Master Degree in Mechanical Engineering

Multi Scale CFD Modelling of Reactive Flows Inside Open-Cell Foams for After Treatment Systems of Internal Combustion Engines

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To my grandmother Graziella,
who taught me to read and write.
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Abstract

Within the context of reducing the pollutant emissions of internal combustion engines, this thesis work aims at the development of CFD models for the simulation of the physical and chemical phenomena occurring in open cell foams for the after treatment system of ICE. In particular, the finite volume open-source CFD code OpenFOAM® is applied. Different approaches, characterised by an increasing level of detail and computational effort, are considered. The most accurate approach is based on a micro-scale analysis of a sample and provides a complete characterisation analysing those parameters that mostly influence the fluid-dynamical, thermal and chemical behaviour of an open-cell foam. Moreover, because of its significative computational effort, the detailed approach is exploited as a support tool for the development of macro-scale numerical models. This up-scaling process has required the implementation of a specific library for the modelling of the macro scale chemical phenomena. The model is tested and its results are discussed and compared to the ones provided by micro scale simulations.

Key-words: OpenFOAM®, CFD, Internal combustion engines, Open-Cell foams, Mass transfer coefficient, Catalytic converter, Chemistry, Micro-scale, Macro-scale.
Il presente lavoro di tesi si vuole inserire all’interno della delicata e complessa catena di progettazione di un catalizzatore trivalente per motori a combustione interna (MCI). È questo un componente che negli ultimi decenni, a fronte soprattutto della sempre maggiore sensibilità verso lo sviluppo sostenibile, ha suscitato un crescente interesse da parte della comunità scientifica internazionale.

La progettazione in ambito motoristico a partire dagli anni ’60 è andata incontro a un notevole mutamento, la cui principale causa è da ricercarsi nello sviluppo di calcolatori sempre più performanti e compatti e nella nascita di nuove branche dell’ingegneria ad essi associate. Tra queste la cosiddetta CFD (Fluidodinamica Computazionale), rappresenta una delle discipline più complesse ed affascinanti, il cui continuo sviluppo fornisce notevoli impulsi allo scenario industriale. Basti pensare che fino anni ’70 la progettazione di un motore, svolta interamente su carta, giungeva a pieno sviluppo dopo anni di prototipazione con rendimenti e prestazioni notevolmente inferiori a quelli attuali. La non piena consapevolezza dei fenomeni fisici richiedeva lunghi tempi di sperimentazione. In questo contesto la CFD è stata una vera e propria rivoluzione, che ha permesso di simulare il funzionamento di un MCI e di “guardarci” all’interno durante il suo ciclo apprezzando i fenomeni che lo regolano.

In questo scenario si colloca il presente lavoro di tesi che impiega la CFD come strumento per la simulazione dei complessi fenomeni che avvengono all’interno di un catalizzatore trivalente. In particolar modo, l’attenzione è rivolta verso l’impiego di un supporto catalitico innovativo: si tratta delle cosiddette schiume a celle aperte. Queste hanno suscitato negli ultimi venti anni un crescente interesse da parte della comunità scientifica sia per le loro interessanti caratteristiche tecnologiche (flessibilità progettuale) sia geometriche (superficie specifica, diametro delle celle, etc.) e primi studi hanno evidenziato la possibilità di realizzare catalizzatori più compatti a pari prestazioni, con un notevole risparmio in termini di metalli nobili impiegati e di costo.

La simulazione CFD tuttavia ha di per sé un grosso limite rappresentato dalle risorse di calcolo disponibili: questo fa sì che ancora oggi (e probabilmente per i prossimi decenni) non sia possibile simulare un motore con un
elevato livello di dettaglio su tutti i suoi singoli componenti. Ciò ha portato alla cosiddetta analisi multi-scala ampiamente applicata in questo lavoro. Questa prevede una analisi su diversi livelli di dettaglio e accuratezza. I risultati ottenuti dalla scala inferiore, più dettagliata, vengono poi impiegati come dati in ingresso per la scala superiore e così via.

Questa tesi vuole presentare un approccio metodologico che permetta di passare da una analisi su micro-scala a una su macro-scala considerando non solo aspetti di natura fluidodinamica e termica (già trattati da precedenti lavori), ma anche di natura chimica (fenomeni imprescindibili all’interno di un catalizzatore) tramite l’implementazione di sottomodelli dedicati.

Nella prima fase dell’indagine viene effettuata la caratterizzazione su micro-scala da cui si estraggono una serie di parametri e gruppi sia dimensionali sia adimensionali, che costituiranno il punto di partenza per le successive simulazioni su macro-scala. In questo primo passo la geometria effettiva della schiuma viene riprodotta partendo da una ricostruzione micro-CT del campione reale. A questo livello si indagano nel dettaglio le differenti metodologie di discretizzazione del dominio (tipo di mesh, generazione di O-grid, numero di celle, etc.), le prestazioni in termini fluidodinamici (perdite di carico) e termici (conduzione della matrice solida e scambio convettivo tra solido e fluido). Successivamente si è introdotto un modello per la chimica dettagliata, il quale ha permesso di ottenere le curve di abbattimento in condizioni stazionarie del monossido di carbonio riferite alla schiuma in esame. Oltre alle tradizionali simulazioni “single-region” (le quali hanno la limitazione di considerare infinita la conduttività del solido), si è implementato un modello più realistico “multi-region”, che considerasse l’effettiva conduttività della matrice e lo scambio termico conseguente tra le due fasi. Questo ha permesso di spiegare delle discrepanze che precedenti autori avevano riscontrato tra simulazioni numeriche e test sperimentali.

Nella seconda fase dell’indagine invece si è descritta in modo dettagliato l’approccio su macro-scala, prima attraverso un confronto tra modello macro e micro in termini sia di costo computazionale sia di accuratezza, in seguito considerando un caso multi reazione. A tal fine sono stati implementati una serie di sottomodelli atti a caratterizzare nel modo più realistico possibile il complesso e delicato processo alla base di un sistema di reazioni catalitiche. I risultati si sono rivelati promettenti e, nonostante la necessità di ulteriori sviluppi del codice, fanno ben sperare per quanto riguarda la sua possibile futura applicazione in fase di progettazione.

**Parole chiave:** OpenFOAM®, Schiume a Cella Aperta, Conversione Catalitica, Chimica, Macro-Scala, Micro-Scala
Introduction

A Fascinating Challenge

In the last decades, the rising sensibility in ecological issues has provided a thriving surge in the development of new-concept vehicles and engines. The necessity of low emissions and sustainable vehicles has probably represented the greatest impulse in the modern automotive (and not only!) industry since its creation in the last decades of the XIX century. Nowadays, this industry is living in a strong contradiction and it is trying to reach the right trade-off between pollutants abatement and vehicle performances. Indeed, on the one hand, the market requires more and more prestant, roaring and powerful vehicles. On the other hand, there is the awareness that global pollution and climate change depend for the most part on the vehicles emissions.

These two facets are strictly related, as the emissions consist of two different kind of pollutants: those deriving from the complete combustion ($CO, H_2O$) of the fuel and those from the incomplete combustion ($CO, HC$). The first ones are unavoidable in a traditional vehicle with Internal Combustion Engines (ICE). On the other hand, the second ones can be eliminated by using an efficient after-treatment system.

The continuous research of power and performances determines a markable over-sizing of engines with a consequent increase of the consumptions. The greater the fuel burned, the greater the $CO_2$ emissions. The fascinating challenge is the design of an efficient, powerful and sustainable engine.

When in the early ’70s three-way catalysts were introduced, the biggest problem was the loss of efficiency in engines because of the increase of the outlet pressure. It caused an important enhancement of the specific consumption and, consequently, an increase of $CO_2$ issued.

Since then, many important progresses have been done due to the more and more stringent standards required by international protocols. Nowadays, it is possible to eliminate the 99% of $CO$, $NO$, and $HC$ more than the ’70s. The most interesting challenge in this scenario is the development of a system with the same performances of traditional catalysts, but that permits to increase the engine efficiency reducing the specific consumption and, therefore,
the emission of greenhouse gases.
In this contest, Computational Fluid-Dynamic analysis has promoted a strong innovation in engine design. It permits to reproduce a particular physical phenomenon by solving mathematical models and analysing its results. It has allowed a sensible reduction of design costs, because prototyping is not necessary at all level of the complex design chain.
In this work, CFD analysis is the instrument that permits to analyse and characterise metal foams performances. These are innovative supports for three-way catalysts, as they are expected to provide a markable economical saving in terms of noble metal involved maintaining the same abatement efficiency. Experimental and numerical investigations have pointed out that it is possible to obtain smaller catalysts than the ones with honeycomb. It will represent an enormous advantage in terms of component cost and in terms of engine performances.
This thesis work is inserted in the long and complex design chain of a three-way catalyst, providing those methodologies which permit to analyse the behaviour of innovative supports, as open-cell are. This represents a mandatory link in the complete design of the component, as it permits to unlock next steps, more and more closer to the final goal.

