to obtain solutions for a set of PDEs by satisfying the integral of the solution on the domain for a family of test functions. Consider the domain $\Omega \subset \mathbb{R}^n$, illustrated in Figure 2.5 for $n = 2$. The weak formulation of $\mathbb{L}(w)$ is given by its actuation on the test function v as (KARNIADAKIS et al., 2005)

$$\left\langle \mathbb{L}(w), v \right\rangle = \int_{\Omega} \mathbb{L}(w) v \, d\mathbf{x} \quad \forall v \in H^1(\Omega), \quad (2.47)$$

where H^1 denotes the Hilbert space, whose functions have their first derivatives belonging to the Lebesgue space L^2 .

For axisymmetric domains, it is multiplied by $2\pi r$ and given by

$$\left\langle \mathbb{L}(w), v \right\rangle = 2\pi \int_{\Omega} r \mathbb{L}(w) v \, d\mathbf{x} \quad \forall v \in H^1(\Omega), \quad (2.48)$$

where r is the radial coordinate.

On $\Gamma_N \subset \partial\Omega$, where Robin boundary condition applies, the weak term is given by (KARNIADAKIS et al., 2005)

$$\left\langle \mathbb{L}(w), v \right\rangle_{\Gamma_N} = \oint_{\Gamma_N} \mathbb{L}(w) \cdot \mathbf{n} v \, ds \quad \forall v \in H^1(\Omega), \quad (2.49)$$

where $\mathbf{n}$ denotes an outward unit vector normal to Ω .

Analogously, for axisymmetric domains, it is given by

$$\left\langle \mathbb{L}(w), v \right\rangle_{\Gamma_N} = 2\pi \oint_{\Gamma_N} r \mathbb{L}(w) \cdot \mathbf{n} v ds \quad \forall v \in H^1(\Omega). \quad (2.50)$$

Considering the Dirichlet boundary condition given by

$$w = w_D \text{ on } \Gamma_D, \quad (2.51)$$

the unknown w belongs to the space $\mathcal{W}$ defined as

$$\mathcal{W} = \{w \in H^1(\Omega) : w = w_D \text{ on } \Gamma_D\}, \quad (2.52)$$

in which $w_D \in H^{1/2}(\Omega)$ (SA et al., 2016).

Thus, from Eqs. (2.33), (2.43) and (2.28) and integrating by parts the terms involving a divergent operator, the weak forms for continuity, energy balance and adsorption kinetics are given by

$$\begin{aligned} \mathbb{M}(P, T, Q) = & \left\langle \frac{\varepsilon_t M_g}{R_g} \frac{1}{T} \frac{\partial P}{\partial t}, v_M \right\rangle - \left\langle \frac{\varepsilon_t M_g}{R_g} \frac{P}{T^2} \frac{\partial T}{\partial t}, v_M \right\rangle + \left\langle \frac{\partial Q}{\partial t}, v_M \right\rangle \\ & + \left\langle \frac{M_g K_s}{R_g \mu_g} \frac{P}{T} \nabla P, \nabla v_M \right\rangle - \left\langle \frac{M_g K_s}{R_g \mu_g} \frac{P}{T} \nabla P, v_M \right\rangle_{\Gamma_N} = 0, \end{aligned} \quad (2.53)$$

$\forall v_M \in H^1(\Omega),$

$$\begin{aligned} \mathbb{E}(P, T, Q) = & \left\langle \frac{\varepsilon_t C p_g M_g}{R_g} \frac{P}{T} \frac{\partial T}{\partial t}, v_E \right\rangle + \left\langle C p_g Q \frac{\partial T}{\partial t}, v_E \right\rangle \\ & + \left\langle (1 - \varepsilon_t) \rho_s C p_s \frac{\partial T}{\partial t}, v_E \right\rangle - \left\langle \varepsilon_t \frac{\partial P}{\partial t}, v_E \right\rangle \\ & + \left\langle \frac{C p_g M_g K_s}{R_g \mu_g} \frac{P}{T} \nabla P \cdot \nabla T, \nabla v_E \right\rangle + \left\langle k_f \nabla T, \nabla v_E \right\rangle \\ & - \left\langle |\Delta H| \frac{\partial Q}{\partial t}, v_E \right\rangle \\ & - \left\langle \frac{C p_g M_g K_s}{R_g \mu_g} \frac{P}{T} \nabla P \cdot \nabla T, v_E \right\rangle_{\Gamma_N} - \left\langle k_f \nabla T, v_E \right\rangle_{\Gamma_N} = 0, \end{aligned} \quad (2.54)$$

$\forall v_E \in H^1(\Omega),$

$$\mathbb{D}(P, T, Q) = \left\langle \frac{\partial Q}{\partial t}, v_D \right\rangle + \left\langle GQ, v_D \right\rangle - \left\langle GQ_{eq}, v_D \right\rangle = 0, \forall v_D \in H^1(\Omega). \quad (2.55)$$

Considering convective heat transfer on the walls,

$$\left\langle k_f \nabla T, v_E \right\rangle_{\Gamma_N} = - \left\langle h_W (T - T_\infty), v_E \right\rangle_{\Gamma_W}. \quad (2.56)$$

Considering mass flow imposition,

$$\left\langle \frac{M_g K_s}{R_g \mu_g} \frac{P}{T} \nabla P, v_M \right\rangle_{\Gamma_N} = \left\langle \dot{m}_{let}, v_M \right\rangle_{\Gamma_L}. \quad (2.57)$$

In the case that no Dirichlet condition is imposed on temperature field, another term remains from the integration by parts on the energy balance, accounting for the heat flux observed on Γ_L due to the inlet/outlet of gases, given by

$$\left\langle k_f \nabla T, v_E \right\rangle_{\Gamma_N} = \left\langle C p_g T \dot{m}_{let}, v_E \right\rangle_{\Gamma_L}. \quad (2.58)$$

Given that v_M , v_E and v_D are arbitrary test functions, Eqs. (2.53)-(2.55) are coupled and the problem reduces to

$$\mathbb{M}(P, T, Q) + \mathbb{E}(P, T, Q) + \mathbb{D}(P, T, Q) = 0. \quad (2.59)$$

The approximated solution of such weak problem is obtained via FEM as presented in Chapter 4, where a discrete system is derived based on shape functions interpolation. Before addressing this and other numerical matters, the next Chapter is focused on the definition of the theoretical concepts of the optimisation problems studied in this work.

3 Optimisation of ANG Tanks

This Chapter is focused on the design of adsorption systems via topology optimisation. The optimisation concept is discussed, followed by the definition of the objective function for the optimisation of ANG tanks. Finally, traditional material models are reviewed and a novel Offset Hyperbolic Tangents (OHT) model is proposed.

3.1 Design Concept

An ANG tank is considered empty when the equilibrium mass of adsorbed gas for atmospheric pressure and temperature (P_{atm} and T_{atm}) is achieved. Similarly, it is considered full when reaching the adsorption equilibrium for the inlet pressure (P_{let}) and atmospheric temperature. Those quantities are expressed by

$$Q_{empty} = \int_{\Omega_{ads}} Q_{eq}(P_{atm}, T_{atm}) d\mathbf{x}, \quad (3.1)$$

$$Q_{full} = \int_{\Omega_{ads}} Q_{eq}(P_{let}, T_{atm}) d\mathbf{x}, \quad (3.2)$$

where Ω_{ads} is the adsorbent domain inside the tank.

At the end of an adsorption or desorption cycle, the actual mass of gas adsorbed inside the tank is given by

$$Q_f = \int_{\Omega_{ads}} Q_{eq}(P_f, T_f) d\mathbf{x}, \quad (3.3)$$

which is well approximated by

$$Q_f \approx \int_{\Omega_{ads}} Q_{eq}(\overline{P}_f, \overline{T}_f) d\mathbf{x}, \quad (3.4)$$

where $\overline{P}_f$ and $\overline{T}_f$ denote the average pressure and temperature within the domain Ω_{ads} at the end of the cycle.

The goal when designing ANG tanks, is to make the temperature $\overline{T_f}$ as near as possible to the atmospheric temperature T_{atm} at the end of both adsorption and desorption cycles. This is often very time demanding due to the adsorbent poor conductivity mentioned above. A possible approach to shorten the cycle length is not to occupy the full volume of the tank with adsorbent, replacing it per some high conductive material in certain regions, as demonstrated in the tank depicted in Figure 3.1. The design trade-off is to not remove too much adsorbent when introducing non-adsorbent material to make the temperature $\overline{T_f}$ nearer to the atmospheric value.

Figure 3.1: Optimisation of ANG tanks through the addition of non-adsorbent materials.

The gain in gas adsorbed obtained in an optimised tank (*opt*) in relation to a tank constituted purely by adsorbent material (*pure*) is represented by γ and denotes the increment in the percentage of mass adsorbed. It is correlated to the variation of adsorbent volume inside the tank by

$$(1 + \gamma_a) = \frac{Q_{eq}(\overline{P_{f,opt}}, \overline{T_{f,opt}}) - Q_{eq}(P_{atm}, T_{atm})}{Q_{eq}(\overline{P_{f,pure}}, \overline{T_{f,pure}}) - Q_{eq}(P_{atm}, T_{atm})} \left(1 - \frac{V_{non}}{V_{tank}}\right). \quad (3.5)$$

Figure 3.2 illustrates the case of a tank which is presenting a final average temperature of 323 K at the end of the adsorption cycle. It is shown how much volume is possible to occupy with non-adsorbent materials according to the reduction of the temperature in order to achieved certain gain in the mass of gas adsorbed. For instance, if the replacement of 5% of the adsorbent bed with some non-adsorbent material leads to the reduction of final average temperature to 300 K, it would be possible to adsorb 30% more gas.

3.2 Manufacturing Considerations

According to Menon & Komarneni (1998), the packing density of adsorbent particles is a key factor for the overall capacity of gas storage in ANG systems. The most promising

Figure 3.2: Isomass curves given by the variation of adsorbent temperature and relative non-adsorbent volume in adsorption cycle.

approaches involve the fabrication of monolithic carbon based on the extrusion, cold pressing or hot isostatic pressing of the activated carbon powder associated with some binder. As a monolith, the void volume between particles is reduced and, therefore, the relative volume of micropores with respect to the total vessel volume is increased, resulting in more gas being adsorbed (QUINN et al., 1994). The fabrication method described in Bose et al. (1991) comprises mixing high surface area carbon particles with a solution of a binder in a solvent, forming a slurry. The use of binders, typically thermoplastic polymers, is important to prevent future powdering of the adsorbent bed when subjected to vibration or strong gas flow. The solvent is then removed, resulting in binder-coated carbon particles, which are compressed to form a compacted adsorbent mass of any desired geometric shape (BOSE et al., 1991).

Hence, ANG tanks can present features of any complexity without prejudice to the manufacturing process. Non-adsorbent parts, can be manufactured through traditional methods, such as machining or casting, and assembled at the desired position inside the tanks. The binder-coated carbon particles can then be poured into segments of the tank and compressed, occupying the whole void space left.

3.3 Objective Function

The optimisation of ANG storing systems can be addressed by focusing on several different objectives. Figure 3.3 illustrates the typical variation of the adsorbed gas mass, pressure and temperature of an ANG tank serving as an on-demand source of fuel, such as in gas-powered vehicles or in residences. Starting from the average density of total gas at the equilibrium, $\overline{(Q + \rho_g)_{ini,a}}$, the tank admits gas while pressure and temperature increase during the filling cycle, reaching the final average total density of $\overline{(Q + \rho_g)_{fin,a}}$. Such average density is conserved inside the tank until its future depletion. While the tank is kept quiescent, its temperature slowly approaches the equilibrium with the atmospheric temperature, T_{atm} , causing its internal pressure to drop due to the gas phase change from gaseous to adsorbed. The stored gas is then delivered through a nearly isothermal desorption, maintaining equilibrium with T_{atm} during the whole emptying cycle.

Figure 3.3: Cycle considered for the optimisation of ANG tanks applied to on-demand consumption.

The goal when designing such tanks is to maximise the total intake of gas during the

filling cycle by mitigating the rise of the adsorbent bed temperature. The optimisation problem consists of

$$\begin{aligned}
& \text{Maximise : } J_a(e) = \left[\int_{\Omega} (Q + \rho_g) dx \right]_{t_{ini,a}}^{t_{fin,a}}, \\
& \text{subjected to : } 0 \leq e \leq 1, \\
& \mathbb{M}(P, T, Q) + \mathbb{E}(P, T, Q) + \mathbb{D}(P, T, Q) = 0.
\end{aligned} \tag{3.6}$$

3.4 Material Model

The design variables are defined as pseudo-porosities representing two materials: adsorbent and non-adsorbent. Given the poor conductivity presented by typical adsorbents, suitable non-adsorbent materials present relatively high conductivity or heat capacity, aiming to improve the heat transfer of the system.

The alternation between adsorbent (*ads*) and non-adsorbent (*non*) materials through the domain can be expressed by a pseudo-porosity e as

$$\mathbb{P}(e) = \begin{cases} \mathbb{P}_{non}, & \text{if } e = 0, \\ \mathbb{P}_{ads}, & \text{if } e = 1, \end{cases} \tag{3.7}$$

where the actual property $\mathbb{P}$ is given by $\mathbb{P}_{ads}$ or $\mathbb{P}_{non}$ depending on e value.

3.4.1 Material Models with Penalisation

A binary law of material defines an ill-posed problem, with multiple local minima. Such issue can be avoided by relaxing the definition and assuming intermediate values, ranging from 0 to 1. Since only 0 and 1 represent existent materials, it is desirable to recover the discrete nature of this material law. The Solid Isotropic Material with Penalisation (SIMP) (BENDSØE; SIGMUND, 1999) addresses this problem by including a penalisation coefficient p , resulting in

$$\mathbb{P}(e) = (1 - e^p) \mathbb{P}_{non} + (e^p) \mathbb{P}_{ads}. \tag{3.8}$$

For structural cases, where $\mathbb{P}_{non} \equiv \mathbb{P}_{void}$ and $\mathbb{P}_{ads} \equiv \mathbb{P}_{solid}$, Bendsøe & Sigmund (1999) recalls that the interpolated material property should not exceed the Hashin-Shtrikman upper bound for any value of the design variable e . In order to meet this requirement it is sufficient that $p \geq 3$. However, such penalisation creates multiple local minima and

makes the final topology very dependent on the initial guess (BENDSØE; SIGMUND, 1999). Thus, a continuation scheme is advisable, by which the penaliser p is slowly increased through the computations.