**CFD Multi-Scale Analysis**

The internal combustion engine is a complex system which involves several phenomena, each characterized by different time and length scales. It is interesting to observe that each scale is essential in the global understanding and optimisation of the functioning of an ICE. These scales can be classified in three different types depending on the component analysed. A three-way catalyst with a open-cell foams, that is the topic of this work, will be analysed under its different scales.
One of the main constraint in CFD analysis is represented by the computational effort which makes not feasible the simultaneous simulation of all scales involved. As a consequence, the so called *multi-scales analysis* (see Fig. 1) is used: different simulations are performed at different scales and with a different level of detail and computational burden, considering only a representative portion of the entire system.

The micro-scale analysis (see Fig. 2(a) and 2(b)) is the most accurate one and provides the guidelines for the choice of the morphological properties of the substrate. Micro Computed Tomography can be applied for the reconstruction of the actual geometry of the foam. It is possible to modify the geometrical parameters by applying mathematical transformations in order
Introduction

Figure 1: Multi-scales analysis

to investigate the effect of each parameter (porosity, specific surface, cell and pore size) on foam performances without affecting its shape. In this way, the number of variables involved in the analysis is reduced. A parametric study on the effect of the inflow velocity can be also performed.

To simulate the detailed chemistry, micro kinetic models are used, so that the elementary reaction steps occurring on the catalyst surface could be described. The adoption of a micro kinetic model is mandatory when the purpose of the analysis is the evaluation of the influence of the catalyst composition on the surface reactivity. On the other hand, when the characterization of the surface reactivity is already available, simplified reaction models can be applied, with a significant reduction of the computational burden. These models (e.g. Languimir-Hinshelwood) describe the macroscopic functionality of the catalyst on the basis of the surface conditions in terms of temperature, pressure and composition. This approach is convenient to study the behaviour of a particular catalysed substrate under varying operating conditions and/or geometrical parameters.

Afterwards, a macro-scale simulation will be considered (see Fig. 3). It allows to simulate parts of components, analysing their behaviour under different conditions with a reasonable computational effort. The micro-structural geometry is not reproduced in details, because it would require an excessive time of simulation. Macro models are implemented in order to reproduce the
effects of the micro-structure. The results extracted from micro-scale simulations are used to set the parameters for the up-scales. These simulations do not want to reproduce the complete geometry of the catalyst, but want to investigate how the fluid-dynamics and chemical properties change passing from a microscopic portion of foam to a simplified engineering component.

The up-scaling approach continues with the analysis of the whole component scale (see Fig. 4). This permits to evaluate the complete behaviour of the component simulating more realistic operating conditions. In this way, it will be possible to design the entire catalyst and to compare the performances of different configurations (open-cells, honeycomb). It will provide important
design guidelines for the optimization of the geometry of the catalyst (structure, ratio between diameter and length). The aim of these simulations is to find the best configuration which allows the higher reduction of pollutant emissions with the lowest impact on engines performances.

Once the catalyst configuration is set, the engine-scale will be tested (see Fig. 5). This means that it would be possible to simulate the entire engine system and its effective behaviour under actual operating conditions. To obtain a model which requires a realistic computational burden, the data provided by the down-scale simulations would be used as support. Along these lines, it will be possible to optimize the complete system without the need for a costly proto-typing.
Introduction

Thesis Outline

The thesis is structured as follows:

- In Chapter 1 a general presentation of open-cell foams and an overview of their main manufacturing processes are reported. A review of the studies published in literature on the topics of this thesis is given. In particular, the possible application of foams to three-way catalysts will be considered.

- In Chapter 2 the governing equations of all phenomena involved in fluxes through foams are presented. An analysis of the flow regime with its dimensional and adimensional parameters is discussed.

- In Chapter 3 the CFD modelling is described. The micro-scale sub-models and the consequent up-scaling and averaged process are presented, focusing on the numerical implementation inside the CFD code used.

- In Chapter 4 a micro-scales analysis is completely performed, reproducing and evaluating all phenomena which occur in micro-structures. The sample in exam will be fully characterised, obtaining those parameters which are needful in the up-scaling process. This section will describe those CFD techniques applied to the micro-analysis: a) the generation of the computational grid for both single-region and multi-regions simulations; b) the geometric characterisation of the sample; c) the fluid-dynamic characterisation and the application of laws for the prediction of the pressure drop; d) the thermal characterisation and the simulation of the conduction in solid matrix and of the conjugate heat-transfer between the fluid flow and the solid matrix; e) the chemical characterisation with the simulations of reaction by using a single and, for the first time, a multi-region modelling.

- In Chapter 5 a complete up-scaling process is performed. The macro-model implemented is described in detail. The macro-scale approach will be validated resorting to representative test cases. Its performances in rating fluid-dynamical and thermo-dynamical quantities are described. After that, chemistry is considered. The macro-chemistry sub-model is so validated and compared to micro-one. In the end, the extension to multi-reactions systems is discussed. A case which is representative of the a simplified three-way catalyst reaction scheme...
is considered, and the performances of the model in multi-reactions problems are largely described.

- In Chapter 6 two test cases are presente. At first, a comparison between two different configurations is done. It permits to obtain important guidelines in three-way catalyst design. Later, en extended reaction model with effective concentrations of pollutants is considered.
Chapter 1

The Open-Cell Foams

1.1 An Overview of the Foams

Foams are cross-linked materials with high porosity; they are constituted by interconnected filaments whose structure may be represented as a sequence of cells repeated in space.

![Foams](image)

(a) Open-cell foam  (b) Close-cell foam

Figure 1.1: Foams

They are a continuous dispersion of a gaseous phase in a solid phase and they can be metallic or not metallic. These are distinguished in two different types on the basis of the continuity of the interconnected solid phase:

- *Open-cell foams* have a complex geometry and the porous geometry is interconnected;
- *Close-cell foams* has spheroidal cavities not connected;

The properties of a foam are provided by its manufacturing process and these can change a lot under different processes. This makes these structures extremely versatile and adaptable to several applications both structural and
functional. Their main properties are light weight, high surface to volume ratio, high mechanical strength and high permeability to the fluid flow that make foams appreciable for various industrial applications like filters, heat exchangers and catalytic reactors [1].

### 1.2 Foams in 3-way catalysts

The possibility to use foams in catalytic processes was proposed for the first time by Twigg and Richardson [2]. The structural properties which make these supports adaptable in heterogeneous catalysis are:

- **High vacuum percentage**: it produces a less resistance to the fluid. The vacuum percentage is more or less the double of the one of the classical reactors.

- **High specific surface**: it is the main parameter involved in a catalytic process. The high specific surface leads to more compact catalysts [3]. However, this causes higher pressure drops than that of monolithic structures with the same dimensions [4]. This can be compensated by an increased mass transfer that allows to downsize the catalyst [5].

- **Radial dispersion**: as the structure is all interconnected, the flux is free to diffuse in the foam. In classical honeycomb reactors, the fluid has principally an axial way of propagation, and it often produces a non-equal distribution of pollutants inside the structure. As a result, the conversion process is non homogeneous and there are zones where the reactions have an extremely low conversion efficiency. On the other hand, the open-cell geometry allows higher flow uniformity which is a critical factor for the pollutant conversion efficiency and for the catalyst durability [6], [7], [8]. The tortuous flow path is expected to enhance the mixing and the heat/mass transfer.

In this context, open-cell foams are interesting as a substitute for the traditional honeycomb monolithic substrate: the use of foam layers having different properties could lead to a more flexible design of the reactor [9]. Up to now, different research groups have investigated foam performances but, due to their great variability in geometrical and chemical properties, there is not a convergence of the results among different authors. This reflects the great variability of both the experimental conditions and the foams physical properties (dimensions, porosity, specific surface, washcoat thickness, composition). The absence of correlations makes the realization and the adoption of this new catalyst substrate difficult, but, on the other hand, proves the
The need of further investigations. The most promising pressure drop correlations are those proposed by Du Plessis et al. [10] and Lacroix [11]. A complete list of correlations based on empirical and analytical models can be found in [12]. Experimental work from Boomsma [13] and Dukhan [14] investigated the effects of compression factor, porosity and pore size for aluminium foams. Along with experimental investigations, CFD approaches have been applied to the study of open cell foams. Two main approaches were adopted for the reproduction of the complex micro-structural geometry:

- idealized and simplified periodic structure: the main advantage of this approach is that the computational domain can be reduced to a single elementary cell, which coincides with the Representative Elementary Volume (REV) of the foam. The best one is the Kelvin Cell Structure, whose performances have been investigated by [15].

- X-ray computed tomography to record the foam micro-structure, using suitable techniques for the generation of the geometry and computational mesh from the scanned images [12]. This is the one used in this thesis.

Up to now numerical simulations studied the foam pressure drop and the heat transfer properties. However, only few studies have been done on the simulation of the mass transfer and the reactions.
1.3 Manufacturing Process

Metal foams are innovative materials patented in 1940 by Benjamin Sosnik. At the beginning, his process was not considered by the scientific community, even if it would create the possibility to produce new materials. Since then, several processes have been patented and realised, allowing the realization of a great variety of foams in terms of material, density, cell dimensions and shape, and homogeneity. Many methods are based on those techniques used to produce polymeric foams; others are thought in order to take advantage of metal properties, like the possibility of being sintered or electrically deposed. These processes can be classified on the basis of the physical state of the metal during the manufacturing. It could be: liquid, solid powder, metal vapour or metal ion. The correct choice of the manufacturing process is based on the metal type, on the relative density and on the cell dimension desired (see Fig. 1.3).

The most widely used method is the direct foaming of the liquid metal. This process uses gas bubbles developed inside the liquid phase: normally these tend to reach the free surface due to the Archimede's force \( F = \rho g V \). The addition of ceramics powder or metal alloys provides an increase of the fluid viscosity; this produces a sensible reduction of the velocity of these bubbles, which tend to stabilise. Nowadays, the direct foaming occurs through...
the injection of air inside a vessel which contains liquid metal, or through the development of gas by a solid reacting powder (e.g. TiH) added to the liquid phase.

In alternative, it is possible to exploit the low melting temperature of eutectic alloys ($\epsilon\upsilon = easy$ and $\tau\iota\kappa\omega = melting$). The solidification of these alloys in an high pressure ($10 \div 50$ atm) hydrogen atmosphere produce the segregation of the gas dissolved in the liquid phase generating bubbles.

The powder foaming is a method developed by the United Aircraft Corporation. This belongs to that engineering branch called Powder Metallurgy because the base material is a mixture of the base metal and a foaming agent. The sintering process consists in the compacting and forming a solid mass of material by heat and/or pressure without melting it to the point of liquefaction. After that, the matrix is heated until the foaming agent is completely decomposed. The decomposition reaction produces hot gasses which melt the structure generating a high porous media. The quantity of foaming agent determines the main characteristics of the foam obtained.

The usage of pre-shaped or sacrificial supports permits to have an high flexibility in terms of characteristic parameters. These are essential when vapour or ions additive processes are used. Metal is deposited over polymeric matrices, which reproduce exactly the negative of the sample. Once the addition is completed, the template has to be removed by liquefying or vaporizing it. This technique permits to realize open-cell foams only, as it is clear. Its main advantage is the high control on pore size and distribution in the sample. However, the maximum porosity that can be reached is about the 80%.

In alternative, the polymeric support can be used as corebox in casting processes. This method permits to realize foams made up of low melting alloys, like $Al$, $Mg$ or $Cu$, as their point of liquefaction has to be lower than the one of the polymers. The main difficulties in the industrialization of this technique is the dismissal of the corebox, making this last process extremely expensive.
Chapter 2

Governing Equations

2.1 Conservation Laws

The governing principles in fluid mechanics are the conservation laws for mass, momentum, energy and chemical species (if chemistry is involved in the problem in exam). These laws are presented in this order in this chapter, and they can be stated in \textit{integral} form, applicable to an extended region or volume, or in \textit{differential} form, applicable to a point a fluid particle. For the problems considered in this work, the hypothesis of continuum can be assumed as valid, since the length and time scales involved are significantly bigger than the molecular characteristic dimension. Indeed, as pointed out by previous works \cite{16} the Knudsen number takes values such that the molecular model with Maxwell equation is not reasonably applicable. Under these assumption, the traditional continuum theory is applied. Two different approaches can be used:

- \textbf{Lagrangian}: it is based on the motion of fluid particles. The fluid particles are followed as they move through a flow field and to describe the entire domain it is necessary to know the properties and trajectory of all particles in fluid. Each characteristic depends on time and its knowledge specifies the entire flow field. This approach is usually used in non-deformable solid mechanics and is not applicable in our models, because of the excessive complexity and computational burden requested.

- \textbf{Eulerian}: flow field characteristics are monitored at fixed locations or in stationary regions of space. Each physical or chemical quantity is a function of four independent variables: the three spatial coordinates, represented by the position vector $\vec{x}$, and time $t$. This is the approach adopted in this work, because of the need to characterise the entire domain with a reasonable computational effort.
This approach implies that a generic quantity can be expressed as \( \phi = \phi(\vec{x}, t) \) and, according to Leibniz’s derivative law, that the time derivative of \( \phi \) is:

\[
\frac{D}{Dt} \phi(\vec{x}, t) = \frac{\partial \phi}{\partial t} + \vec{U} \cdot \nabla (\phi) \tag{2.1}
\]

In 2.1 it is possible to identify two different contributions:

- \( \frac{\partial \phi}{\partial t} \): the unsteady term which represents the direct time dependence of the generic \( \phi \) quantity.
- \( \vec{U} \cdot \nabla (\phi) \): the flux term which represents the dependence of the generic \( \phi \) quantity from the motion field surrounding.

The application of the Reynolds transport theorem to the equation above permits to make same considerations in the integral form. Considering a control volume \( V(t) \) having a closed boundary surface \( S(t) \) with outward normal \( \vec{n} \), the 2.1 can be written:

\[
\frac{D}{Dt} \int_{V(t)} \phi dV = \int_{V(t)} \frac{\partial \phi}{\partial t} dV + \oint_{S(t)} \phi \vec{U} \cdot \vec{n} dS \tag{2.2}
\]

This equation is based on the distinction between a material and control volume. The first one represents the actual fluid volume to which the conservation laws should be applied and it is time dependent. The second one is a volume defined by the observer in order to characterize the fluid motion, it can depend on time or not. The term \( \vec{U} \) in 2.2 is the relative speed between the material and control volume. In this work the control volume is fixed and so \( \vec{U} \) represents the effective fluid speed. It implies that in the following integral equations the control volume will be indicated as \( V \) as it is not a function of time.

### 2.1.1 Conservation of Mass

Setting aside nuclear reactions and relativistic effects, mass is neither created or destroyed. This can be expressed by the following equation:

\[
\frac{DM}{Dt} = 0 \tag{2.3}
\]

where \( M \) is the mass of the material volume.

\[
M = \int_{V(t)} \rho dV \tag{2.4}
\]

Using the previous equations 2.1 e 2.2, the mass conservation law can be written:
• **Differential form**
\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{U}) = 0
\]  
(2.5)

• **Integral form**
\[
\int_V \frac{\partial \rho}{\partial t} \, dV + \oint_S \rho \vec{U} \cdot ndS = 0
\]  
(2.6)

where \(V\) and \(S\) are the control volume and its boundary surface and \(\vec{U}\) is the fluid speed.

### 2.1.2 Conservation of Momentum

The momentum conservation is developed from Newton’s second law:

\[
\frac{D \vec{I}}{Dt} = \sum \vec{F}
\]  
(2.7)

where \(\vec{I}\) is the momentum and \(\vec{F}\) are the forces applied to the material domain. Momentum is defined as:

\[
\vec{I} = \int_{V(t)} \rho \vec{U} \cdot dV
\]  
(2.8)

It is possible to distinguish between two different kinds of forces:

• **Body Forces**: these are distributed through the fluid and are proportional to the mass (or electric charge, electric current, etc.). Body forces commonly arise from gravitational, magnetic, electrostatic, or electromagnetic force fields. In this thesis, \(\vec{g}\) represents the body forces per unit mass and carries the units of an acceleration. In this way, body forces can be written as:

\[
\vec{F}_v = \int_{V(t)} \rho \vec{g} dV
\]  
(2.9)

• **Surface Forces**: these act on fluid elements through direct contact with the surface of the element. \(\overline{\vec{f}}\) represents the surface forces per unit area and carries the units of stress.

\[
\vec{F}_s = \oint_{S(t)} \overline{\vec{f}} \cdot \vec{n} dS
\]  
(2.10)

Using the previous equations, the momentum conservation law can be written as follows:
• Differential form
\[ \frac{\partial \rho \vec{U}}{\partial t} + \vec{\nabla} \cdot (\rho \vec{U} \vec{U}) = \vec{g} + \vec{\nabla} \cdot \vec{\sigma} \] (2.11)

• Integral form
\[ \int_V \frac{\partial \rho \vec{U}}{\partial t} dV + \oint_S \rho \vec{U} \vec{U} \cdot \vec{n} dS = \int_V \rho \vec{g} dV + \oint_S \vec{\sigma} \cdot \vec{n} dS \] (2.12)