Figure 3.4 shows the impact of the penalisation coefficient to the property being interpolated by SIMP. Taking the pair Steel-Carbon as an example, it can be seen that the resulting property for intermediate values of the design variable, e , tends to Steel ($k = 47.00 \text{ Wm}^{-1}\text{K}^{-1}$ and $W = 0.00 \text{ cm}^3\text{g}^{-1}$) as $p \rightarrow \infty$, while it tends to Activated Carbon ($k = 0.21 \text{ Wm}^{-1}\text{K}^{-1}$ and $W = 0.33 \text{ cm}^3\text{g}^{-1}$) as $p \rightarrow 0$.

Borrvall & Petersson (2003) introduced a scheme more suitable to deal with the interpolation of permeabilities, which are separated by several orders of magnitude and would require extremely high values for p . This material model is based on the inverse permeability, S , and it is given by

$$S(e) = \frac{1}{K(e)} = S_{non} + (S_{ads} - S_{non}) \frac{1+p}{e+p} e, \quad (3.9)$$

where S_{ads} and S_{non} are given by

$$S_{[ads,non]} = \frac{1}{K_{[ads,non]}}. \quad (3.10)$$

The adsorbent permeability (K_{ads}) is in the order of $1.00 \times 10^{-10} \text{ m}^2$ (SAHOO et al., 2011), while the non-adsorbent (K_{non}) material must be an impermeable medium, in which the permeability should be as low as $1.00 \times 10^{-22} \text{ m}^2$. For such properties, the resulting permeability based on Borrvall's scheme is shown in Figure 3.5.

3.4.2 Offset Hyperbolic Tangents (OHT) Material Model

SIMP and Borrvall's models present some disadvantages when dealing with discrepant properties, such as the interpolation from $K_{ads} = 1.00 \times 10^{-10} \text{ m}^2$ to $K_{non} = 1.00 \times 10^{-22} \text{ m}^2$. A material model based on hyperbolic tangents is able to offer a better discrimination of materials, being defined as

$$\mathbb{P}(e) = \left(1 - m(e)\right) \mathbb{P}_{non} + m(e) \mathbb{P}_{ads}, \quad (3.11)$$

in which

$$m(e) = \frac{\tanh\left(p(e - e_c)\right) + 1}{2}, \quad (3.12)$$

where the transition from one material to the other is centred on the value e_c .

(a) Thermal Conductivity (k) (b) Specific Micro-Pore Volume (W)**Figure 3.4:** SIMP for Steel and Carbon properties.

In the case of Steel-Carbon pair, it can be seen that the hyperbolic tangent approach is suitable to interpolate all the material properties with its generic form, as seen in Figure 3.6.

When optimising adsorption systems, materials presenting intermediate properties often constitute the best solution from the optimiser's perspective. For instance, in the case of seeking an optimised placement of Steel on a Carbon bed, the conductivity of

Figure 3.5: Borrvall's material model for Steel and Carbon Permeability (K).

the non-adsorbent material is more than 200 times larger than adsorbent's and Steel adsorption capacity is null. Therefore, a material presenting half of Steel's conductivity and half of Carbon's adsorption would be a good choice, if feasible.

It is then necessary to adopt a material model which forces the optimiser to clearly choose one or other material. The material model based on hyperbolic tangents presented in Eq. (3.11) is suitable for this sort of requirement. However, when choosing the material change centred on the same e_c for all the properties, the existence of hybrid materials prevails despite the penalisation imposed, as shown in Figure 3.7a. Such issue is solved by defining different values of e_c for different properties. For the property A , where the functional of interest $J(A_{ads})$ (adsorbent property in the whole domain) is higher than $J(A_{non})$ (non-adsorbent property in the whole domain), the phase change is centred on $e_c = 0.5 + \epsilon$. Conversely, for a property B which presents $J(B_{non})$ higher than $J(B_{ads})$, $e_c = 0.5 - \epsilon$ is adopted. In the absence of an offset, there would be intermediate properties at $e = 0.5$ regardless of the penalisation value. Figure 3.7 illustrates such material model for the offset $\epsilon = 0.02$. The function $m(e)$ in the Offset Hyperbolic Tangents (OHT) material model is then given by

$$m(e) = \frac{\tanh\left(p(e + s\epsilon - 0.5)\right) + 1}{2}, \quad (3.13)$$

where

$$s = \text{sgn}\left(J(\mathbb{P}_{non}) - J(\mathbb{P}_{ads})\right), \quad (3.14)$$

with sgn denoting the signum function.

A comparison between OHT and traditional material models is presented in Chapter 5, highlighting its advantages for the problems studied in this work. In the next Chapter, the numerical implementation of the adsorption problem and the topology optimisation algorithm is detailed, along with the necessary verifications.

(a) Thermal Conductivity (k) (b) Specific Micro-Pore Volume (W) (c) Permeability (K)

Figure 3.6: Hyperbolic tangent material model for Steel and Carbon properties with $e_c = 0.5$.

(a) $e_c = 0.5$ for A and B

(b) $e_c = 0.52$ for A and $e_c = 0.48$ for B

Figure 3.7: Material model for properties A and B.

4 Numerical Implementation and Verification

In this Chapter, the discretisation of the weak forms is presented in detail and an adjoint system is derived in view of the implementation of a gradient-based topology optimisation. The solution of the adsorption problem and the optimisation algorithm are then described along with several numerical verifications.

4.1 Discrete Adsorption Problem

The weak forms of the adsorption problem derived in Section 2.4 are approximated over a finite element, ω , by (REDDY; GARTLING, 2010)

$$P(\mathbf{x}, t) \cong \sum_{n=1}^N \phi_n(\mathbf{x}) P_n(t) = \mathbf{\Phi}^T \mathbf{P}, \quad (4.1)$$

$$T(\mathbf{x}, t) \cong \sum_{m=1}^M \psi_m(\mathbf{x}) T_m(t) = \mathbf{\Psi}^T \mathbf{T}, \quad (4.2)$$

where $\mathbf{P}$ and $\mathbf{T}$ are, respectively, the vectors with the nodal values of pressure and temperature, N and M denotes the number of nodes used for each unknown and ϕ and ψ are the shape functions, which are assembled in matrices $\mathbf{\Phi}$ and $\mathbf{\Psi}$.

Analogously, the mass of adsorbed gas per volume of adsorbent (Q) is interpolated over finite elements by the shape function ξ as

$$Q(\mathbf{x}, t) \cong \sum_{l=1}^L \xi_l(\mathbf{x}) Q_l(t) = \mathbf{\Xi}^T \mathbf{Q}. \quad (4.3)$$

The interpolation of the total porosity (ε) and all other material properties (ρ_s , Cp_s , K_s and K_s) is also done by using ξ , which is given by

$$\varepsilon(\mathbf{x}, t) \cong \sum_{l=1}^L \xi_l(\mathbf{x}) \varepsilon_l(t) = \mathbf{\Xi}^T \boldsymbol{\varepsilon}. \quad (4.4)$$

Making $v_M = \phi$, $v_E = \psi$ and $v_D = \xi$, results in the discrete equations given by

$$\mathbf{W}(\mathbf{T}) \dot{\mathbf{P}} + \mathbf{S}(\mathbf{P}, \mathbf{T}) \dot{\mathbf{T}} + \mathbf{Y}_M \dot{\mathbf{Q}} + \mathbf{Z}(\mathbf{P}, \mathbf{T}) \mathbf{P} = \mathbf{0}, \quad (4.5)$$

$$\mathbf{J} \dot{\mathbf{P}} + \mathbf{N}(\mathbf{P}, \mathbf{T}, \mathbf{Q}) \dot{\mathbf{T}} + \mathbf{Y}_E \dot{\mathbf{Q}} + \mathbf{L}(\mathbf{P}, \mathbf{T}) \mathbf{T} + \mathbf{K} \mathbf{T} = \mathbf{0}, \quad (4.6)$$

$$\mathbf{Y}_D \dot{\mathbf{Q}} + \mathbf{R}(\mathbf{T}) \mathbf{Q} = \mathbf{V}(\mathbf{P}, \mathbf{T}), \quad (4.7)$$

which results in the following system:

$$\begin{aligned} & \begin{bmatrix} \mathbf{W}(\mathbf{T}) & \mathbf{S}(\mathbf{P}, \mathbf{T}) & \mathbf{Y}_M \\ \mathbf{J} & \mathbf{N}(\mathbf{P}, \mathbf{T}, \mathbf{Q}) & \mathbf{Y}_E \\ \mathbf{0} & \mathbf{0} & \mathbf{Y}_D \end{bmatrix} \begin{Bmatrix} \dot{\mathbf{P}} \\ \dot{\mathbf{T}} \\ \dot{\mathbf{Q}} \end{Bmatrix} \\ & + \begin{bmatrix} \mathbf{Z}(\mathbf{P}, \mathbf{T}) & \mathbf{0} & \mathbf{0} \\ \mathbf{0} & \mathbf{L}(\mathbf{P}, \mathbf{T}) + \mathbf{K} & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{R}(\mathbf{T}) \end{bmatrix} \begin{Bmatrix} \mathbf{P} \\ \mathbf{T} \\ \mathbf{Q} \end{Bmatrix} \\ & = \begin{Bmatrix} \mathbf{0} \\ \mathbf{0} \\ \mathbf{V}(\mathbf{P}, \mathbf{T}) \end{Bmatrix}, \end{aligned} \quad (4.8)$$

whose matrices are assembled based on the coefficients defined in Appendix A.1.

The system given in Eq. (4.8) is rewritten for the n -th timestep as

$$\mathbf{F}_t(\mathbf{w}_n) \dot{\mathbf{w}}_n + \mathbf{F}_s(\mathbf{w}_n) \mathbf{w}_n = \mathbf{F}_r(\mathbf{w}_n), \quad (4.9)$$

where the state variable $\mathbf{w}_n$, constituted by pressure, temperature and adsorbed gas, is given by

$$\mathbf{w}_n = \begin{Bmatrix} \mathbf{P}_n \\ \mathbf{T}_n \\ \mathbf{Q}_n \end{Bmatrix}. \quad (4.10)$$

The discretisation of the equations in time by using backward Euler method results

in a lower-triangular system given by

$$\begin{bmatrix} \mathbf{I} & \mathbf{0} & \cdots & \mathbf{0} & \mathbf{0} \\ \mathbf{C}_P(\mathbf{w}_0) & \mathbf{C}_C(\mathbf{w}_1) & \cdots & \mathbf{0} & \mathbf{0} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \mathbf{0} & \mathbf{0} & \cdots & \mathbf{C}_P(\mathbf{w}_{N-1}) & \mathbf{C}_C(\mathbf{w}_N) \end{bmatrix} \begin{bmatrix} \mathbf{w}_0 \\ \mathbf{w}_1 \\ \vdots \\ \mathbf{w}_{N-1} \\ \mathbf{w}_N \end{bmatrix} = \begin{bmatrix} \mathbf{W}_{ini} \\ \mathbf{F}_r(\mathbf{w}_1) \\ \vdots \\ \mathbf{F}_r(\mathbf{w}_{N-1}) \\ \mathbf{F}_r(\mathbf{w}_N) \end{bmatrix}, \quad (4.11)$$

where $\mathbf{W}_{ini}$ denotes the initial state conditions and

$$\mathbf{C}_P(\mathbf{w}_n) = -\frac{\mathbf{F}_t(\mathbf{w}_n)}{\Delta t}, \quad (4.12)$$

$$\mathbf{C}_C(\mathbf{w}_n) = \frac{\mathbf{F}_t(\mathbf{w}_n)}{\Delta t} + \mathbf{F}_s(\mathbf{w}_n). \quad (4.13)$$

4.2 Discrete Adjoint System for the Adsorption Problem

In the optimisation problem given in Eq. (3.6), the functional of interest $J(\mathbf{w}(\mathbf{e}), \mathbf{e})$ is constrained to the PDE system $\mathbf{F}(\mathbf{w}, \mathbf{e}) = \mathbf{0}$ given in Eq. (4.11). Such problem is expressed by the following augmented Lagrangian as

$$J = \int_{t_{ini}}^{t_{fin}} \left(\delta_{t_{fin}} - \delta_{t_{ini}} \right) B + \boldsymbol{\lambda}^T \left(\mathbf{F}_t \dot{\mathbf{w}} + \mathbf{F}_s \mathbf{w} - \mathbf{F}_r \right) dt, \quad (4.14)$$

where B denotes the total gas mass, given by:

$$\int_{\Omega} (Q + \rho_g) dx, \quad (4.15)$$

and, for simplicity

$$\delta_{t_{fin}} - \delta_{t_{ini}} = \delta(t - t_{fin}) - \delta(t - t_{ini}), \quad (4.16)$$

where δ denotes Dirac's delta operator, making the term $(\delta_{t_{fin}} - \delta_{t_{ini}})B$ to be equal to the difference in the total gas mass between the beginning and the end of the adsorption cycle.