2.1.3 Conservation of Energy

The energy conservation is developed from the first thermodynamic law:
\[ \frac{DE}{Dt} = \dot{L} + \dot{Q} \] (2.13)

where \( E \) is the total internal energy possessed by the material domain. When applied to a material volume \( V(t) \) with surface \( S(t) \), the total energy can be expressed as a function of the internal energy per unit mass \( e \) and the kinetic energy per unit mass \( \frac{1}{2} |\vec{U}|^2 \):
\[ E = \int_{V(t)} \rho \left( e + \frac{1}{2} |\vec{U}|^2 \right) dV \] (2.14)

\( \dot{L} \) is the mechanical power given by body and surface forces:
\[ \dot{L} = \int_{V(t)} \rho \vec{g} \cdot \vec{U} dV + \oint_{S(t)} \left( \vec{\sigma} \cdot \vec{U} \right) \cdot \vec{n} dS \] (2.15)

\( \dot{Q} \) is the thermal power given by thermal heat flux \( \vec{q} \) and by external or internal sources or sinks \( Q_H \):
\[ \dot{Q} = -\oint_{S(t)} \vec{q} \cdot \vec{n} dS + Q_H \] (2.16)

Using the previous equations the energy conservation law can be written:

• Differential form
\[ \frac{\partial}{\partial t} \left( \rho \left( e + \frac{1}{2} |\vec{U}|^2 \right) \right) + \vec{\nabla} \cdot \left( \rho \left( e + \frac{1}{2} |\vec{U}|^2 \right) \vec{U} \right) = \vec{g} \cdot \vec{U} + \vec{\nabla} \cdot \left( \vec{\sigma} \cdot \vec{U} \right) - \vec{\nabla} \cdot \vec{q} + Q \] (2.17)

• Integral form
\[ \int_V \frac{\partial}{\partial t} \left( \rho \left( e + \frac{1}{2} |\vec{U}|^2 \right) \right) dV + \oint_S \rho \left( e + \frac{1}{2} |\vec{U}|^2 \right) \vec{U} \cdot \vec{n} dS = \]
\[ \int_V \rho \vec{g} \cdot \vec{U} dV + \oint_S \left( \vec{\sigma} \cdot \vec{U} \right) \cdot \vec{n} dS - \oint_S \vec{q} \cdot \vec{n} dS + Q_H \] (2.18)
2.1.4 Conservation of Chemical Species

The species conservation is developed from the Lavoisier’s law:

- **Differential form**

\[
\frac{\partial \rho Y_k}{\partial t} + \nabla \cdot (\rho Y_k \vec{U}) = -\nabla \cdot \vec{j}_k + R_k \tag{2.19}
\]

- **Integral form**

\[
\int_V \frac{\partial \rho Y_k}{\partial t} dV + \oint_S \rho Y_k \vec{U} \cdot \vec{n} dS = -\oint_S \vec{j}_k \cdot \vec{n} dS + \int_V R_k dV \tag{2.20}
\]

where \( Y_k \) is the mass fraction of the \( k \)-th specie, \(-\nabla \cdot \vec{j}_k\) represents the diffusive flux and the term \( R_k \) takes into account the generation and destruction of the \( k \)-th specie due to the chemical reactions. The equations 2.19 and 2.20 need to be solved for all \( N_c - 1 \) chemical species and the set of equations is closed by a continuity equation expressed as follows:

\[
\sum_{k=1}^{N_c} Y_k = 1 \tag{2.21}
\]

2.2 Constitutive Laws

These laws are mathematical models that allow the description of the entire domain under specific conditions or phenomena.

This section will present the models for the thermophysical characterisation of the fluid, the equation of state, the stress tensor \( \sigma \), the energy flux \( \vec{q} \) and the diffusive flux \( \vec{j}_k \). On the other side, the models for mass diffusion and reactions will be described in a following dedicated section.

A newtonian fluid will be considered with the following set of equations:

- **Thermophysical Characterization**: the classical thermodynamic theory provides an efficient model, which can well describe the link between energy and temperature. Internal energy and enthalpy per mass unit \( e \) and \( h \) are so expressed as a function of temperature \( T \) and of a parameter called specific heat \( c_v \) or \( c_p \):

\[
e = c_v T \tag{2.22}
\]

\[
h = c_p T \tag{2.23}
\]

where \( h = e + pv \).

\( c_v \) and \( c_p \) depend on temperature. In fact, it is not reasonable the
hypothesis of ideal gas because of the big variation of temperature due to chemical reactions. This dependence is expressed through the Janaf polynomial model:

\[ c_p = R \left( ((\alpha_4 T + \alpha_3) T + \alpha_2) T + \alpha_1 \right) T + \alpha_0 \]  

(2.24)

where the coefficients \( \alpha_i \) are available in dedicated tables provided by OpenFOAM®.

- **Equation of State:** it allows to define the thermophysical behaviour of a fluid, establishing a correlation between the main variables of the system:

\[ \rho = \rho(p, T) \]  

(2.25)

A first necessary hypothesis is that the fluid analysed in this work could be approximated by a perfect gas. Under this condition it is possible to write:

\[ \rho = \frac{p}{R^* T} \]  

(2.26)

where \( R^* = \frac{R}{MM} \). \( R \) is the universal constant for gases (equal to 8.314 J mol\(^{-1}\) K\(^{-1}\)) and \( MM \) is the molar mass of the considered specie (or the weighted average molar mass in a mix). It can be possible to use other more complex models to describe the equation of state (Van der Waals, Dieterici, Virial equation, etc.), but their complexity is not supported by a significant higher accuracy.

- **Stress Tensor:** the characterisation of the stress tensor is derived from the solid mechanic theory, where the stress tensor is splitted into two tensors: the hydrostatic and the deviatoric tensors.

\[ \overline{\sigma} = \overline{\sigma} - p\overline{I} \]  

(2.27)

\( p\overline{I} \) is the hydrostatic stress tensor. It is calculated as the mean of the principal normal stresses and in fluid-dynamic it represents the pressure component of stresses.

\( \overline{\sigma} \), the deviatoric tensor, is calculated using Newton’s viscosity law:

\[ \overline{\sigma} = 2\mu\overline{D} + \lambda \left( \nabla \cdot \overline{U} \right) \overline{I} \]  

(2.28)

\[ \overline{D} = \frac{1}{2} \left[ \nabla \overline{U} + \left( \nabla \overline{U} \right)^T \right] \]  

(2.29)
where \( \lambda \) is equal to \(- (2/3) \mu \) under the Stokes’ hypothesis. 
\( \mu \) is the dynamic viscosity and for Newtonian fluid, it is a function of the only thermodynamical quantities.
In this thesis \( \mu \) is calculated using the Sutherland model:

\[
\mu = \frac{A_s \sqrt{T}}{1 + \frac{T}{T_s}}
\]

where \( A_s = 1.4792 \cdot 10^{-6} Pa/(s\sqrt{K}) \) and \( T_s = 116 K \).

• **Energy Flux**: the energy flux can be expressed using the Fourier Law, that returns the thermal flux as a function of the temperature \( T \) and the thermal conductivity \( \kappa \):

\[
\vec{q} = -\kappa \nabla T
\]

\( \kappa \), expressed in \( \frac{W}{mK} \), can be considered constant. In fact, its dependence from temperature is not so strong to justify the usage of a dedicated model.

• **Diffusive Flux**: it is well modelled by the Fick’s law:

\[
\vec{j}_k = -\rho D_{k,mix} \nabla Y_k
\]

where \( D_{k,mix} \) represents the diffusion coefficient of the k-th specie in the mix.

### 2.3 Navier-Stokes Equations

By the union of conservative and constitutive laws it is possible to write the complete set of equations used:

• **Mass conservation**:

\[
\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \vec{U}) = 0
\]

• **Momentum conservation**:

\[
\frac{\partial \rho \vec{U}}{\partial t} + \nabla \cdot (\rho \vec{U} \vec{U}) = \vec{g} - \nabla \left( p + \frac{2}{3} \mu \nabla \cdot \vec{U} \right) + \nabla \cdot \left[ \mu \left( \nabla \vec{U} + \nabla \vec{U}^T \right) \right]
\]
• **Energy conservation:**

\[
\frac{\partial}{\partial t} \left( \rho \left( e + \frac{1}{2} |\vec{U}|^2 \right) \right) + \vec{\nabla} \cdot \left( \rho \left( e + \frac{1}{2} |\vec{U}|^2 \right) \vec{U} \right) = \rho \vec{g} \cdot \vec{U} \\
- \vec{\nabla} \cdot \left[ \left( p + \frac{5}{3} \mu \vec{\nabla} \cdot \vec{U} \right) \vec{U} \right] + \vec{\nabla} \cdot \left[ \mu \left( \vec{\nabla} \vec{U} + \vec{\nabla} \vec{U}^T \right) \vec{U} \right] \\
+ \vec{\nabla} \cdot \left( \kappa \vec{\nabla} T \right) + Q \tag{2.35}
\]

• **Specie conservation:**

\[
\frac{\partial \rho Y_k}{\partial t} + \vec{\nabla} \cdot \left( \rho Y_k \vec{U} \right) = \vec{\nabla} \cdot \left( \rho \mathcal{D}_{k,mix} \vec{\nabla} Y_k \right) + \mathcal{R}_k \tag{2.36}
\]

• **Equation of state:**

\[
\frac{p}{\rho} = R^* T \tag{2.37}
\]

### 2.4 Flow Regimes

Viscous flows generically fall into two categories: *laminar* and *turbulent*. The difference between these two behaviours was studied for the first time by Reynolds in 1883. He called laminar the regime where the fluid moves in parallel layers with no unsteady macroscopic mixing. This is the regime of a smooth ordered flow. On the contrary, turbulence is a chaotic state of fluid flow that may be simultaneously beneficial and problematic. A turbulent flow is marked by:

• **Fluctuations**: an unsteady behaviour of the dependent-field quantities (pressure, velocity, temperature, etc.) can be seen, even if the boundary conditions are steady. These fluctuations seem to be chaotic, irregular and unpredictable.

• **Non-linearity**: the problem is not linear and it can be clearly seen in the convective terms in the Navier-Stokes equations.

• **Vorticity**: turbulence is characterized by fluctuating vorticity. The swirling structures that can be identified in a turbulent flow are called *eddies*, each with its own length scale.

• **Dissipation**: the vortex mechanism transfers energy from bigger to smaller scales. This process is called *energy cascade* and provides the dissipation of the energy owned by eddies. The smaller the scale, the
bigger the velocity gradients and the energy dissipated by viscous effects increased. The dissipation process is shown in Fig. 2.1, and three main scales can be identified. The Integral scale is the biggest scale that an eddy can reach. The Taylor scale is the scale under which the dissipation cannot be considered negligible anymore. As a consequence, the fluid can be considered inviscid for scales bigger than the Taylor one. The Kolmogorov scale is the smallest scale that can be reached, as the fluid dissipates all energy it has.

\[ \text{Figure 2.1: Energy cascade} \]

- **Diffusivity**: because of the fluctuations, turbulent flows are characterised by a rapid rate of mixing and diffusion of species, momentum and heat compared to equivalent laminar flows.

The main parameter which can discriminate between the different regimes is the Reynolds Number:

\[ Re = \frac{\rho UL}{\mu} \]  

(2.38)

where \( U \) and \( L \) are respectively the velocity and the characteristic linear dimension of the problem in exam. The Reynolds Number represents the ratio between the inertial forces and the viscous ones. When \( Re \) is low the regime will be laminar; it means that it will be dominated by viscous forces. On the contrary, when \( Re \) is high, the regime will be dominated by inertial forces and it will manifest a turbulent behaviour.

These considerations are generally valid for flows in pipes. In a generic porous media, Seguin [17] and Ingham [18] suggested to classify four different regimes on the basis of a new definition of Reynolds number \( \left( Re_c = \frac{\rho U_D d_c}{\mu} \right) \). It considers the Darcy velocity \( U_D \), i.e. the no-disturbed velocity at the inlet of the porous media, and the average cell size \( d_c \). These regimes are:
• **Darcy regime**: $Re_c < 1$. It is dominated by viscous forces and the pressure drop is proportional to the Darcy velocity:

\[
\frac{\Delta p}{L} = \mu d U_D
\]  

(2.39)

• **Forchheimer regime**: $1 \div 10 < Re_c < 150$. The flow is dominated by inertial forces and the relation between pressure drop and velocity becomes non-linear:

\[
\frac{\Delta p}{L} = \mu d U_D + \frac{1}{2} \rho f U_D^2
\]  

(2.40)

• **post-Forchheimer regime**: $150 < Re_c < 300$. Laminar wake oscillations appear.

• **fully-turbulent regime**: $Re_c > 300$. The flow becomes chaotic and highly unsteady.

Della Torre et al. [19] pointed out that in porous media, like an open-cell foam, the dissipation mechanism depends essentially on the superposition of two different contributions. The first one is provided by the high stresses at the interface between stagnation and flow regions. It is evident especially at low $Re_c$ passing from Darcy to Forchheimer regimes, because of the increasing of the inertial forces, while, at high $Re_c$, the dissipation seems to stabilize when the flow is inertia dominated. The second contribution is given by the form drag, i.e. the continuum distortion of fluid flow due to the solid matrix. It is essentially an inertial contribution which increases linearly with velocity.

Turbulence should increase the dissipative contribution to pressure drop, however, it has been demonstrate by Della Torre et al. [19] that the effect of a turbulent model in a CFD micro-simulation of a porous media is negligible. Indeed, no significant differences has been highlighted between laminar, RANS or DNS simulation, with or without turbulent model. The explanation of this behaviour is that while inertial contribution generated by the form drag increases with $Re_c$, the one given by shear stress remains constant and its contribution to pressure drop becomes negligible compared to the whole.
pressure drop. This is the main difference between a flow in a porous media and a flow in pipe. Inside pipes there is not a form drag contribution and the whole pressure drop is generated by the shear stress at the wall. This is the reason why it is possible to use a laminar model, even if the fluid is turbulent, obtaining a sufficiently accurate prediction of dissipation with a reasonable computational effort. This is the approach used in this work.
Chapter 3

CFD Models

This chapter aims to present the CFD models developed in this work. The need to simulate different scales required the implementation of specific libraries, that will be explained later. These are developed on the basis of the open-source finite volume code OpenFOAM®.

3.1 Micro-Scale Model

This section explains how the Navier-Stokes equations are implemented in OpenFOAM® for the micro-scale simulations of catalytic surface reactions. The model consists of two main cores:

- a finite volume (FV) solver, which describes the fluid-dynamic and the chemical phenomena occurring in the homogeneous fluid phase;

- a finite area (FA) solver, which describes the phenomena related to the catalytic specie conversion occurring on the washcoat surface.

3.1.1 FV solver

This solver is based on the solution of Navier-Stokes equations 2.33, 2.34, 2.35, 2.36, 2.37. It is coupled to the FA solver by means of two source terms added in 2.35, 2.36 $Q^{f\rightarrow w}$ and $R^{f\rightarrow w}$, which take into account the energy and specie transfer occurring between the boundary cell and washcoat surface. A reasonable assumption is to consider a Schmidt number ($Sc = \frac{\nu}{D_{k,mix}}$) equal to 1, approximating the transport coefficient $D_{k,mix}$ with the cinematic viscosity $\nu$. It provides a lower computational effort and relocate the complexity of the problem in the calculus of viscosity, provided by the Sutherland model. This assumption is not valid in the FA solver, where a more detailed model is implemented. With regard to the gas phase chemistry
modelling, an Arrhenius-type expression is adopted to determine $R_k$, in this way:

$$R_k = AT^\beta e^{-\frac{E_{att}}{RT}}$$  \hspace{1cm} (3.1)

$\beta$ is an exponent which allows to increase the dependence of the reaction rate from temperature. In this work it is always set equal to zero. $E_{att}$ is the activation energy, i.e. the minimum energy that produces a chemical transformation.

$A$ is the Arrhenius constant. It is quite constant with temperature and depends essentially on the reaction type. Shock theory suggests that $A$ is the product of two different factors:

- a probability factor that depends on molecular geometry. It measures the probability that reactants interact with each other in a particular way
- a frequency factor which measures the frequency of shocks between molecules and depends on the molecular dimension.

![Figure 3.1: Activation energy](image)

![Figure 3.2: Physical and chemical significance of activation energy](image)

### 3.1.2 FA solver

The conversion of reactants into products involves their convective mass-transfer towards the catalytic surface on the washcoat, as well as adsorption of reactants and desorption of products at the active sites.