The vector of Lagrange multipliers, $\boldsymbol{\lambda}$, is given by

$$\boldsymbol{\lambda} = \begin{Bmatrix} \boldsymbol{\lambda}_M \\ \boldsymbol{\lambda}_E \\ \boldsymbol{\lambda}_D \end{Bmatrix}. \quad (4.17)$$

The derivative of the reduced functional J in respect to a design variable e_i is given by

$$\begin{aligned} \frac{dJ}{de_i} = & \int_{t_{ini}}^{t_{fin}} \left(\delta_{t_{fin}} - \delta_{t_{ini}} \right) \left(\frac{\partial B}{\partial e_i} + \frac{\partial B}{\partial \mathbf{w}} \frac{d\mathbf{w}}{de_i} \right) dt \\ & + \int_{t_{ini}}^{t_{fin}} \boldsymbol{\lambda}^T \left(\left(\frac{\partial \mathbf{F}_t}{\partial e_i} + \frac{\partial \mathbf{F}_t}{\partial \mathbf{w}} \frac{d\mathbf{w}}{de_i} \right) \dot{\mathbf{w}} + \mathbf{F}_t \frac{d\dot{\mathbf{w}}}{de_i} + \left(\frac{\partial \mathbf{F}_s}{\partial e_i} + \frac{\partial \mathbf{F}_s}{\partial \mathbf{w}} \frac{d\mathbf{w}}{de_i} \right) \mathbf{w} \right. \\ & \left. + \mathbf{F}_s \frac{d\mathbf{w}}{de_i} - \frac{\partial \mathbf{F}_r}{\partial e_i} - \frac{\partial \mathbf{F}_r}{\partial \mathbf{w}} \frac{d\mathbf{w}}{de_i} \right) dt. \end{aligned} \quad (4.18)$$

Integrating the term involving $d\dot{\mathbf{w}}/de_i$ by parts, it results in

$$\frac{dJ}{de_i} = \Theta_{sen} + \Theta_{b,ini} + \Theta_{b,fin} + \Theta_{adj}, \quad (4.19)$$

where

$$\Theta_{sen} = \int_{t_{ini}}^{t_{fin}} \left(\delta_{t_{fin}} - \delta_{t_{ini}} \right) \frac{\partial B}{\partial e_i} + \boldsymbol{\lambda}^T \left(\frac{\partial \mathbf{F}_t}{\partial e_i} \dot{\mathbf{w}} + \frac{\partial \mathbf{F}_s}{\partial e_i} \mathbf{w} - \frac{\partial \mathbf{F}_r}{\partial e_i} \right) dt, \quad (4.20)$$

$$\Theta_{b,ini} = - \boldsymbol{\lambda}^T \mathbf{F}_t \frac{d\mathbf{w}}{de_i} \Big|_{t_{ini}}, \quad (4.21)$$

$$\Theta_{b,fin} = \boldsymbol{\lambda}^T \mathbf{F}_t \frac{d\mathbf{w}}{de_i} \Big|_{t_{fin}}, \quad (4.22)$$

$$\Theta_{adj} = \int_{t_{ini}}^{t_{fin}} \frac{d\mathbf{w}}{de_i} \left[\left(\delta_{t_{fin}} - \delta_{t_{ini}} \right) \frac{\partial B}{\partial \mathbf{w}} - \frac{\partial(\boldsymbol{\lambda}^T \mathbf{F}_t)}{\partial t} + \boldsymbol{\lambda}^T \left(\mathbf{F}_s + \frac{\partial \mathbf{F}_t}{\partial \mathbf{w}} \dot{\mathbf{w}} + \frac{\partial \mathbf{F}_s}{\partial \mathbf{w}} \mathbf{w} - \frac{\partial \mathbf{F}_r}{\partial \mathbf{w}} \right) \right] dt. \quad (4.23)$$

Since the term $d\mathbf{w}/de_i$ is unknown for $t > t_{ini}$, the terms $\Theta_{b,fin}$ and Θ_{adj} cannot be evaluated explicitly. Given that $\boldsymbol{\lambda}$ is arbitrary, it can be chosen in order to nullify these terms (DAHL et al., 2008). To ensure $\Theta_{b,fin} = 0$ it is necessary to choose $\boldsymbol{\lambda}$ such that $\boldsymbol{\lambda}(t_{fin}) = \mathbf{0}$. In adsorption systems, although P_{ini} and T_{ini} are imposed and do not depend on the design variables, the initial density of gas adsorbed, Q_{ini} , is dependent on the volume of adsorbent material inside the domain. The derivative of the state variable in respect to e_i is given by

$$\frac{d\mathbf{w}}{de_i} \Big|_{t_{ini}} = \begin{Bmatrix} 0 \\ 0 \\ Q_{eq}(P_{ini}, T_{ini}) \frac{dm(e_i)}{de_i} \end{Bmatrix}, \quad (4.24)$$

where the equilibrium adsorbed density Q_{eq} is given in Eq. (2.24) and the material model interpolation function $m(e_i)$ is given in Eq. (3.13).

The term Θ_{adj} is null when the expression between brackets is equal to zero, which

can be rewritten as

$$\left(\delta_{t_{fin}} - \delta_{t_{ini}}\right) \frac{\partial B}{\partial \mathbf{w}} - \dot{\boldsymbol{\lambda}}^T \mathbf{F}_t - \boldsymbol{\lambda}^T \frac{\partial \mathbf{F}_t}{\partial \mathbf{w}} \frac{d\mathbf{w}}{dt} + \boldsymbol{\lambda}^T \left(\mathbf{F}_s + \frac{\partial \mathbf{F}_t}{\partial \mathbf{w}} \frac{d\mathbf{w}}{dt} + \frac{\partial \mathbf{F}_s}{\partial \mathbf{w}} \mathbf{w} - \frac{\partial \mathbf{F}_r}{\partial \mathbf{w}} \right) = 0, \quad (4.25)$$

resulting in

$$\left(\delta_{t_{fin}} - \delta_{t_{ini}}\right) \frac{\partial B}{\partial \mathbf{w}} - \dot{\boldsymbol{\lambda}}^T \mathbf{F}_t + \boldsymbol{\lambda}^T \left(\mathbf{F}_s + \frac{\partial \mathbf{F}_s}{\partial \mathbf{w}} \mathbf{w} - \frac{\partial \mathbf{F}_r}{\partial \mathbf{w}} \right) = 0. \quad (4.26)$$

The Lagrange multiplier $\boldsymbol{\lambda}$ is obtained by the solution of the adjoint problem given by

$$\begin{aligned} \left(\mathbf{F}_t(\mathbf{w})\right)^T \dot{\boldsymbol{\lambda}}(t) - \left(\mathbf{F}_s(\mathbf{w}) + \frac{\partial \mathbf{F}_s(\mathbf{w})}{\partial \mathbf{w}} \mathbf{w} - \frac{\partial \mathbf{F}_r(\mathbf{w})}{\partial \mathbf{w}}\right)^T \boldsymbol{\lambda}(t) &= \left(\delta_{t_{fin}} - \delta_{t_{ini}}\right) \frac{\partial B}{\partial \mathbf{w}}, \\ \boldsymbol{\lambda}(t_{fin}) &= \mathbf{0}. \end{aligned} \quad (4.27)$$

Such system poses a terminal value problem, which can be converted in an initial value problem by substituting the time variable t per $\tau = t_{fin} - t$. A new system is then defined in terms of $\bar{\boldsymbol{\lambda}}(\tau) = \boldsymbol{\lambda}(t_{fin} - t)$, given by

$$\begin{aligned} \left(\mathbf{F}_t(\mathbf{w})\right)^T \dot{\bar{\boldsymbol{\lambda}}}(\tau) + \left(\mathbf{F}_u(\mathbf{w})\right)^T \bar{\boldsymbol{\lambda}}(\tau) &= \left(\delta_{\tau_{fin}} - \delta_{\tau_{ini}}\right) \frac{\partial B}{\partial \mathbf{w}}, \\ \bar{\boldsymbol{\lambda}}(\tau_{ini}) &= \mathbf{0}, \end{aligned} \quad (4.28)$$

where, for simplicity

$$\mathbf{F}_u(\mathbf{w}) = \mathbf{F}_s(\mathbf{w}) + \frac{\partial \mathbf{F}_s(\mathbf{w})}{\partial \mathbf{w}} \mathbf{w} - \frac{\partial \mathbf{F}_r(\mathbf{w})}{\partial \mathbf{w}}. \quad (4.29)$$

Let the Laplace transform of $\bar{\boldsymbol{\lambda}}(\tau)$ to be expressed as

$$\mathcal{L}\{\bar{\boldsymbol{\lambda}}(\tau)\} = \bar{\boldsymbol{\Lambda}}(s). \quad (4.30)$$

The Laplace transformation of each term in the Eq. (4.28) results in

$$\mathcal{L} \left\{ \left(\mathbf{F}_t(\mathbf{w})\right)^T \dot{\bar{\boldsymbol{\lambda}}}(\tau) \right\} = \left(\mathbf{F}_t(\mathbf{w})\right)^T \left(s \bar{\boldsymbol{\Lambda}}(s) - \bar{\boldsymbol{\lambda}}(\tau_{ini}) \right), \quad (4.31)$$

$$\mathcal{L} \left\{ \left(\mathbf{F}_u(\mathbf{w})\right)^T \bar{\boldsymbol{\lambda}}(\tau) \right\} = \left(\mathbf{F}_u(\mathbf{w})\right)^T \bar{\boldsymbol{\Lambda}}(s), \quad (4.32)$$

$$\mathcal{L} \left\{ \left(\delta_{\tau_{fin}} - \delta_{\tau_{ini}} \right) \frac{\partial B}{\partial \mathbf{w}} \right\} = \int_0^\infty e^{-s\tau} \left(\delta_{\tau_{fin}} - \delta_{\tau_{ini}} \right) \frac{\partial B}{\partial \mathbf{w}} d\tau = \left(e^{-s\tau_{fin}} - e^{-s\tau_{ini}} \right) \mathcal{L} \left\{ \frac{\partial B}{\partial \mathbf{w}} \right\}. \quad (4.33)$$

Following, the inverse Laplace transform must be performed to go back to the reverse time domain τ , which for the last term is given by

$$\mathcal{L}^{-1} \left\{ \left(e^{-s\tau_{fin}} - e^{-s\tau_{ini}} \right) \mathcal{L} \left\{ \frac{\partial B(\tau)}{\partial \mathbf{w}} \right\} \right\} = H(\tau - \tau_{fin}) \frac{\partial B(\tau - \tau_{fin})}{\partial \mathbf{w}} - H(\tau - \tau_{ini}) \frac{\partial B(\tau - \tau_{ini})}{\partial \mathbf{w}}, \quad (4.34)$$

where H denotes the Heaviside step function, which is applied to the function B shifted by τ_{fin} and τ_{ini} .

The adjoint problem in Eq. (4.28) is then given by

$$\begin{aligned} \left(\mathbf{F}_t(\mathbf{w}) \right)^T \dot{\bar{\boldsymbol{\lambda}}}(\tau) + \left(\mathbf{F}_u(\mathbf{w}) \right)^T \bar{\boldsymbol{\lambda}}(\tau) &= H_{\tau_{fin}} \frac{\partial B_{\tau_{fin}}}{\partial \mathbf{w}} - H_{\tau_{ini}} \frac{\partial B_{\tau_{ini}}}{\partial \mathbf{w}}, \\ \bar{\boldsymbol{\lambda}}(\tau_{ini}) &= \mathbf{0}, \end{aligned} \quad (4.35)$$

where, for simplicity

$$H_{\tau_{fin}} \frac{\partial B_{\tau_{fin}}}{\partial \mathbf{w}} - H_{\tau_{ini}} \frac{\partial B_{\tau_{ini}}}{\partial \mathbf{w}} = H(\tau - \tau_{fin}) \frac{\partial B(\tau - \tau_{fin})}{\partial \mathbf{w}} - H(\tau - \tau_{ini}) \frac{\partial B(\tau - \tau_{ini})}{\partial \mathbf{w}}. \quad (4.36)$$

The discretisation of the adjoint system in time via backward Euler method results in

$$\begin{bmatrix} \mathbf{I} & \mathbf{0} & \cdots & \mathbf{0} & \mathbf{0} \\ \mathbf{A}_P(\mathbf{w}_0) & \mathbf{A}_C(\mathbf{w}_1) & \cdots & \mathbf{0} & \mathbf{0} \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \mathbf{0} & \mathbf{0} & \cdots & \mathbf{A}_P(\mathbf{w}_{N-1}) & \mathbf{A}_C(\mathbf{w}_N) \end{bmatrix} \begin{bmatrix} \bar{\boldsymbol{\lambda}}_0 \\ \bar{\boldsymbol{\lambda}}_1 \\ \vdots \\ \bar{\boldsymbol{\lambda}}_{N-1} \\ \bar{\boldsymbol{\lambda}}_N \end{bmatrix} = \begin{bmatrix} \mathbf{0} \\ \mathbf{A}_R(\mathbf{w}_1) \\ \vdots \\ \mathbf{A}_R(\mathbf{w}_{N-1}) \\ \mathbf{A}_R(\mathbf{w}_N) \end{bmatrix}, \quad (4.37)$$

where

$$\mathbf{A}_P(\mathbf{w}_n) = \left(-\frac{\mathbf{F}_t(\mathbf{w}_n)}{\Delta t} \right)^T, \quad (4.38)$$

$$\mathbf{A}_C(\mathbf{w}_n) = \left(\frac{\mathbf{F}_t(\mathbf{w}_n)}{\Delta t} + \mathbf{F}_s(\mathbf{w}_n) + \frac{\partial \mathbf{F}_s(\mathbf{w}_n)}{\partial \mathbf{w}_n} \mathbf{w}_n - \frac{\partial \mathbf{F}_r(\mathbf{w}_n)}{\partial \mathbf{w}_n} \right)^T, \quad (4.39)$$

$$\mathbf{A}_R(\mathbf{w}_n) = H_{\tau_{fin}} \frac{\partial B_{\tau_{fin}}}{\partial \mathbf{w}_n} - H_{\tau_{ini}} \frac{\partial B_{\tau_{ini}}}{\partial \mathbf{w}_n}. \quad (4.40)$$

The solution of the system above, in terms of $\bar{\lambda}(\tau)$, is then reversed in time to obtain $\lambda(t)$. Therefore, the derivative of the functional J in respect to e_i is now known and given by

$$\frac{dJ}{de_i} = \Theta_{sen} + \Theta_{b,ini}. \quad (4.41)$$

4.3 Adsorption Problem Implementation

Several open source software are available for computational fluid dynamics. Some examples are OpenFOAM (WELLER et al., 1998), based on the Finite Volume Method (FVM); FEniCS (LOGG, 2007) and Fluidity (PIGGOTT et al., 2008), based on Finite Element Method (FEM); SU2 (PALACIOS et al., 2013), able to handle both FVM and FEM; PyFR (WITHERDEN et al., 2014), based on flux reconstruction. This work adopts FEniCS and its module Dolfin-Adjoint, which are described in this Section.

FEniCS (LOGG, 2007) is open-source software focused on the automated solution of differential equations. Its form compiler (FFC) interprets a discrete form of the weak variational equation, which is written in a high-level language similar to the mathematical syntax, and generates a C++ code for finite element assembly conforming to the Unified Form-Assembly Code (UFC) (ALNÆS et al., 2014). This process relies on the Finite Element Automatic Tabulator (FIAT) (KIRBY, 2004), which numerically builds the finite element basis functions used by FFC. The process is concluded by combining the UFC code with mesh and coefficient data, in order to assemble the FEM tensors. The tensors from the resulting FEM system are given in SciPy format, enabling its solution by several linear algebra packages. However, FEniCS offers native support to PETSc, Epetra, uBLAS and MTL4, allowing to easily specify the desired linear solvers and pre-conditioners. The communication between all FEniCS modules is handled by Dolfin library, providing a unified environment.