Moreover, due to reactions, heat is released and accumulated in the substrate and transfer to both the solid and the fluid. As a consequence, FA solver is based on three main sub-models:

- a diffusion model for $D_{k,mix}$;
- a surface reaction model for $\dot{\Omega}_k$;
Figure 3.3: Diffusion, reaction and heat transfer phenomena towards the washcoat

- a heat-transfer model for $Q$

The diffusion model provides the description of the mass transfer between the fluid phase and the washcoat surface. For each chemical specie it is possible to define a diffusion coefficient $D_{k,mix}$ in the mixture. It depends on the binary diffusion coefficients $D_{k,j}$, which describes the diffusion of the k-th specie in the j-th one, and on concentrations $c_k$ according to the following law:

$$D_{k,mix} = \frac{1 - c_k}{\sum_{\forall j \neq k} \left( \frac{c_k}{D_{k,j}} \right)} \quad (3.2)$$

The binary gas diffusion coefficient $D_{k,j}$ is calculated by means of the Chapman-Enskog equation:

$$D_{k,j} = 1.85 \cdot 10^{-3} \cdot T^{1.5} \cdot \left( \frac{1}{MM_k} + \frac{1}{MM_j} \right)^{0.5} \frac{p \left( \frac{\sigma_k + \sigma_j}{2} \right)^2 \Omega_D}{\epsilon} \quad (3.3)$$

This equation shows a strong dependence of the diffusivity from the temperature. It marks the significative influence that it has on the reaction rate especially at high temperature. Diffusivity also depends on molar mass ($MM$), on the collision diameter ($\sigma$) and on the collision integral ($\Omega_D$), evaluated on the basis of the Lennard-Jones potential ($\epsilon_0$). There are in literature several formulations of the collision integral; however many of the expressions are valid only in a strict range of temperature.

This is the reason why, according to [20], the following correlation is adopted:

$$\Omega_D = \left( \frac{1.06036}{kT^0.1290} \right) + \left( \frac{0.19300}{\epsilon^{0.476357}} \right) + \left( \frac{1.03587}{\epsilon^{1.529962}} \right) + \left( \frac{1.76474}{\epsilon^{3.894117}} \right) \quad (3.4)$$

The values of $\sigma$ and $\epsilon$ used in this model are listed in Tab. 3.1.
The reaction model describes the specie conversion on the catalytic surface. It is an Arrhenius-type model which allows to consider the competition between the different chemical species in reacting on active sites and it is adapted for solid surfaces. In this way it is possible to take into account all phenomena of adsorption and de-adsorption that take place, as shown in Fig. 3.4.

This model is the Langmuir-Hinshelwood theory, modified by Koltsakis et al. [21] for three way catalyst applications. They consider the main reactions occurring on washcoat surface:

1. CO oxidation

\[
CO + \frac{1}{2}O_2 \rightarrow CO_2
\]

(3.5)

2. H₂ oxidation

\[
H_2 + \frac{1}{2}O_2 \rightarrow H_2O
\]

(3.6)

### Table 3.1: Lennard-Jones Potentials and Collision Diameters of the chemicals species analyzed

<table>
<thead>
<tr>
<th>Specie</th>
<th>ε₀</th>
<th>σ [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>59.7</td>
<td>2.827</td>
</tr>
<tr>
<td>H₂O</td>
<td>809.1</td>
<td>2.641</td>
</tr>
<tr>
<td>N₂</td>
<td>71.4</td>
<td>3.788</td>
</tr>
<tr>
<td>O₂</td>
<td>106.7</td>
<td>3.467</td>
</tr>
<tr>
<td>CO</td>
<td>91.7</td>
<td>3.690</td>
</tr>
<tr>
<td>CO₂</td>
<td>195.2</td>
<td>3.941</td>
</tr>
<tr>
<td>CH₄</td>
<td>148.6</td>
<td>3.758</td>
</tr>
</tbody>
</table>

Figure 3.4: Transport and diffusion mechanism: (a) reactants absorption on washcoat surface, (b) diffusion and interaction on washcoat surface, (c) products de-adsorption in fluid phase
3. *fast HC oxidation*

\[ C_x H_y + \left( x + \frac{y}{4} \right) O_2 \rightarrow x CO_2 + \frac{y}{2} H_2 O \]  

(3.7)

4. *slow HC oxidation*

\[ C_x H_y + \left( x + \frac{y}{4} \right) O_2 \rightarrow x CO_2 + \frac{y}{2} H_2 O \]  

(3.8)

5. *fast HC steam water reforming*

\[ C_x H_y + x H_2 O \rightarrow x CO + \left( x + \frac{y}{2} \right) H_2 \]  

(3.9)

6. *NO\(_x\) reduction*

\[ 2CO + 2NO \rightarrow 2CO_2 + N_2 \]  

(3.10)

This reaction scheme has been chosen with the need to find a reasonable compromise between minimization of tunable parameters and model representability in real-world operating condition. Koltsakis et al. [21] have chosen these 6-reaction scheme considering the reactions that are more significant for the main pollutants, i.d. CO, HC and NO, while \(H_2\) oxidation is considered due to the high heat released.

Langmuir-Hinshelwood theory provides the reaction rate for the previous reactions:

\[ \dot{\Omega}_1 = \frac{A_1 e^{-\frac{E_1}{RT}} c_{CO} c_{O_2}}{G} \]  

(3.11)

\[ \dot{\Omega}_2 = \frac{A_2 e^{-\frac{E_2}{RT}} c_{H_2} c_{CO_2}}{G} \]  

(3.12)

\[ \dot{\Omega}_3 = \frac{A_3 e^{-\frac{E_3}{RT}} c_{C_2H_6} c_{CO_2}}{G} \]  

(3.13)

\[ \dot{\Omega}_4 = \frac{A_4 e^{-\frac{E_4}{RT}} c_{C_2H_6} c_{H_2O}}{G} \]  

(3.14)

\[ \dot{\Omega}_5 = \frac{A_5 e^{-\frac{E_5}{RT}} c_{C_2H_6} c_{H_2O}}{G} E_{q_5} \]  

(3.15)

\[ \dot{\Omega}_6 = A_6 e^{-\frac{E_6}{RT}} c_{CO}^{0.5} c_{NO_x}^{0.5} \]  

(3.16)

where \(G\) is the inhibition factor calculated as following:

\[ G = T_w \left( 1 + K_1 c_{CO} + K_2 c_{C_2H_6} \right)^2 \left( 1 + K_3 c_{CO}^2 c_{C_2H_6}^2 \right) \left( 1 + K_4 c_{NO_x}^{0.7} \right) \]  

(3.17)
The following expressions for the adsorption equilibrium constants are provided by [21],[22],[23] for Pt containing catalysts:

\[ K_1 = 65.5e^{\frac{261}{T}} \]  
\[ K_2 = 2.08 \cdot 10^{-3} e^{\frac{361}{T}} \]  
\[ K_3 = 3.98e^{\frac{11.611}{T}} \]  
\[ K_4 = 4.79 \cdot 10^5 e^{-\frac{3733}{T}} \]

Because of the lack of data and informations about the fast HC steam water reforming reaction Koltsakis et al. suggested to use a traditional Langmuir-Hinshelwood model coupled to the chemical equilibrium theory by the definition of:

\[ Eq_5 = 1 - \frac{c_x^{\alpha A} + 0.5y_{s,H_2} c_x c_{s,CO} c_{s,H_2}^x c_{s,H_2}^y c_{s,H_2}^z}{K_P(T)} \]  

where \( K_P(T) \) is the chemical equilibrium constant.

Given a generic reaction involving gas species:

\[ \alpha A + \beta B \rightleftharpoons \gamma C + \delta D \]

\( K_P(T) \) is the ratio between the chemical constant of the direct and inverse reaction computed as below:

\[ K_P = \frac{p_{\gamma C} p_{\delta D}^\gamma}{p_{\alpha A} p_{\beta B}^\beta} \]

where \( p_i \) are the partial pressures of the species. Correlations for the chemical equilibrium constant as a function of temperature can be found in dedicated handbooks [24].

However, the Gibbs potential theory provides a simplified correlation for \( K_P(T) \):

\[ K_P = e^{\frac{\Delta G_0}{R T}} \]

In 6.6 the parameter \( m \) is defined:

\[ m = -0.19 \left( 1 - 6.26e^{-m_1 c_{s,CO}} \right) \]

where \( m_1 \) is a tunable factor.

The heat transfer model provides the calculus of the source term \( Q \) which takes into account the heat generated or required by the chemical reactions. This term implies the need of a model which can well describe the heat exchanged between the fluid and washcoat:
Two different models can be used to model the problem:

- **Single-Region**: there is only one domain, the fluid one. The solid temperature $T_w$ is imposed as boundary condition;

- **Multi-Regions**: Both fluid and solid domain are considered. Heat flux and interface temperature are calculated coupling the Navier-Stokes equations for the fluid domain and the Fourier equation for the solid domain. This model is more complex than the previous one and requires an higher computational effort. However, it provides a more detailed solution.

In this work a comparison between these two model will be provided. It permits to explain some differences between numerical and experimental data pointed out by previous works [16].

**Calculus of the global Reaction Rate**

Experimental activities [25] have highlighted an important dependence of the global conversion from temperature. In Fig.3.1.2 the typical behaviour of the reaction rate with temperature is represented. It is possible to define two areas divided by the so called *light-off temperature* $T_L$. This is defined as the temperature at which the catalyst has a reaction rate equal to the 50% of
the maximum reaction rate that it reaches. 
If $T < T_L$ the conversion process is kinetic dominated. It means that the value of $\Omega_k$ is the bottle neck of the process. In this case the percentage of conversion has an exponential law with temperature.
If $T > T_L$ the conversion process is diffusion dominated. It means that the value of $j_k$ is the bottle neck of the process, because the kinetic is completely activated at high temperatures. In this case the percentage of conversion has a linear law with temperature.
To calculate the previous conversion curve, it is necessary to couple the two solvers with $Q^{f\rightarrow w}$ and $R^{f\rightarrow w}$ using the sub-models defined before. A possible approach consists of the solution of the balance equations both for mass and energy, considering their accumulation in the washcoat. For the k-th specie it is possible to write:

$$\frac{\delta \rho Y_{w,k}}{\delta t} = -\nabla \cdot j_k - \dot{\Omega}_k$$

$$\frac{\delta \rho c_w T_w}{\delta t} = +H_r$$

where the derivative $\frac{\delta \rho Y_{w,k}}{\delta t}$ and $\frac{\delta \rho c_w T_w}{\delta t}$ terms are called accumulation terms. They represent the level of mass and energy accumulation in the washcoat. In 3.28 accumulation is provided by the diffusion term $\nabla \cdot j_k$ and the generation and destruction of the generical k-th specie due to chemical reaction $\dot{\Omega}_k$.
According to the Fick’s Law 2.32, it is possible to express the diffusive term in this way:

$$j_k = -\rho \ D_{k,mix} \ (Y_{k,f} - Y_{k,w})$$

where $Y_{k,f}$ and $Y_{k,w}$ are the concentration of the k-th specie in the first fluid cell adjacent to the washcoat surface and in the washcoat.
In 3.29 energy accumulation is provided by the heat exchanged between fluid and solid $Q^{f\rightarrow w}$ and the one generated by reaction $H_r$.
Using the previous relations 3.27 and 3.30 in 3.28 and 3.29 it is possible to obtain:

$$\frac{\delta \rho Y_{w,k}}{\delta t} = \rho \ D_{k,mix} \frac{(Y_{k,f} - Y_{k,w})}{\Delta L} - \dot{\Omega}_k$$

$$\frac{\delta \rho c_w T_w}{\delta t} = h \frac{S}{V} (T_f - T_w) + H_r$$

where $\Delta L$ is the distance between washcoat surface and the first fluid cell centre.
These two differential equation are solved step-by-step to obtain the source terms $Q^{f\rightarrow w}$ and $R^{f\rightarrow w}$ included in 2.35 and 2.36 solved by FV-solver. This method highlights some limitations especially in steady-state simulations, as
it requires a time evolution to describe the phenomena. This is the reason why it cannot be simply coupled with steady state FV-solver based on SIMPLE algorithm and an iterative method and an elevate computational effort are required for the solution of 3.31 and 3.32.

For steady-state simulations, a simplified procedure has been implemented on the basis of Baruah theory [20]. The main assumption is that there is no mass accumulation in the washcoat when the global kinetics becomes controlled by the mass transfer process. It means that the accumulation term in 3.31 is null, because all the reactants diffused on the washcoat are supposed to react on the active sites. This provides a very small concentration of these species in the solid phase, \( Y_{k,w} \approx 0 \) and so the concentration gradient between the solid and fluid phase of the reactants can be approximated by fluid phase concentration itself.

In conclusion, these assumptions and considerations provide that \( R_k^{f\rightarrow w} \) can be defined as the minimum between \( \Omega_k \) and \( \rho D_{k,mix} \frac{(Y_{k,f} - Y_{k,w})}{\Delta L} \). In this way, at low temperature when \( T < T_L \), the specie conversion is limited by the reaction kinetics; conversely, at high temperature, the diffusion of the reactants represents the limiting factor.

3.2 Macro-Scale Model

3.2.1 Averaging Operators and their Properties

In order to obtain the set of equations for a macro-scale analysis, it is necessary to apply averaging operators to the corresponding micro-scale equations. Two different kind of operators are identified:

- *Local-volume averaging:* this operator permits to calculate average quantities weighted on a reference volume, known as Representative Elementary Volume (REV). The idea of this operator is the following:

\[
\langle \phi \rangle^V = \frac{1}{V} \int_V \phi dV
\]  

(3.33)

The value of \( \langle \phi \rangle^V \) is assigned to any point in the REV. For a multiphase domains, as the one analysed in this work, it is possible to write:

\[
\langle \phi_i \rangle^V = \Phi_i \langle \phi_i \rangle^i
\]  

(3.34)

where \( i \) at the superscript identifies the i-th phase. \( \Phi_i \) is the ratio between the volume \( V_i \) occupied by the i-th phase and the total REV \( V \). In case of two phases, it is called porosity. After the volume averaging
is done, it is possible to relate the averaged property with the effective one as follows:

$$\phi = \langle \phi \rangle^{i} + ^{i} \phi$$  \hspace{1cm} (3.35)$$

where the term $^{i} \phi$ represents the distribution of the $\phi$ property in the reference volume. This theory, called Theory of Local Volume Average ([26], [27],[28]), permits to obtain the following formulations of the principle operators used in the Navier-Stokes equations:

$$\langle \vec{\nabla} \phi \rangle^{V} = \vec{\nabla} \left( \Phi \langle \phi^{i} \rangle \right) + \frac{1}{V} \oint_{S_{i}} \phi \vec{n} dS$$  \hspace{1cm} (3.36)$$

$$\langle \vec{\nabla} \cdot \phi \rangle^{V} = \vec{\nabla} \cdot \left( \Phi \langle \phi^{i} \rangle \right) + \frac{1}{V} \oint_{S_{i}} \phi \cdot \vec{n} dS$$  \hspace{1cm} (3.37)$$

$$\langle \frac{\partial \phi}{\partial t} \rangle^{V} = \frac{\partial}{\partial t} \left( \Phi \langle \phi^{i} \rangle \right) - \frac{1}{V} \oint_{S_{i}} \phi \vec{U} \cdot \vec{n} dS$$  \hspace{1cm} (3.38)$$

where $S_{i}$ is the surface of the interface between the different phases and $\vec{U}$ is the relative velocity between the different phases. In the problem in exam, it is the fluid velocity as the solid phase is fixed.

- **Time averaging**: as previously pointed out, at high $Re_c$ fluid becomes fully turbulent. This means that unsteady phenomena involve the fluid motion even if the boundary conditions are all steady. These phenomena need to be described when the up-scaling process is done. This is the reason why the time averaging operator ([18]) is defined:

$$\overline{\phi} = \frac{1}{\Delta t} \int_{\Delta t} \phi dt$$  \hspace{1cm} (3.39)$$

The time decomposition can be so expressed:

$$\phi = \overline{\phi} + \phi'$$  \hspace{1cm} (3.40)$$

where $\phi'$ represents the time fluctuations of $\phi$ around $\overline{\phi}$. An interesting property is that $\overline{\phi'} = 0$.

These operators are related by the following relation if the medium is rigid and not time dependant:

$$\langle \overline{\phi} \rangle^{V} = \langle \overline{\phi} \rangle^{V}$$  \hspace{1cm} (3.41)$$

In order to up-scale the instantaneous governing equations, it is necessary to apply both the local volume and time averaging operators. It implies that:

$$\phi = \langle \overline{\phi} \rangle^{i} + ^{i} \phi + ^{i} \phi' + \left( ^{i} \phi' \right) = \langle \overline{\phi} \rangle^{V} + ^{i} \phi + \left( ^{i} \phi' \right)$$  \hspace{1cm} (3.42)$$
By Eq. 3.42 it is possible to derive and demonstrate that \( \langle \phi' \rangle^i = \left( \langle \phi \rangle^i \right)' \), \( \bar{\phi} = \bar{i}\phi \) and that \( i\langle \phi' \rangle = (i\phi)' \).