4.3.1 System Decoupling Verification

It is reported by several authors (SAHOO et al., 2011; MOTA et al., 2004; VASILIEV et al., 2014) that the gradient of pressure observed inside ANG tanks is very small. Therefore, the validity of decoupling the full system presented in Eq. (4.8) is assessed in this Section. Such decoupling is interesting with respect to the topology optimisation implementation, in order to reduce the computational cost.

When decoupling the full adsorption problem in sub-problems, each timestep is formed

by a sequence of variables updates. The decoupled solution starts with the solution of the continuity equation to obtain the pressure (P) distribution in the domain by keeping the temperature (T) and the adsorbed density (Q) fixed. Based on the new pressure field, the adsorbed density is updated based on the adsorption kinetics, which does not involve spatial derivatives and is explicitly given by pressure and temperature. Finally, the temperature field is obtained by solving the energy balance considering fixed pressure and adsorbed density from the previous step.

The solution of the adsorption problem is then given by

$$\mathbf{W} \dot{\mathbf{P}} + \mathbf{Z} \mathbf{P} = \mathbf{F}, \quad (4.42)$$

$$\mathbf{N} \dot{\mathbf{T}} + \mathbf{L} \mathbf{T} + \mathbf{K} \mathbf{T} = \mathbf{H}, \quad (4.43)$$

whose matrices are assembled based on the coefficients given in Appendix A.3.

The numerical implementation of such system is verified by reproducing the results obtained in Sahoo et al. (2011). The adsorption of Methane on Activated Carbon in an axisymmetric tank for the flow rates of 1 L min^{-1} , 10 L min^{-1} and 30 L min^{-1} (volume of methane at 300 K and P_{atm}) is considered. The domain depicted in Figure 4.1 has $L_o = 0.20 \text{ m}$, $L_i = 0.03 \text{ m}$, $R_o = 0.05 \text{ m}$ and $R_i = 0.01 \text{ m}$. The convection heat transfer coefficient on the wall Γ_W is considered to be $h = 5 \text{ W m}^{-2} \text{ K}^{-1}$. Due to axisymmetry assumptions, the simulations are based on two-dimensional domains meshed in 43 781 triangular finite elements. The material adopted are listed in Appendix B.

The maximum temperature at the center of the tank and the total mass of gas adsorbed for each flow rate case are presented in Figures 4.2-4.4. The plots of the evolution of the central temperature include the datasets of two experiments per each flow rate reported in Sahoo et al. (2011). It can be seen that the numerical implementation of the adsorption problem proposed in this Section approximates satisfactorily the experimental results reported.

Numerical simulations are also reported in Sahoo et al. (2011), which reinforce the accuracy of the results obtained here. The distributions of temperature inside the tanks after each one the flow rates imposed are presented in Figure 4.5. Such distributions present good agreement with the plots reported in the aforementioned work.

Figure 4.1: Custom axisymmetric tank domain (SAHOO et al., 2011).

Figure 4.2: Flow rate of 1 L min^{-1} : Comparison with the experimental results in (SAHOO et al., 2011).

4.3.2 Pressure Loading Verification

This Section verifies the sensitivity of adsorption cycles to the smoothness factor σ defined in Eq. (2.35). Let consider the domain depicted in Figure 4.6, where $R_i = 0.05 \text{ m}$, $R_o = 0.20 \text{ m}$, $L_o = 1.00 \text{ m}$, subjected to a smooth pressure increase from $P_{ini} = 0.10 \text{ MPa}$ to $P_{let} = 1.00 \text{ MPa}$ in a 3600 s cycle. The temperature at the inlet region Γ_L

Figure 4.3: Flow rate of 10 L min⁻¹: Comparison with the experimental results in (SAHOO et al., 2011).

Figure 4.4: Flow rate of 30 L min⁻¹: Comparison with the experimental results in (SAHOO et al., 2011).

during adsorption is kept constant and equal to the entering gas due to the local thermal equilibrium assumption with the gas entering the tank at 293 K.

Figure 4.7 shows the evolution of the total gas mass inside the tank for three different values of σ . It can be seen that the curves are nearly coincidental after 500 s, demonstrating a low sensitivity to the history of pressure increase at the inlet. As smoothness is decreased, the cycle approaches the case in which the pressure variation is imposed

(a) 1 L min^{-1} at $t = 7200 \text{ s}$ (b) 10 L min^{-1} at $t = 630 \text{ s}$ (c) 30 L min^{-1} at $t = 204 \text{ s}$ **Figure 4.5:** Temperature distribution at the end of the adsorption cycle.

promptly. Figure 4.8 shows how the final total gas mass converges to this case as $\sigma \rightarrow 0$. Therefore, in the scope of this work, it is considered that any $\sigma \leq 0.1$ ($\sigma^{-1} \geq 10$) ensures negligible impact to the functional of interest.

4.3.3 Impermeability Verification

When distributing a impermeable material, such as Steel, in an ANG tank, it is important to ensure that gas will not flow across it. The impermeability can be numerically represented by assigning very low values to K_s , given that ideal impermeable media would

Figure 4.6: Adsorption domain adopted for verifying the sensitivity of adsorption cycles to the smoothness factor σ .

Figure 4.7: Total mass of gas along the adsorption cycle for different smoothness factors.

have $K_{non} = 0$. Consider the domain in Figure 4.9 representing a section of an axisymmetric tank, constituted of impermeable non-adsorbent and permeable adsorbent phases. The region Γ_L denotes the inlet region ($R_i = 0.05$ m) and Γ_W denotes walls subjected to heat convection ($R_o = 0.20$ m and $L_o = 1.00$ m). The domain is subjected to a smooth pressure rise on Γ_L following Eq. (2.35) from $P_{ini} = 0.10$ MPa to P_{let} with $\sigma = 0.05$. The permeabilities of $K_{ads} = 3.67 \times 10^{-10}$ m² for Activated Carbon and $K_{non} = 1.00 \times 10^{-22}$ m² for Steel are considered.

Figure 4.10b demonstrates the inaccessibility of the squared Carbon region on the right to the gas for $P_{let} = 1.00$ MPa in a cycle lasting $t_f = 600$ s. The pressure on the full right

Figure 4.8: Smoothness factor convergence.

Figure 4.9: Adsorption domain constituted by Activated Carbon and Steel.

half of the domain stays approximately unchanged during the whole cycle, being equal to P_{ini} . The permeability of 1.00×10^{-22} has shown to be able to reproduce impermeability even for high pressures and long cycles. In Figure 4.10c a cycle with $P_{let} = 8.00$ MPa and $t_f = 3600s$ is considered, demonstrating that the Carbon region on the right is still not accessed by the gas, although it permeated a slightly larger portion of Steel insulation.

(a) Permeability divided by viscosity ($K_s \mu_g^{-1}$) (b) $P_{let} = 1.00$ MPa at $t_f = 600$ s (c) $P_{let} = 8.00$ MPa at $t_f = 3600$ s**Figure 4.10:** Pressure distribution on Carbon-Steel domain.

4.3.4 Mesh and Timestep Convergence

The accuracy of the FEM model is dependent on the mesh and timestep resolutions adopted. The goal of this Section is to identify suitable refinement schemes for the adsorption problems studied here. Let consider the domain depicted in Figure 4.11 subjected to an adsorption cycle following a smooth pressure variation from $P_{ini} = 0.10$ MPa to $P_{let} = 1.00$ MPa in a 3600 s cycle with $\sigma = 0.1$.

This convergence study is based on the total gas mass intake observed in the adsorption cycle, according to the functional defined in Eq. (3.6). Figure 4.12 presents the variation in the value of such functional for different element sizes, where $\bar{h}^{-1}$ denotes the inverse of the average mesh cell diameter. Very small changes in the functional value are seen for resolutions higher than 50, implying that such value is sufficient for obtaining

Figure 4.11: Adsorption domain adopted for verifying mesh and timestep convergence.

accurate results. It is important to remark that in topology optimisation problems, higher resolutions can be adopted depending on the desired complexity of the resulting topology.

Figure 4.12: Mesh convergence.

Similarly, the timestep adopted in the implicit Euler method for time discretisation can influence the model accuracy. Figure 4.13 presents the total gas mass intake functional for different timesteps Δt . It can be seen that satisfactory convergence is achieved for $\Delta t = 10$ ($\Delta t^{-1} = 0.1$).

4.4 Topology Optimisation Implementation

An important aspect of topology optimisation implementation is the method of obtaining the sensitivities of the functional with respect to the design variables. In this

Figure 4.13: Timestep convergence.

work, it is based on the solution of an adjoint problem, which is derived in Section 4.2. Figure 4.14 presents three different approaches for obtaining the adjoint code starting from the continuous forward equations, in the context of the FEniCS packages UFL and UFC. It can be derived by *symbolic differentiation* of the forward PDE, through packages such as SAGE (STEIN; JOYNER, 2005). The derivation can also be addressed at source code level, treating the forward model as a sequence of elementary instructions by source-to-source compiler tool for *algorithmic differentiation*, such as Tapenade (HASCOET; DAUVERGNE, 2008). Another method consists in the derivation of the discrete forward equations, representing a middle-level approach that can be easily automated without depending on low-level implementation details. This work adopts the latter approach aided by the *libadjoint* library (FUNKE, 2012).

4.4.1 Design Variables Filtering

Topology optimisation presents inherent issues such as checker-board instability and mesh dependency, which are usually mitigated by filtering the sensitivities as described in Sigmund & Petersson (1998). Such method modifies the sensitivity of each design variable based on the values of its neighbours. An alternative approach is to modify the design variables based on the solution of a modified Helmholtz-type PDE, as introduced

Figure 4.14: Methods for obtaining the adjoint code (FUNKE, 2012).

in Lazarov & Sigmund (2011), given by

$$-z^2 \nabla^2 \mathbf{e} + \mathbf{e} = \boldsymbol{\phi}, \quad (4.44)$$

where the distribution $\boldsymbol{\phi}$ is smoothed to $\mathbf{e}$, according to the filter length parameter z .

The weak form of the modified Helmholtz-type PDE is given by

$$\mathbb{H} = \left\langle \mathbf{e}, v_H \right\rangle + \left\langle z^2 \nabla \mathbf{e}, \nabla v_H \right\rangle = \left\langle \boldsymbol{\phi}, v_H \right\rangle, \quad (4.45)$$

$$\forall v_H \in H^1(\Omega).$$

The discrete filtering system is given by

$$\mathbf{Z} \mathbf{e} = \boldsymbol{\phi}, \quad (4.46)$$

where $\mathbf{Z}$ and $\boldsymbol{\phi}$ are defined in Appendix A.4.

When applying the Helmholtz filter, despite the functional and PDE systems being expressed in terms of filtered pseudo-densities, $\mathbf{e}_j$, the optimisation problem is performed on the field of non-filtered pseudo-densities, $\boldsymbol{\phi}_j$, resulting in

$$\begin{aligned} \text{Maximise : } J_a(\boldsymbol{\phi}) &= \left[\int_{\Omega} \left(Q(\mathbf{e}) + \rho_g(\mathbf{e}) \right) dx \right]_{t_{ini,a}}^{t_{fin,a}}, \\ \text{subjected to : } 0 &\leq \boldsymbol{\phi} \leq 1, \\ \mathbb{M}(P, T, Q) + \mathbb{E}(P, T, Q) + \mathbb{D}(P, T, Q) &= 0, \\ -z^2 \nabla^2 \mathbf{e} + \mathbf{e} &= \boldsymbol{\phi}. \end{aligned} \quad (4.47)$$

Such variable change impacts functionals sensitivities. The implicit derivative of Eq. (4.46) with respect to ϕ_j results in

$$\frac{d\mathbf{Z}}{d\phi_j}\mathbf{e} + \mathbf{Z}\frac{d\mathbf{e}}{d\phi_j} = \frac{d\phi}{d\phi_j}, \quad (4.48)$$

where the first term is null, given that $\mathbf{Z}$ is not dependent on pseudo-porosities, and the right-hand side is

$$\frac{d\phi}{d\phi_j} = \boldsymbol{\delta}_{jk}, \quad (4.49)$$

in which $\boldsymbol{\delta}_{jk}$ denotes the Kronecker's delta column vector, being null in all lines, except for the j -th, which is equal to 1.

The sensitivity of the functional J to the non-filtered pseudo-porosity ϕ_j is then given by

$$\frac{dJ}{d\phi_j} = \left(\frac{dJ}{d\mathbf{e}}\right)^T \frac{d\mathbf{e}}{d\phi_j} = \left(\frac{dJ}{d\mathbf{e}}\right)^T \mathbf{Z}^{-1} \boldsymbol{\delta}_{jk}. \quad (4.50)$$

4.4.2 Optimisation Algorithm

The optimisation algorithm follows the flow represented in Figure 4.15. In the optimisation loop, the sensitivities are obtained via Dolfin-Adjoint (FUNKE, 2012) based on the equilibrium equations solved on FEniCS. An optimiser receives the sensitivities and output a new distribution of design variables, aiming to improve the functional of interest. The relative functional variation is defined by considering the last two iterations by

$$\omega = \frac{J_{it} - \frac{J_{it-1} + J_{it-2}}{2}}{\frac{J_{it-1} + J_{it-2}}{2}}. \quad (4.51)$$

When the functional relative variation is non-negative and smaller than a tolerance ω_{min} or when the maximum number of iterations it_{max} is reached, the loop is broken. The penalisation p is then increased by Δp , following the continuation method, and the loop is restarted. This algorithm is performed until reaching the maximum penalisation p_{max} , when the final topology is defined.

The optimiser adopted in all the cases presented in this work is the limited memory Broyden-Fletcher-Goldfarb-Shanno optimiser with box constraints (L-BFGS-B) (BYRD et al., 1995) implemented in `scipy.optimize` package (JONES et al., 2011). Optimisation problems requiring volume constraints can be approached based on other optimisers contained in this package, such as SLSQP and COBYLA, or via an IPOpt (WACHTER;

Figure 4.15: Optimisation activity diagram.

BIEGLER, 2006) interface also available in Dolfin-Adjoint.

4.4.3 Adjoint Sensitivites Verification

The topology optimisation relies on the accurate computation of the sensitivity of the objective functions to the design variables. The gradients computed based on the adjoint problem described in Section 4.2 can be verified through a Taylor remainder convergence test. Given a reduced functional $\hat{J}(m)$ subjected to an arbitrary perturbation δm , the first-order Taylor remainder tends to zero at $\mathcal{O}(h)$ while the second-order tends at $\mathcal{O}(h^2)$. That means that by halving h the first-order error also halves while the second-order error is divided by four. Taylor remainders expressions are given in Eq. (4.52). By evaluating the second-order remainder based on the $\nabla \hat{J}$ obtained via adjoint approach, its correctness can be determined by observing $\mathcal{O}(h^2)$ convergence.

$$\begin{aligned}
 |\hat{J}(m + h\delta m) - \hat{J}(m)| &\rightarrow 0 \quad \text{at } \mathcal{O}(h), \\
 |\hat{J}(m + h\delta m) - \hat{J}(m) - h\nabla \hat{J} \cdot \delta m| &\rightarrow 0 \quad \text{at } \mathcal{O}(h^2).
 \end{aligned}
 \tag{4.52}$$

Due to current Dolfin-Adjoint limitations, varying Dirichlet boundary conditions will produce inaccurate gradients. Thus, the variation of the inlet pressure on Γ_L is done

through the Nitsche's method (JUNTUNEN; STENBERG, 2012) by

$$\frac{\partial P}{\partial n} = \frac{1}{\delta}(P_{let} - P) \quad \text{on } \Gamma_L, \quad (4.53)$$

in which $P \rightarrow P_{let}$ as $\delta \rightarrow 0$.

Such condition is imposed to the system by enforcing

$$\left\langle \frac{M_g K_s P}{R_g \mu_g T} \nabla P, v_M \right\rangle_{\Gamma_N} = \left\langle \frac{M_g K_s P}{R_g \mu_g T} \frac{1}{\delta} (P_{let} - P), v_M \right\rangle_{\Gamma_L}. \quad (4.54)$$

Let consider the same cycle adopted in Section 4.3.2, with $\sigma = 0.1$, and the functional of total gas mass intake along such cycle, given by Eq. (3.6). From an initial homogeneous distribution of design variables $\mathbf{e} = \mathbf{0.5}$ the domain is subjected to a pseudo-random perturbation δe scaled to different values of h as shown in Figure 4.16.

Figure 4.16: Original (top) and Perturbed Pseudo-Porosity fields for (from the top) $h = 1.00 \times 10^{-3}$, $h = 5.00 \times 10^{-4}$, $h = 2.50 \times 10^{-5}$, $h = 1.25 \times 10^{-5}$, $h = 6.25 \times 10^{-6}$.

Table 4.1 presents the errors for each perturbation following the first and second Taylor remainder expressions. It demonstrates the correctness of $\nabla \hat{J}$ as the convergence order of second-order Taylor remainders are approximately 2.0.

Such verification of the sensitivities, associated with the afore presented verifications concerning the adsorption problem, sustains the numerical implementation in all its aspects. In the following Chapter, optimisation problems are approached based on the

Table 4.1: Taylor Remainder Convergence.

	h	Taylor Remainder	Convergence Order
1st Order	1.00×10^{-3}	1.47×10^{-3}	
1st Order	5.00×10^{-4}	7.36×10^{-4}	0.99929
1st Order	2.50×10^{-5}	3.68×10^{-4}	0.99964
1st Order	1.25×10^{-5}	1.84×10^{-4}	0.99982
1st Order	6.25×10^{-6}	9.21×10^{-5}	0.99991
2nd Order	1.00×10^{-3}	1.43×10^{-6}	
2nd Order	5.00×10^{-4}	3.58×10^{-7}	1.99989
2nd Order	2.50×10^{-5}	8.94×10^{-8}	1.99996
2nd Order	1.25×10^{-5}	2.23×10^{-8}	2.00007
2nd Order	6.25×10^{-6}	5.59×10^{-9}	2.00013

method derived here, resulting in several optimised adsorbent bed topologies.

5 Results and Discussion

This Chapter starts by comparing the OHT and traditional material models. Thereafter, the topology optimisation method derived in this work is adopted for designing ANG tanks for on-demand consumption of fuel.

5.1 Definition of Standard Domains and Cycles for the Design of ANG Tanks

The following Sections are focused on the design of ANG tanks for on-demand fuel consumption based on the idea presented in Section 3.1, in which non-adsorbent materials are distributed in the adsorbent bed. The objective function adopted is given by the total mass intake of gas during adsorption cycles of pre-defined length, as presented in Section 3.3. The major drawback when designing these tanks is the exothermic nature of the adsorption reaction, which increases the adsorbent bed temperature and hinders reaching of the equilibrium density of adsorbed gas. Such behaviour poses several limitations to the range of applicability of ANG tanks and asks for some thermal management, which can be done passively or actively. A passive method is based merely on the heat transfer with the environment, without the addition of any external work for cooling. In the case of aiding the tank filling by the imposition of forced convection, cold walls or any other sort of cooling method which requires additional work, the thermal management is considered to be active. In the latter, exergy analyses must be done in order to quantify how efficient is the system as a whole, although such analyses are beyond the scope of this work.

The domains considered here represent tanks constituted by adsorbent beds wrapped by a thin sheet of metallic material subject to heat exchange through convection on its walls, denoted by Γ_W . The contribution of such wall is assumed to be negligible (SAHOO

et al., 2011) and it is not included in the model. In fact, being a thin metallic sheet, its Biot number (Bi) is very small and the heat conduction inside it is much faster than the heat convection away from the surface.

The domains studied here represent two-dimensional reductions of three-dimensional tanks. The first domain, presented in Table 5.1, consists in an approximation of a very long prismatic tank with fixed cross-section. Since ANG tanks operate in a much lower pressure than its CNG pairs, prismatic tanks can offer a good trade-off between stress concentration and packing density or efficiency in space usage. Based on symmetry, only one quarter of such section is optimised. The gas inlet is considered to be distant from such section, making the pressure homogeneous on the whole domain and, consequently, the convective term in the energy balance null.

<p>Domain</p> <p>Dimensions: $L = 0.25$ m</p> <p>Materials: Appendix B</p> <p>Cycle</p> <p>Temperatures: $T_{ini,\infty} = 293$ K</p> <p>Initial Pressure: $P_{ini} = 0.10$ MPa</p> <p>Final Pressure: $P_{let} = 1.00$ MPa</p> <p>Smoothness: $\sigma = 0.1$, Eq.(2.35)</p>
<p>FEM</p> <p>Mesh Elements: 31 999 (simplex)</p> <p>Mesh Cell Diameter: 2.50×10^{-3} m</p> <p>Timestep: $\Delta t = 10$ s</p>

Table 5.1: Standard domain and cycle for prismatic tanks.

The second domain is presented in Table 5.2, consisting of an axisymmetric tank represented by its radial section. In this case, pressure gradient is observed across the domain, originated by the gas inlet region denoted by Γ_L . In some of the optimisation studies presented in this Chapter, low temperature is imposed on the region denoted by

Γ_F .

Table 5.2: Standard domain and cycle for cylindrical tanks.

The third and last domain adopted in this work is presented in Table 5.3. It follows the axisymmetry assumption but is focused on assessing the influence of complex shapes on the optimisation of ANG tanks beds. Despite not modelling any specific scenario, such domain presents typical features observed in tanks fitted along other components in constrained spaces. Similar to the previous domain, gas inlet occurs on the region Γ_L and cold temperature is imposed on Γ_F in some of the optimisation cases studied. As it will be seen in the sequence of this Chapter, concave and convex corners play an important role in the behaviour of ANG tanks, being, therefore, essential for the scope of this work.

Table 5.3: Standard domain and cycle for a custom axisymmetric tank.

5.2 Evaluation of the OHT Material Model for the Design of ANG Tanks

This Section is focused on studying the properties of the OHT material model. It is initially compared with SIMP and then tested for the dependency on the initial guess and penalisation continuation when adopted in the design of ANG tanks.

5.2.1 OHT vs. Traditional Material Models

The OHT material model proposed in Section 3.4.2 aims to mitigate the theoretical advantage of intermediate materials arising from the relaxation of the optimisation problem. This Section compares OHT with the traditional SIMP, emphasizing the relevance of the offset imposed to the model.

The optimisation of a prismatic tank, defined in Table 5.4 is chosen to test different material models. Figure 5.1 shows the evolution of the distribution of the design variables for three different material models. The first column is based on SIMP, in which the penalisation was continued from $p = 1$ to $p = 5$, with $\Delta p = 1$. The central column shows the evolution for a material model based on hyperbolic tangents without an offset, expressed by the Eq. (3.13) with $\epsilon = 0.0$, in which the penalisation is continued from $p = 1$ to $p = 51$, with $\Delta p = 5$. The right column shows the evolution of the same problem when an offset is defined by imposing $\epsilon = 0.02$. It is important to note that the penalisation coefficients in SIMP and OHT material models do not present a clear correlation, in a way that $p = 51$ in OHT does not represent, necessarily, a more penalised material model than $p = 5$ in SIMP.

It can be seen that the adoption of SIMP causes the pseudo-porosity values to be near $e = 0.92$, given that such value offers a reasonable increase of the thermal conductivity for an adsorption capacity near the full-carbon phase. Even when very high penalisation is imposed to the material model, such anomaly will still occur around the phase transition region. If such region is translated from $e = 1.0$ to $e = 0.5$ by adopting an hyperbolic tangent material model, the resulting evolution of the optimisation will be similar to the central column in Figure 5.1. Again, the values of the design variables are all concentrated around the phase transition region, taking advantage from the desired properties from each phase. In this optimisation problem, the offset tangents material model, presented in the third column, is the only one able to avoid unfeasible intermediate properties and define a clear topology. In this last case, as the penalisation increases the intermediate

pseudo-porosity of $e = 0.5$ becomes increasingly less advantageous for the functional of interest.

Figure 5.2 complements the points aforementioned by presenting the convergence of each one of the optimisations performed. Each drop seen in the curves are due to the increase of the penalisation, following the continuation scheme adopted. In SIMP and non-offset hyperbolic tangents material models, a theoretical maximum based on unfeasible materials is carried along the iterations, unaffected by the penalisation increase. In the case of OHT, the functional value decreases along the iterations as it recovers the binary nature of the problem as the penalisation is increased.

Prismatic Tank (Table 5.1)	Domain
	Heat Convection: $h_{\Gamma_W} = 100 \text{ Wm}^{-2}\text{K}^{-1}$
	Cycle
	Time Length: $t_{fin,a} = 10\,800 \text{ s}$, Fig. (3.3)
	Optimisation
	Iterations per Step: $it_{max} = 20$
	Tolerance: $\omega_{min} = 1.0 \times 10^{-6}$
	Filter Radius: $z = 5 \times 10^{-3} \text{ m}$, Eq.(4.44)

Table 5.4: Optimisation definitions for a prismatic tank subjected to forced convection.

Figure 5.1: Pseudo-porosity fields evolution (top-down) for SIMP (left), non-offset hyperbolic tangents (centre) and offset hyperbolic tangents (right) material models for prismatic tank optimisation.

(a) SIMP

(b) Non-offset hyperbolic tangents

(c) Offset hyperbolic tangents

Figure 5.2: Functional convergence for different material models.

5.2.2 Dependency on the Initial Guess and Penalisation

Topology optimisation problems are non-convex and often lead to different solutions depending on the initial guess and on the strategy adopted for the penalisation continuation on the OHT material model. This Section is limited to the numerical study of such dependency, while the subsequent Sections are focused on the actual design of ANG tanks.

Let consider the optimisation of the prismatic tank defined in Table 5.5. Figure 5.3 demonstrates the independency of the final topology with respect to the initial guess. The evolution of the optimisation starting from an homogeneous pseudo-porosity distribution $\mathbf{e} = \mathbf{0.5}$ is shown on the left column while one starting from an arbitrary initial guess is shown on the right. In both cases, the distribution of pseudo-porosities goes towards a full-carbon domain during the first optimisation iterations, following an identical evolution after that toward the same final layout. The optimisation of this tank is resumed in Section 5.4.1, where a thorough analysis is presented.

Prismatic Tank (Table 5.1)	Domain
	Heat Convection: $h_{\Gamma_W} = 100 \text{ Wm}^{-2}\text{K}^{-1}$
	Cycle
	Time Length: $t_{fin,a} = 10\,800 \text{ s}$, Fig. (3.3)
	Optimisation
	Material Model: $\epsilon = 0.02$, Eq. (3.13)
	$p = [1, 51]$, $\Delta p = 5$
	Iterations per Step: $it_{max} = 20$
	Tolerance: $\omega_{min} = 1.0 \times 10^{-6}$
	Filter Radius: $z = 5 \times 10^{-3} \text{ m}$, Eq.(4.44)

Table 5.5: Optimisation definitions for a prismatic tank subjected to forced convection.

The cylindrical tank optimisation presented in Table 5.6 is ran from a material model which is already significantly penalised ($p_{ini} = 20$). In this case, different initial guesses result in different final layouts as seen in Figure 5.4, where the distributions on the top of each block show the evolution of the homogeneous initial guess, while the bottom ones refers to an arbitrary initial distribution of pseudo-porosity. Despite the different layouts obtained for each case, the final objective function values are very similar: 2.31 kg of total

Figure 5.3: Pseudo-porosity fields evolution for homogeneous (left) and arbitrary (right) initial guesses for prismatic tank optimisation starting with $p_{ini} = 1$.

gas intake for the homogeneous initial guess and 2.28 kg for the arbitrary.

Cylindrical Tank (Table 5.2)	Domain	
	Materials:	$Cp_{non} = 1880 \text{ J kg}^{-1} \text{ K}^{-1}$
	Heat Convection:	$h_{(\Gamma_W \cup \Gamma_F)} = 5 \text{ W m}^{-2} \text{ K}^{-1}$
	Cycle	
	Time Length:	$t_{fin,a} = 3600 \text{ s}$, Fig. (3.3)
	Optimisation	
	Material Model:	$\epsilon = 0.02$, Eq. (3.13)
		$p = [20, 100]$, $\Delta p = 10$
	Iterations per Step:	$it_{max} = 10$
	Tolerance:	$\omega_{min} = 1.0 \times 10^{-6}$
	Filter Radius:	$z = 5 \times 10^{-3} \text{ m}$, Eq.(4.44)

Table 5.6: Optimisation definitions for a cylindrical domain with non-adsorbent material with high heat capacity.

The dependence of the final layouts on the initial guesses can be mitigated by following a continuation approach starting from a material model presenting low penalisation. Figure 5.5 shows the evolution of the pseudo-porosity distribution for an optimisation starting with penalisation $p_{ini} = 1$. Similar to the prismatic case, shown in Figure 5.3, the initial optimisation steps take the pseudo-porosities to a full-carbon distribution, following the same evolution from then on. The final layout for this case results in a total gas intake of 2.30 kg, which is very similar to the 2.31 kg observed for the case starting the penalisation from $p_{ini} = 20$. This particular case also highlights the non-convexity of such optimisation problem, where a particular distribution of pseudo-porosities in a moderately penalised material model complies the objective function better than a less penalised one following a smooth continuation. The optimisation of this tank is approached in detail in Section 5.3.3.

5.3 Design of ANG Tanks with Passive Thermal Management

In this Section, tanks filled without the aid of any external work for managing the temperature of the adsorbent bed are studied.

Figure 5.4: Pseudo-porosity fields evolution for homogeneous (top image on each block) and arbitrary (bottom) initial guesses for cylindrical tank optimisation starting with $p_{ini} = 20$.

Figure 5.5: Pseudo-porosity fields evolution for homogeneous (top image on each block) and arbitrary (bottom) initial guesses for cylindrical tank optimisation starting with $p_{ini} = 1$.

5.3.1 Tanks Subjected to Natural Convection

The optimisation of a cylindrical tank subjected to natural convection is defined in 5.7. It starts from an homogeneous distribution of the design variables at $\mathbf{e} = \mathbf{0.5}$ and the penalisation is smoothly increased from $p_{ini} = 20$ to $p_{max} = 100$, following the flowchart shown in Figure 4.15 with $it_{max} = 10$ and $\omega_{min} = 1.0 \times 10^{-6}$. The pseudo-porosity distribution is subjected to Helmholtz filtering with radius $z = 5 \times 10^{-3}$, which is equal to the double of the characteristic mesh cell diameter.

In Figure 5.6, the resulting topology is shown along with its three-dimensional revolution. The distribution of the pseudo-porosities obtained from the optimiser is shown in Figure 5.6a, where the colour scale ranges from grey, representing Steel ($e = 0.0$), to black, representing Activated Carbon ($e = 1.0$). Given the properties of the material model adopted, the interpretation of binary distribution of materials inside the domain is made on the 0.5 threshold. Figure 5.6b shows the convergence of the objective function, which presents a very smooth behaviour. The total density of gas, that is, the sum of gaseous and adsorbed phase density, is shown in Figure 5.6c for a domain fully occupied by Carbon ($\mathbf{e} = \mathbf{1.0}$) and for the optimised distribution of Steel. It can be seen that the gas inlet was reduced approximately in 3/4 in order to allow the growth of a metallic region along the center of tank extending the zone of high density of gas adsorbed, which was before limited to the inlet neighbourhood. It is due to the fact that the gas entering the domain is at room temperature (293 K) and creates a region of low temperature, which was extended because of the higher thermal conductivity of the Steel in relation to Activated Carbon, as shown in the temperature distribution plotted in Figure 5.6d. However, the increase of the gas density in this zone comes with the loss of adsorbent volume, as detailed in Section 3.1, making the net gain in the total mass of gas admitted being only 1.06%.

Cylindrical Tank (Table 5.2)	Domain	
	Heat Convection:	$h_{(\Gamma_W \cup \Gamma_F)} = 5 \text{ W m}^{-2} \text{K}^{-1}$
	Cycle	
	Time Length:	$t_{fin,a} = 10\,800 \text{ s}$, Fig. (3.3)
	Optimisation	
	Material Model:	$\epsilon = 0.02$, Eq. (3.13) $p = [20, 100]$, $\Delta p = 10$
	Iterations per Step:	$it_{max} = 10$
	Tolerance:	$\omega_{min} = 1.0 \times 10^{-6}$
	Filter Radius:	$z = 5 \times 10^{-3} \text{ m}$, Eq.(4.44)

Table 5.7: Optimisation definitions for a cylindrical domain subjected to natural convection.

Figure 5.6: Optimised design for a cylindrical domain subjected to natural convection.

5.3.2 Sensitivity to Thermal Conductivity

The non-adsorbent material considered when designing ANG tanks is not restricted to Steel only. Other metals with higher thermal conductivity, such as Aluminium, may be suitable in some cases. Aiming to verify that, a hypothetical material presenting conductivity four times higher than Steel is considered in the cycle defined in Table 5.8. Figure 5.7 shows a clear increase in the complexity of the metallic region connected to the inlet. Besides advancing further along the domain, this region presents more and thinner legs when compared to the optimisation performed with standard Steel properties - Figure 5.6. A new non-adsorbent region is also created from the wall opposite to the gas inlet, which would not compensate the loss in volume in the previous case. Figure 5.7d shows a clear reduction of the overall temperature within the domain, resulting in a net gain of 2.13% in the total mass of gas admitted. Therefore, the increase of the thermal conductivity of the non-adsorbent material has a positive impact on the optimisation of the ANG tanks considered in this work.

Cylindrical Tank (Table 5.2)	Domain	
	Materials:	$k_{non} = 188 \text{ W m}^{-2} \text{ K}^{-1}$
	Heat Convection:	$h_{(\Gamma_W \cup \Gamma_F)} = 5 \text{ W m}^{-2} \text{ K}^{-1}$
	Cycle	
	Time Length:	$t_{fin,a} = 10\,800 \text{ s}$, Fig. (3.3)
	Optimisation	
	Material Model:	$\epsilon = 0.02$, Eq. (3.13)
		$p = [20, 100]$, $\Delta p = 10$
	Iterations per Step:	$it_{max} = 10$
	Tolerance:	$\omega_{min} = 1.0 \times 10^{-6}$
	Filter Radius:	$z = 5 \times 10^{-3} \text{ m}$, Eq.(4.44)

Table 5.8: Optimisation definitions for a cylindrical domain with non-adsorbent material with high thermal conductivity.

Figure 5.7: Optimised design for a cylindrical domain with non-adsorbent material with high thermal conductivity.

5.3.3 Sensitivity to Heat Capacity

Extending the previous Section, the impact of the increase of the heat capacity of the non-adsorbent material is studied here. Materials presenting enough high heat capacity can be used to roughly approximate the impact of the insertion of Phase Change Materials (PCM) regions inside the domain - see Toledo et al. (2013) for more details about PCM operation. The specific heat capacity of Steel is multiplied by four, resulting in the problem defined in Table 5.9. Figure 5.8 shows the resulting topology for this case, where the non-adsorbent regions are not necessarily connected to the gas inlet or to the walls. The occurrence of this layout is due to the fact that materials with high heat capacity act as heat sinks. This approach seems more promising than using high conductive materials as it is reflected in the high gas density through the whole domain observed in Figure 5.8c. In the comparison with the homogeneous case, the the amount of gas admitted during the filling cycle is 6.30% higher when compared with the domain filled with Carbon only. The relative gain is even higher for shorter cycles. Table 5.10 defines a cycle lasting 3600 s, keeping all the other parameters the same. It can be seen in Figure 5.9 that more non-adsorbent islands were formed in order to take advantage of its high heat capacity. Such islands represent hoops as depicted in the revolved three-dimensional topology. It is important to highlight that this optimised domain admits more gas in 3600 s (2.31 kg) than the homogeneous does in 10 800 s (2.30 kg). This fact makes the use materials with high heat capacity very promising in fast-filling ANG tanks. Table 5.11 defines an even shorter cycle of 1200 s. In Figure 5.10, it can be seen that the non-adsorbent islands becomes smaller and are located nearer the axis of symmetry, in order to reduce the loss in adsorbent volume. However, the improvement is much smaller than on the previous ones: 2.89%. In this case, the cooling effect is constrained by the poor thermal conductivity of the Activated Carbon, given that the cycle is very short. That is, the non-adsorbent islands posses a very small radius of influence around them, as can be clearly seen in Figure 5.10d.

Cylindrical Tank (Table 5.2)	Domain	
	Materials:	$Cp_{non} = 1880 \text{ Jkg}^{-1}\text{K}^{-1}$
	Heat Convection:	$h_{(\Gamma_W \cup \Gamma_F)} = 5 \text{ W m}^{-2}\text{K}^{-1}$
	Cycle	
	Time Length:	$t_{fin,a} = 10\,800 \text{ s}$, Fig. (3.3)
	Optimisation	
	Material Model:	$\epsilon = 0.02$, Eq. (3.13)
		$p = [20, 100]$, $\Delta p = 10$
	Iterations per Step:	$it_{max} = 10$
	Tolerance:	$\omega_{min} = 1.0 \times 10^{-6}$
Filter Radius:	$z = 5 \times 10^{-3} \text{ m}$, Eq.(4.44)	

Table 5.9: Optimisation definitions for a cylindrical domain with non-adsorbent material with high heat capacity.

Cylindrical Tank (Table 5.2)	Domain	
	Materials:	$Cp_{non} = 1880 \text{ Jkg}^{-1}\text{K}^{-1}$
	Heat Convection:	$h_{(\Gamma_W \cup \Gamma_F)} = 5 \text{ W m}^{-2}\text{K}^{-1}$
	Cycle	
	Time Length:	$t_{fin,a} = 3600 \text{ s}$, Fig. (3.3)
	Optimisation	
	Material Model:	$\epsilon = 0.02$, Eq. (3.13)
		$p = [20, 100]$, $\Delta p = 10$
	Iterations per Step:	$it_{max} = 10$
	Tolerance:	$\omega_{min} = 1.0 \times 10^{-6}$
Filter Radius:	$z = 5 \times 10^{-3} \text{ m}$, Eq.(4.44)	

Table 5.10: Optimisation definitions for a cylindrical domain with non-adsorbent material with high heat capacity in 3600 s filling cycle.

Figure 5.8: Optimised design for a cylindrical domain with non-adsorbent material with high heat capacity.

Figure 5.9: Optimised design for a cylindrical domain with non-adsorbent material with high heat capacity in 3600 s filling cycle.

Cylindrical Tank (Table 5.2)	Domain	
	Materials:	$Cp_{non} = 1880 \text{ Jkg}^{-1}\text{K}^{-1}$
	Heat Convection:	$h_{(\Gamma_W \cup \Gamma_F)} = 5 \text{ W m}^{-2}\text{K}^{-1}$
	Cycle	
	Time Length:	$t_{fin,a} = 1200 \text{ s}$, Fig. (3.3)
	Optimisation	
	Material Model:	$\epsilon = 0.02$, Eq. (3.13)
		$p = [20, 100]$, $\Delta p = 10$
	Iterations per Step:	$it_{max} = 10$
	Tolerance:	$\omega_{min} = 1.0 \times 10^{-6}$
	Filter Radius:	$z = 5 \times 10^{-3} \text{ m}$, Eq.(4.44)

Table 5.11: Optimisation definitions for a cylindrical domain with non-adsorbent material with high heat capacity in 1200 s filling cycle.

Figure 5.10: Optimised design for a cylindrical domain with non-adsorbent material with high heat capacity in 1200 s filling cycle.

5.4 Design of ANG Tanks with Active Thermal Management

This Section considers tanks filled with the aid of some external work for the thermal management, such as the imposition of forced convection or low temperature at some point of the domain. The latter approach is adopted in Vasiliev et al. (2014), where fins linked to a very cold wall, at 233 K, are distributed radially along an adsorbent cylinder.

5.4.1 Tanks Subjected to Forced Convection

The resulting topology depicted in Figure 5.11 shows perfectly symmetric fins connecting the central region of the section to the walls subjected to forced convection. Such symmetry is due to the use of a regular mesh constituted by equal elements. Figure 5.11d shows that the fins made the maximum temperature inside the domain drop from 325 K to 310 K, allowing 5.46% more gas to be admitted during the filling cycle. An instability is seen on Figure 5.11b for the convergence of the objective function due to the increase of the penaliser from $p_{ini} = 20$ to $p = 30$.

Prismatic Tank (Table 5.1)	Domain	
	Heat Convection:	$h_{\Gamma_W} = 100 \text{ Wm}^{-2}\text{K}^{-1}$
	Optimisation	
	Material Model:	$\epsilon = 0.02$ $p = [1, 51], \Delta p = 5, \text{ Eq. (3.13)}$
	Iterations per Step:	$it_{max} = 20$
	Tolerance:	$\omega_{min} = 1.0 \times 10^{-6}$
	Filter Radius:	$z = 5 \times 10^{-3} \text{ m, Eq.(4.44)}$

Table 5.12: Optimisation definitions for a prismatic domain subjected to forced convection.

Figure 5.11: Optimised design for a prismatic domain subjected to forced convection.

5.4.2 Sensitivity to Forced Convection and Cold Walls

In order to study the impact of different thermal boundary conditions, the complex-shaped axisymmetric domain defined in 5.3 is adopted. Initially, forced convection is considered by imposing $h = 100 \text{ Wm}^{-1}\text{K}^{-1}$, as defined in Table 5.13. The resulting topology shown in Figure 5.12 presents the trend of growing Steel fins from concave corners. Such behaviour is justified by the temperature distribution in the homogeneous case observed in Figure 5.12d. These corners are the regions with steepest temperature gradient from points on the wall towards the inside of the domain. Accordingly, the curved shape acquired by the fins coincide almost perfectly with the path of maximum gradient. Based on this approach, the optimised domain is able to admit 1.23% more gas than the homogeneous one. By increasing the convective coefficient to $h = 700 \text{ Wm}^{-1}\text{K}^{-1}$, small changes are observed. The most prominent change in the topology shown in Figure 5.12 is the fork of one of the fins. However, a very reticent relative gain is obtained in relation to the first case: 1.94% in total gas mass admitted. Therefore, the energy required to increase the convective heat transfer in the second case is reasonable. The case defined in Table 5.15 keeps the natural convection on the walls expect for the region Γ_F , which is kept at the fixed temperature of 273 K. As seen in Figure 5.14, the low temperature makes the corners on Γ_F preferred for the creation of fins. In Figure 5.14c, it can be clearly seen that the vicinity of the fins connected to the cold wall becomes the zone presenting the highest densities of gas, improving the total gas admission during the filling cycle in 7.51% when compared to the homogeneous case.

Custom Axisymmetric Tank (Table 5.3)	Domain	
	Heat Convection:	$h_{(\Gamma_W \cup \Gamma_F)} = 100 \text{ W m}^{-2} \text{K}^{-1}$
	Cycle	
	Time Length:	$t_{fin,a} = 3600 \text{ s}$, Fig. (3.3)
	Optimisation	
	Material Model:	$\epsilon = 0.02$, Eq. (3.13) $p = [20, 100]$, $\Delta p = 10$
	Iterations per Step:	$it_{max} = 10$
	Tolerance:	$\omega_{min} = 1.0 \times 10^{-6}$
	Filter Radius:	$z = 5 \times 10^{-3} \text{ m}$, Eq.(4.44)

Table 5.13: Optimisation definitions for a custom axisymmetric domain subjected to forced convection with $h = 100 \text{ Wm}^{-2} \text{K}^{-1}$.

Custom Axisymmetric Tank (Table 5.3)	Domain	
	Heat Convection:	$h_{(\Gamma_W \cup \Gamma_F)} = 700 \text{ W m}^{-2} \text{K}^{-1}$
	Cycle	
	Time Length:	$t_{fin,a} = 3600 \text{ s}$, Fig. (3.3)
	Optimisation	
	Material Model:	$\epsilon = 0.02$, Eq. (3.13) $p = [20, 100]$, $\Delta p = 10$
	Iterations per Step:	$it_{max} = 10$
	Tolerance:	$\omega_{min} = 1.0 \times 10^{-6}$
	Filter Radius:	$z = 5 \times 10^{-3} \text{ m}$, Eq.(4.44)

Table 5.14: Optimisation definitions for a custom axisymmetric domain subjected to forced convection with $h = 700 \text{ Wm}^{-2} \text{K}^{-1}$.

Figure 5.12: Optimised design for a custom axisymmetric domain subjected to forced convection with $h = 100 \text{ Wm}^{-2}\text{K}^{-1}$.

Figure 5.13: Optimised design for a custom axisymmetric domain subjected to forced convection with $h = 700 \text{ Wm}^{-2}\text{K}^{-1}$.

Custom Axisymmetric Tank (Table 5.3)	Domain	
	Heat Convection:	$h_{\Gamma_W} = 5 \text{ Wm}^{-2}\text{K}^{-1}$
	Cold Finger:	$T_{\Gamma_F} = 273 \text{ K}$
	Cycle	
	Time Length:	$t_{fin,a} = 3600 \text{ s}$, Fig. (3.3)
	Optimisation	
	Material Model:	$\epsilon = 0.02$, Eq. (3.13)
		$p = [20, 100]$, $\Delta p = 10$
	Iterations per Step:	$it_{max} = 10$
	Tolerance:	$\omega_{min} = 1.0 \times 10^{-6}$
	Filter Radius:	$z = 5 \times 10^{-3} \text{ m}$, Eq.(4.44)

Table 5.15: Optimisation definitions for a custom axisymmetric domain subjected to natural convection and connected to a cold finger.

Figure 5.14: Optimised design for a cylindrical domain with forced convection.

5.4.3 Sensitivity to Shape Complexity

The cases tested in the previous Section are repeated for a cylindrical tank, in order to identify the contribution of the external shape complexity to the optimisation. Forced convection is imposed on the cylindrical tank, as defined in Table 5.16. As seen in Figure 5.15, such convection urges the appearance of metallic fins on the wall opposite to the inlet. The main reason for such fins appearing there is the adiabatic condition imposed on the bottom line due to the axisymmetry. In the temperature distribution shown for the homogeneous case in Figure 5.15d it can be seen that the axisymmetry makes the gradient along the bottom line near the walls to be the steepest.

By shortening the cycle defined in Table 5.16 to 3600 s, the volume occupied by the fins are slight smaller, although maintaining the roughly the same layout. The fins on the middle of the vertical walls are longer because the gradient of temperature there is approximately the same of the one observed on the bottom line for a short cycle, as shown in Figure 5.16d.

Keeping natural convection on the short cycle and imposing a cold region on Γ_F results in the topology shown in Figure 5.17. The presence of such condition stimulate the grow of fins from Γ_F and leads to a net gain in the mass of gas admitted of 2.47%.

Cylindrical Tank (Table 5.2)	Domain
	Heat Convection: $h_{(\Gamma_W \cup \Gamma_F)} = 700 \text{ W m}^{-2} \text{K}^{-1}$
	Cycle
	Time Length: $t_{fin,a} = 10\,800 \text{ s}$, Fig. (3.3)
	Optimisation
	Material Model: $\epsilon = 0.02$, Eq. (3.13)
	$p = [20, 100]$, $\Delta p = 10$
	Iterations per Step: $it_{max} = 10$
	Tolerance: $\omega_{min} = 1.0 \times 10^{-6}$
	Filter Radius: $z = 5 \times 10^{-3} \text{ m}$, Eq.(4.44)

Table 5.16: Optimisation definitions for a cylindrical domain with forced convection in 10 800 s filling cycle.

Figure 5.15: Optimised design for a cylindrical domain with forced convection in 10 800 s filling cycle.

Cylindrical Tank (Table 5.2)	Domain	
	Heat Convection:	$h_{(\Gamma_W \cup \Gamma_F)} = 700 \text{ W m}^{-2} \text{K}^{-1}$
	Cycle	
	Time Length:	$t_{fin,a} = 3600 \text{ s}$, Fig. (3.3)
	Optimisation	
	Material Model:	$\epsilon = 0.02$, Eq. (3.13) $p = [20, 100]$, $\Delta p = 10$
	Iterations per Step:	$it_{max} = 10$
	Tolerance:	$\omega_{min} = 1.0 \times 10^{-6}$
	Filter Radius:	$z = 5 \times 10^{-3} \text{ m}$, Eq.(4.44)

Table 5.17: Optimisation definitions for a cylindrical domain with forced convection in 3600 s filling cycle.

Cylindrical Tank (Table 5.2)	Domain	
	Heat Convection:	$h_{\Gamma_W} = 5 \text{ W m}^{-2} \text{K}^{-1}$
	Cold Finger:	$T_{\Gamma_F} = 273 \text{ K}$
	Cycle	
	Time Length:	$t_{fin,a} = 3600 \text{ s}$, Fig. (3.3)
	Optimisation	
	Material Model:	$\epsilon = 0.02$, Eq. (3.13) $p = [20, 100]$, $\Delta p = 10$
	Iterations per Step:	$it_{max} = 10$
	Tolerance:	$\omega_{min} = 1.0 \times 10^{-6}$
	Filter Radius:	$z = 5 \times 10^{-3} \text{ m}$, Eq.(4.44)

Table 5.18: Optimisation definitions for a cylindrical domain subjected to natural convection and connected to a cold finger.

Figure 5.16: Optimised design for a cylindrical domain with forced convection in 3600 s filling cycle.

Figure 5.17: Optimised design for a cylindrical domain with natural convection and cold finger.

5.4.4 Sensitivity to Tank Dimensions

Prismatic tanks with different sizes of cross section are optimised aiming to evaluate the sensitivity of the method to tank dimensions. The optimisation of the narrow tanks defined in Table 5.20 is performed with the proportional reduction of the Helmholtz filter radius. In the resulting topology presented in Figure 5.18, it is seen a smaller penetration of the fins towards the center of the domain. However, the distance between the tips of opposite fins are barely the same when compared to the optimised topology for the analogous 0.25 m tank presented in Figure 5.11. This distance is determined by Activated Carbon heat conduction. Figure 5.18c shows very small gradients in the distribution of gas density when compared to the 0.25 m reference. While in the homogeneous reference the minimal density observed is 24.74 kg, here it is 29.47 kg, making the loss of adsorbent volume to fins less advantageous. In fact, the improvement of gas intake is much smaller in the small domain: 0.39 kg.

Table 5.19 defines a large prismatic tank, with the proportional increase of the Helmholtz radius filter. The resulting topology shown in Figure 5.19 presents many more fins than in the smaller tanks. The pseudo-porosity distribution in Figure 5.19a shows the formation of perfect squared region on the middle of the domain where the value of the design variables is very near to $e = 1.0$. The grey margin presents a thickness of approximately 0.12 m, suggesting that beyond this point the loss in volume for fins is not compensatory. It can be seen in Figure 5.19b that many pseudo-porosity distributions were rejected by L-BFGS-B while the penalisation was weak, evolving to a smooth convergence for higher penalisation. Figure 5.19c makes clear that little improvement could be achieved in the central tank region. The focus of the optimisation was to adsorb more gas near the walls, leaving the central region almost unchanged. The improvement in the mass of gas admitted is roughly equivalent to the gain presented for the 0.25 m reference: 5.54%.

5.4.5 Sensitivity to Filling Pressure

The optimisation of ANG tanks are highly dependent on its filling pressure. Aiming to demonstrate the topology changes caused by the pressure increase, the problem described in Table 5.13 is used as reference. By increasing the filling pressure from 1.00 MPa to 3.00 MPa, the topology shown in Figure 5.20 is obtained. In contrast to the resulting topology for 1.00 MPa, it can be seen that the higher gas flow rate is enough to cool down a large area around the inlet. Therefore, fins connected to the inlet region are less interesting in this case, given that a large volume of cold adsorbent would be lost. Fins

Prismatic Tank (Table 5.1)	Domain	
	Dimensions:	$L = 0.10 \text{ m}$
	Heat Convection:	$h_{\Gamma_W} = 100 \text{ Wm}^{-2}\text{K}^{-1}$
	Cycle	
	Time Length:	$t_{fin,a} = 10\,800 \text{ s}$, Fig. (3.3)
	Optimisation	
	Material Model:	$\epsilon = 0.02$, Eq. (3.13)
		$p = [20, 100]$, $\Delta p = 10$
	Iterations per Step:	$it_{max} = 10$
	Tolerance:	$\omega_{min} = 1.0 \times 10^{-6}$
	Filter Radius:	$z = 2 \times 10^{-3} \text{ m}$, Eq.(4.44)

Table 5.19: Optimisation definitions for a small prismatic domain subjected to forced convection.

Prismatic Tank (Table 5.1)	Domain	
	Dimensions:	$L = 0.40 \text{ m}$
	Heat Convection:	$h_{\Gamma_W} = 100 \text{ Wm}^{-2}\text{K}^{-1}$
	Cycle	
	Time Length:	$t_{fin,a} = 10\,800 \text{ s}$, Fig. (3.3)
	Optimisation	
	Material Model:	$\epsilon = 0.02$, Eq. (3.13)
		$p = [20, 100]$, $\Delta p = 10$
	Iterations per Step:	$it_{max} = 10$
	Tolerance:	$\omega_{min} = 1.0 \times 10^{-6}$
	Filter Radius:	$z = 8 \times 10^{-3} \text{ m}$, Eq.(4.44)

Table 5.20: Optimisation definitions for a small prismatic domain subjected to forced convection.

are then place on the nearest concave corner, producing a slight temperature reduction in the region, which results in an improvement of 0.23% on the intake mass of gas. Such gain is much smaller than the one obtained for the reference case, demonstrating that the addition of fins are more suitable on the design of low pressure ANG tanks.

By increasing the filling pressure to 5.00 MPa, as defined in Table 5.22, the fins are

Figure 5.18: Optimised design for a small prismatic domain subjected to forced convection.

placed farther than the inlet region, as shown in Figure 5.21. This shift is explained by extending the points listed on the 3.00 MPa case. The 5.00 MPa pressure intensified the cooling effect produced near the inlet region, as seen in Figure 5.21d. Interestingly, the improvement achieved here is slightly higher than in the 3.00 MPa case: 0.58%. Such improvement is mainly due to the creation of a fin on the next concave corner, which was able to reduce the maximum temperature inside the optimised tank to around 320 K.

Figure 5.19: Optimised design for a large prismatic domain subjected to forced convection.

Custom Axisymmetric Tank (Table 5.3)	Domain	
	Heat Convection:	$h_{(\Gamma_W \cup \Gamma_F)} = 100 \text{ W m}^{-2} \text{K}^{-1}$
	Cycle	
	Time Length:	$t_{fin,a} = 3600 \text{ s}$, Fig. (3.3)
	Final Pressure:	$P_{let} = 3.00 \text{ MPa}$
	Optimisation	
	Material Model:	$\epsilon = 0.02$, Eq. (3.13)
		$p = [20, 100]$, $\Delta p = 10$
	Iterations per Step:	$it_{max} = 10$
	Tolerance:	$\omega_{min} = 1.0 \times 10^{-6}$
	Filter Radius:	$z = 5 \times 10^{-3} \text{ m}$, Eq.(4.44)

Table 5.21: Optimisation definitions for a custom axisymmetric domain subjected to 3.00 MPa filling pressure and forced convection with $h = 100 \text{ Wm}^{-2} \text{K}^{-1}$.

Custom Axisymmetric Tank (Table 5.3)	Domain	
	Heat Convection:	$h_{(\Gamma_W \cup \Gamma_F)} = 100 \text{ W m}^{-2} \text{K}^{-1}$
	Cycle	
	Time Length:	$t_{fin,a} = 3600 \text{ s}$, Fig. (3.3)
	Final Pressure:	$P_{let} = 5.00 \text{ MPa}$
	Optimisation	
	Material Model:	$\epsilon = 0.02$, Eq. (3.13)
		$p = [20, 100]$, $\Delta p = 10$
	Iterations per Step:	$it_{max} = 10$
	Tolerance:	$\omega_{min} = 1.0 \times 10^{-6}$
	Filter Radius:	$z = 5 \times 10^{-3} \text{ m}$, Eq.(4.44)

Table 5.22: Optimisation definitions for a custom axisymmetric domain subjected to 5.00 MPa filling pressure and forced convection with $h = 100 \text{ Wm}^{-2} \text{K}^{-1}$.

Figure 5.20: Optimised design for a custom axisymmetric domain subjected to 3 MPa filling pressure and forced convection with $h = 100 \text{ Wm}^{-2}\text{K}^{-1}$.

Figure 5.21: Optimised design for a custom axisymmetric domain subjected to 5 MPa filling pressure and forced convection with $h = 100 \text{ Wm}^{-2}\text{K}^{-1}$.

6 Conclusions

The main goal of the research presented in this work was to formulate and evaluate the use of topology optimisation for designing adsorption systems. Among the several applications of such systems, Adsorbed Natural Gas (ANG) tanks have been chosen to be the focus of this work. Accordingly, a comprehensive model for ANG tanks is presented, including the kinetics of adsorption and the variation of adsorbent properties in function to the porosities. The solution of the resulting set of PDEs governing the adsorption problem is obtained via the Finite Element Method (FEM). The procedure to assemble the FEM matrices from the PDEs weak form is described in detail. The concept of including non-adsorbent materials inside ANG tanks aiming to improve their thermal management is then introduced. The optimisation of the distribution of adsorbent and non-adsorbent materials inside the tank is approached via topology optimisation. The implementation of this method is based on the calculation of the sensitivities via the adjoint method for transient systems, which is comprehensively presented. Resulting optimised topologies are presented for ANG tanks applied to on-demand consumption. The optimisation of tanks with different shapes is tackled and the impact of parameters such as material properties, filling pressure, cycle duration and tank dimensions are studied.

A major scientific contribution presented in this work is the derivation of the full formulation of a gradient-based PDE-constrained optimisation of adsorption systems. Such derivation includes the statement of the weak and discrete formulation of the adsorption problem for FEM implementation and the derivation of the adjoint problem from the augmented Lagrangian form of the functional of interest. Additionally, a material model based on hyperbolic tangents (OHT) is introduced. Such model has shown to be more efficient than traditional ones for the design of biphasic structures. It is due to its novel penalisation approach combined with offsets.

Several ANG tanks optimised according to the distribution of cooling material across

the adsorbent bed are presented in this work. Designs include axisymmetric and prismatic tanks subjected to natural convection and active thermal boundary conditions. By the results presented, it is concluded that small improvement is achievable by the addition of metallic fins in tanks subjected to natural convection. For the cycles and domain sizes considered, tanks subjected to natural convection presented insufficient improvement in order to justify the cost of including regions constituted by non-adsorbent material across the adsorbent bed. Similarly, small improvement is observed in high pressure tanks. The relative improvement achievable in high pressure tanks is smaller than the ones working at low pressure. It suggests that the design concept adopted by this work is more suitable for low pressure ANG tanks.

In contrast, the insertion of non-adsorbent regions in ANG tanks is very effective when associated with cold regions. It is due to the fact that materials with high conductivity depend on meaningful temperature gradients in order to aid heat transfer across the tank. Such fact is reinforced by the resulting topologies presenting metallic regions around tanks concave corners, where the temperature gradients are higher. Also, materials presenting high heat capacity constitute a suitable solution for passive thermal management. In opposition to phases presenting typical metallic properties, materials with high heat capacity are not dependent on the existence of cold regions in the domain. Results have shown that islands constituted by materials presenting high heat capacity act as a heat sink, creating a zone of influence in the temperature field.

Altogether, adsorbent's low conductivity can represent a limiting issue. In fast adsorption cycles, any optimisation attempt is hindered by the extremely low conductivity of adsorbent materials. It is demonstrated by the reduction of the zone of influence of regions constituted by high capacity materials as the cycles considered gets shorter. Therefore, the design concept presented in this work is complementary to further development of adsorbent materials.

This thesis provides the basis for several future work. The formulation presented here is easily extended to storage and transport applications, by including the desorption cycle in the objective function. Additionally, since results have shown that complex-shaped tanks present better performance than traditional ones. Therefore, it is promising to complement the optimisation of the adsorbent bed with the optimisation of the external shape, by either shape or topology optimisation. Furthermore, given the promising results obtained for non-adsorbent material with high heat capacity, the use of Phase Change Materials (PCMs) is very promising for any application. It consists of including an additional governing equation in order to model the phase change kinetics, leading to new

source terms in the energy balance.

Due to the numerical focus of this work, manufacturing issues have been addressed marginally only. Yet, the literature review in this matter indicated relative ease for conforming adsorbent beds in any desired geometry by pouring and compacting a slurry constituted by binder-coated carbon particles inside tank segments. Manufacturing complexity depend mainly on the construction of non-adsorbent parts, which can be done via traditional methods such as machining and casting, in the case of metals. However, despite such preliminary indications, further research on this topics is necessary.

Finally, the work presented here is naturally extendible to any other adsorption application. Fluid separation, refrigeration and Carbon Capture and Storage (CCS) are some of the possible applications for adsorption systems that could be explored based on this research.

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Appendix A. Finite Element Coefficients

This chapter presents the integral form of the coefficients of the FEM systems given in Chapter 4.

A.1 Full Adsorption Problem

$$W(T) = \int_{\omega} [2\pi r] \frac{M_g(\Xi^T \varepsilon_t)}{R_g(\Psi^T \mathbf{T})} \Phi \Phi^T d\mathbf{x}. \quad (\text{A.1})$$

$$S(P, T) = \int_{\omega} [2\pi r] \frac{M_g(\Xi^T \varepsilon_t)(\Phi^T \mathbf{P})}{R_g(\Psi^T \mathbf{T})^2} \Phi \Psi^T d\mathbf{x}. \quad (\text{A.2})$$

$$\begin{aligned} Z(P, T) &= \int_{\omega} [2\pi r] \frac{M_g(\Xi^T \mathbf{K}_s)(\Phi^T \mathbf{P})}{R_g \mu_g(\Psi^T \mathbf{T})} \nabla \Phi \nabla \Phi^T d\mathbf{x} \\ &\quad - \int_{\gamma_w} [2\pi r] \frac{M_g(\Xi^T \mathbf{K}_s)(\Phi^T \mathbf{P})}{R_g \mu_g(\Psi^T \mathbf{T})} \Phi \nabla \Phi^T ds. \end{aligned} \quad (\text{A.3})$$

$$J = \int_{\omega} [2\pi r] (\Xi^T \varepsilon_t) \Psi \Phi^T d\mathbf{x}. \quad (\text{A.4})$$

$$\begin{aligned} N(P, T, Q) &= \int_{\omega} [2\pi r] \frac{C p_g M_g(\Xi^T \varepsilon_t)(\Phi^T \mathbf{P})}{R_g(\Psi^T \mathbf{T})} \Psi \Psi^T d\mathbf{x} \\ &\quad + \int_{\omega} [2\pi r] C p_g (\Xi^T \mathbf{Q}) \Psi \Psi^T d\mathbf{x} \\ &\quad + \int_{\omega} [2\pi r] (1 - \Xi^T \varepsilon_t) (\Xi^T \mathbf{C} \mathbf{p}_s) (\Xi^T \rho_s) \Psi \Psi^T d\mathbf{x}. \end{aligned} \quad (\text{A.5})$$

$$L(P, T) = - \int_{\omega} [2\pi r] \frac{Cp_g M_g (\Xi^T \mathbf{K}_s) (\Phi^T \mathbf{P})}{R_g \mu_g (\Psi^T \mathbf{T})} (\nabla \Phi^T \mathbf{P}) \nabla \Psi \nabla \Psi^T d\mathbf{x}. \quad (\text{A.6})$$

$$K = \int_{\omega} [2\pi r] (\Xi^T \mathbf{k}_f) \nabla \Psi \nabla \Psi^T d\mathbf{x} - \int_{\gamma_W} [2\pi r] (\Xi^T \mathbf{k}_f) \Psi \nabla \Psi^T ds. \quad (\text{A.7})$$

$$Y_M = \int_{\omega} [2\pi r] \Phi \Xi^T dx. \quad (\text{A.8})$$

$$Y_E = \int_{\omega} -[2\pi r] |\Delta H| \Psi \Xi^T dx. \quad (\text{A.9})$$

$$Y_D = \int_{\omega} [2\pi r] \Xi \Xi^T dx. \quad (\text{A.10})$$

$$R(T) = \int_{\omega} [2\pi r] (\Xi^T \mathbf{G}) \Xi \Xi^T dx. \quad (\text{A.11})$$

$$V(P, T) = \int_{\omega} [2\pi r] (\Xi^T \mathbf{G}) (\Xi^T \mathbf{Q}_{\text{eq}}) \Xi dx. \quad (\text{A.12})$$

A.2 Adsorption Problem after Decoupling the Adsorbed Density Field

$$F = - \int_{\omega} [2\pi r] \left(\Xi^T \frac{\partial \mathbf{Q}}{\partial t} \right) \Phi d\mathbf{x}. \quad (\text{A.13})$$

$$H = \int_{\omega} [2\pi r] |\Delta H| \left(\Xi^T \frac{\partial \mathbf{Q}}{\partial t} \right) \Psi d\mathbf{x}. \quad (\text{A.14})$$

A.3 Adsorption Problem after Decoupling the Pressure Field

$$W = \int_{\omega} [2\pi r] (\Xi^T \varepsilon_t) (\Xi^T \frac{\partial \rho_g}{\partial t}) \Phi \Phi^T d\mathbf{x}. \quad (\text{A.15})$$

$$\begin{aligned} Z &= \int_{\omega} [2\pi r] \frac{(\Xi^T \mathbf{K}_s)(\Xi^T \rho_g)}{\mu_g} \nabla \Phi \nabla \Phi^T d\mathbf{x} \\ &\quad - \int_{\gamma_W} [2\pi r] \frac{(\Xi^T \mathbf{K}_s)(\Xi^T \rho_g)}{\mu_g} \Phi \nabla \Phi^T ds. \end{aligned} \quad (\text{A.16})$$

$$F = - \int_{\omega} [2\pi r] \left(\Xi^T \frac{\partial \mathbf{Q}}{\partial t} \right) \Phi d\mathbf{x}. \quad (\text{A.17})$$

$$\begin{aligned} N &= \int_{\omega} [2\pi r] (\Xi^T \varepsilon_t) C p_g (\Xi^T \rho_g) \Psi \Psi^T d\mathbf{x} \\ &+ \int_{\omega} [2\pi r] \left(1 - (\Xi^T \varepsilon_t) \right) (\Xi^T C p_s) (\Xi^T \rho_s) \Psi \Psi^T d\mathbf{x} \\ &\quad + \int_{\omega} [2\pi r] C p_g (\Xi^T \mathbf{Q}) \Psi \Psi^T d\mathbf{x}. \end{aligned} \quad (\text{A.18})$$

$$L = - \int_{\omega} [2\pi r] \frac{C p_g M_g (\Xi^T \mathbf{K}_s) (\Phi^T \mathbf{P})}{R_g \mu_g (\Psi^T \mathbf{T})} (\nabla \Phi^T \mathbf{P}) \nabla \Psi \nabla \Psi^T d\mathbf{x}. \quad (\text{A.19})$$

$$\begin{aligned} K &= \int_{\omega} [2\pi r] (\Xi^T \mathbf{k}_f) \nabla \Psi \nabla \Psi^T d\mathbf{x} \\ &\quad - \int_{\gamma_W} [2\pi r] (\Xi^T \mathbf{k}_f) \Psi \nabla \Psi^T ds. \end{aligned} \quad (\text{A.20})$$

$$H = \int_{\omega} [2\pi r] (\Xi^T \varepsilon_t) \left(\Xi^T \frac{\partial \mathbf{P}}{\partial t} \right) \Psi d\mathbf{x} + \int_{\omega} [2\pi r] |\Delta H| \left(\Xi^T \frac{\partial \mathbf{Q}}{\partial t} \right) \Psi d\mathbf{x}. \quad (\text{A.21})$$

A.4 Helmholtz Filtering

The interpolation of the pseudo-porosities is done over a finite element by using the shape function ξ as

$$\mathbf{e}(\mathbf{x}, t) \cong \sum_{l=1}^L \xi_l(\mathbf{x}) \mathbf{e}(t) = \mathbf{\Xi}^T \mathbf{e}. \quad (\text{A.22})$$

Making $v_H = \xi$, the FEM system is assembled based on the coefficients

$$Z = \int_{\omega} \mathbf{\Xi} \mathbf{\Xi}^T d\mathbf{x} + \int_{\omega} z^2 \nabla \mathbf{\Xi} \nabla \mathbf{\Xi}^T d\mathbf{x}, \quad (\text{A.23})$$

$$\mathbf{\phi} = \int_{\omega} (\mathbf{\Xi}^T \mathbf{\phi}) \mathbf{\Xi} d\mathbf{x}. \quad (\text{A.24})$$

Appendix B. Material Properties

Table B.1: Methane properties (SAHOO et al., 2011; SAHOO; RAMGOPAL, 2014).

Property	Symbol	Value	Unit
Specific Heat	Cp_g	14 890	$\text{J kg}^{-1}\text{K}^{-1}$
Thermal Conductivity	k_g	34.30×10^{-3}	$\text{W m}^{-1}\text{K}^{-1}$
Molar Mass	M_g	16.03×10^{-3}	kg mol^{-1}
Critical Pressure	P_{cr}	4.60×10^6	Pa
Boiling Point Temperature	T_{boil}	111.2	K
Critical Temperature	T_{cr}	191	K
Thermal Expansion of Liquefied Gases	α_e	2.50×10^{-3}	K^{-1}
Density at Boiling Point	ρ_{boil}	422.62	kg m^{-3}
Viscosity	μ_g	12.50×10^{-6}	Pa s

Table B.2: Activated Carbon properties (SAHOO et al., 2011).

Property	Symbol	Value	Unit
Bulk Specific Heat	Cp_s	650	$\text{J kg}^{-1}\text{K}^{-1}$
Bulk Thermal Conductivity	k_s	0.54	$\text{W m}^{-1}\text{K}^{-1}$
Micro-Pores Dispersion	n_s	1.8	
Specific Volume of Micro-Pores	w	0.33×10^{-3}	$\text{m}^3 \text{kg}^{-1}$
Particle Diameter	ϕ_s	1.00×10^{-3}	m
Macro-Porosity	ε_M	0.3	
Micro-Porosity	ε_m	0.5	
Bulk Density	ρ_s	1428.57	kg m^{-3}
Micro-Pore Tortuosity	τ_s	2.08	

Table B.3: Adsorption parameters for Methane on Activated Carbon (SAHOO et al., 2011; SAHOO; RAMGOPAL, 2014).

Parameter	Symbol	Value	Unit
Effective Gas Diffusivity	D_0	8.00×10^{-7}	$\text{m}^2 \text{s}^{-1}$
Characteristic Energy	E_0	25 040	J mol^{-1}
Activation Energy of Adsorption	E_a	6000	J mol^{-1}
Activation Energy of Desorption ¹	E_d	22 000	J mol^{-1}
Affinity Coefficient	β	0.35	
Isosteric Heat of Adsorption	ΔH	$-16\,000 \times 10^3$	J mol^{-1}

¹ Calculated from E_a and ΔH values (CHRISTMANN, 1991).

Table B.4: Steel properties.

Parameter	Symbol	Value	Unit
Specific Heat	Cp_s	470	$\text{J kg}^{-1}\text{K}^{-1}$
Thermal Conductivity	k_s	47	$\text{W m}^{-1}\text{K}^{-1}$
Density	ρ_s	7900	kg m^{-3}
Permeability ¹	K_s	1.00×10^{-22}	m^2

¹ Approximation adopted for representing impermeable medium.