When these operators are applied to compressible flows, the averaging process produces fluctuations between density and other properties. To avoid this behaviour, a density whighted averaging is defined. It is called **Favre averaging** and it is so expressed:

\[
\bar{\phi} = \frac{\rho * \phi}{\rho^*}
\]  (3.43)

and satisfies the following property:

\[
\phi = \bar{\phi} + \phi''
\]  (3.44)

\[
\bar{\rho} * \bar{\phi} = 0
\]  (3.45)

This definition can be extended in case of volume averaging in the following way:

\[
\langle \phi \rangle^i = \frac{\langle \rho * \phi \rangle^i}{\langle \rho^* \rangle^i}
\]  (3.46)

### 3.2.2 Averaging of Navier-Stokes Equations

By applying the previous operators to the Navier-Stokes equations, it is possible to write:

- **Mass conservation:**

  \[
  \frac{\partial \Phi \langle \rho \rangle^f}{\partial t} + \nabla \cdot \left( \langle \rho \rangle^f \langle \tilde{U} \rangle^f \right) = 0
  \]  (3.47)

- **Momentum conservation:**

  \[
  \frac{\partial}{\partial t} \left( \Phi \langle \rho \rangle^f \langle \tilde{U} \rangle^f \right) + \nabla \cdot \left( \langle \rho \rangle^f \langle \tilde{U} \rangle^f \langle \tilde{U} \rangle^f \right) = \nabla \cdot \left( \mu \left( \nabla \langle \tilde{U} \rangle^f + \nabla \langle \tilde{U} \rangle^f \right) \right) + \\
  \nabla \cdot \left( \frac{\partial}{\partial t} \langle \tilde{U} \rangle + \nabla \cdot \nabla \langle \tilde{U} \rangle + \nabla \cdot \nabla \langle \tilde{U} \rangle + R_P + R_V \right)
  \]  (3.48)
• **Energy conservation:**

\[
\frac{\partial}{\partial t} \left( \Phi \langle \rho \rangle \left\langle e + \frac{1}{2} \| \mathbf{U} \|^2 \right\rangle \right) + \nabla \cdot \left( \Phi \langle \rho \rangle \langle \tilde{e} + 1 \rangle \frac{\mathbf{U}}{2} \right) = \mathbf{g} \cdot \langle \mathbf{U} \rangle + \nabla \cdot \left( \Phi \langle \rho \rangle \langle \tilde{e} + 1 \rangle \frac{\mathbf{U}}{2} \right) \quad (3.49)
\]

• **Specie conservation:**

\[
\frac{\partial}{\partial t} \left( \Phi \langle \rho \rangle \langle \tilde{Y}_k \rangle \right) + \nabla \cdot \left( \Phi \langle \rho \rangle \langle \tilde{Y}_k \rangle \frac{\mathbf{U}}{2} \right) = \nabla \cdot \left( \Phi \langle \rho \rangle \langle \tilde{Y}_k \rangle \frac{\mathbf{U}}{2} \right) + \nabla \cdot \left( \Phi \kappa \langle \tilde{T} \rangle \langle \tilde{Y}_k \rangle \right) + \ldots \quad (3.50)
\]

• **Equation of state:**

\[
\frac{p}{\rho} = R^* T \quad (3.51)
\]

This set of equations is valid only for the fluid phase. As a result these are coupled with the energy equation for the solid phase.

\[
\frac{\partial}{\partial t} \left[ (1 - \Phi) \langle \rho \rangle c_s \langle \tilde{T} \rangle \right] = \nabla \cdot \left[ (1 - \Phi) \kappa_s \nabla \langle \tilde{T} \rangle \right] + Q^{w-f} \quad (3.52)
\]

where \( Q^{w-f} = -Q^{f-w} \).

In the previous equations extra-terms appear because of the averaging process.

The **resistance source term** is related to those terms that appear in Eq. 3.48. It is important to underline the actual physical meaning of each one of these terms in order to introduce mathematical model which can describe them:

• \( \mathbf{\overline{\mathbf{T}}} \): it represents the turbulent Reynolds stress divided by the density.

\[
\mathbf{\overline{\mathbf{T}}} = \langle \mathbf{\overline{\mathbf{U}}}^n \rangle \langle \mathbf{\overline{\mathbf{U}}}^n \rangle \quad (3.53)
\]
• $\overline{D}$: it represents the dispersion associated to spatial deviations of time averaged velocity.

$$\overline{D} = \langle \tilde{i} \tilde{U} \tilde{j} \tilde{U} \rangle$$  \hspace{1cm} (3.54)

• $\overline{D_T}$: it represents the turbulent dispersion to both time fluctuations and space deviations of the instantaneous velocity from the averaged one.

$$\overline{D_T} = \langle \tilde{i} \tilde{U}^n \tilde{j} \tilde{U}^n \rangle$$  \hspace{1cm} (3.55)

• $\vec{R}_P$: it is associated to the form drag.

$$\vec{R}_P = \frac{1}{V} \int_{S_i} \vec{n} \bar{p} dS$$  \hspace{1cm} (3.56)

• $\vec{R}_V$: it describes the viscous part of the total drag.

$$\vec{R}_V = \frac{1}{V} \int_{S_i} \mu \left( \nabla \vec{U} + \nabla \vec{U}^T \right) \vec{n} dS$$  \hspace{1cm} (3.57)

The terms with the superscript $^E$ represent the corresponding terms in the energy equation.

Previous works [28] have pointed out that the terms $\mathcal{T}$ and $\mathcal{D}_T$, related to the turbulent fluctuations, give a negligible contribution. It explains the fact that the choice of the turbulence model has no impact in the prediction of the pressure drop, as it is principally provided by the form drag terms ($R_P$). Once the physical meaning is understood, it is important to find a model which can model these terms. In particular, it is possible to define:

$$- \nabla \cdot \overline{\mathcal{T}} - \nabla \cdot \overline{\mathcal{D}_T} + \nabla \cdot \overline{\mathcal{D}} - \vec{R}_P + \vec{R}_V = \vec{\Phi}$$  \hspace{1cm} (3.58)

$\vec{\Phi}$ is a vector which represents the contribution of pressure gradient given by the porous media, it depends on the instantaneous fluid and thermo-physical properties. The application of the Buckingham-II ([28]) theorem permits to define a non dimensional parameter which can describe this term.

$$\Pi_1 = \frac{\vec{\Phi}^{U^2}}{U \mu}$$  \hspace{1cm} (3.59)

The idea is to compute the different values of $\Pi_1$ under different $Re_c$ using micro-scale simulations, to interpolate these value obtaining a general
law which permits to compute the value of $\Phi$ that had to be used in the momentum averaged equation.

The **inter-phase convective term** is expressed by the term $Q^{e\rightarrow f}$. It is the same already defined in Eq. 3.27. To define the correct value of $h$ the idea is to evaluate in micro-scales simulations the $Nu$ under different $Re_c$ and to interpolate these values by means of a potential function. In this way it would be possible to express under different conditions the correct value of $h$ that had to be used to compute $Q^{e\rightarrow f}$.

The **reaction terms** in averaged Navier-Stokes equations are both $(\langle R_k \rangle)^f$ and $R_k$. The first one is the easiest term to describe: it is the averaged source term derived from reactions in homogeneous phase. As it is clear, this term is strictly related to that one described in the FV solver for micro simulations. It is generally modelled by using a simple Arrhenius reaction model.

The biggest difficulties are in the characterisation of the term $R_k$. It represents the effective catalytic contribution and it is the averaged quantity of the reaction rate computed in micro simulations by the FA solver. As it is clear, this term describes surface reactions in micro simulation but, in macro simulation, it is necessary a volume reaction rate because the micro-structure is no reproduced, and so there is not the washcoat surface where reactions occur. This required an obvious rescaling of the pre-exponential constants, in order to take into account this facet. The rescaling factor is a length strictly connected with the washcoat thickness. This permits to consider those catalytic volume reactions performed in the washcoat volume. This implementation permits to estimate the reaction rate as if the problem is entirely kinetic-dominated. The term $\nabla \cdot (\Phi (\langle p \rangle)^f (\langle D_{k,mix} \rangle)^f \nabla (\langle Y_k \rangle)^f)$ describes the averaged diffusive behaviour in the only homogeneous phase. It does not consider those phenomena related to the adsorption and desorption of chemical species in the washcoat. As previously explained, these facets are not negligible when $T > T_L$ because they mark the bottleneck of the entire conversion process. In the micro-model these phenomena are described by Chapman-Enskog diffusive model, applied only for those cell close to the interface fluid-solid. During the up-scaling and averaging this contribution is lost, as the geometry is not reproduced.

To reproduce the effective behaviour, the diffusion-limit term has been implemented in a dedicated model which permits to compute the effective reaction rate. This permits to calculate both the reaction velocity $\dot{\Omega}_k$ for the k-th specie by using a detailed chemistry model (e.g. Langmuir-Hinshelwood) and the diffusive contribution by using the Fick’s law (2.32). Like in the micro model, the Baruah assumption is retained valid and so it is assumed that reactant concentrations in solid phase is equal to zero when the catalytic
process is diffusion-dominated.

In conclusion, as previously implemented for micro models, a comparison between $\dot{\Omega}_k$ and $\rho \mathcal{D}_{k,mix} \frac{(Y_{k,f} - Y_{k,w})}{\Delta L}$ is done and it is set that:

$$R_k^* = \min \left( \dot{\Omega}_k, \rho \mathcal{D}_{k,mix} \frac{(Y_{k,f} - Y_{k,w})}{\Delta L} \right)$$ \tag{3.60}

where $Y_{k,f}$ is the k-th specie concentration in the fluid phase, $Y_{k,w} \approx 0$ for Baruah assumption and $\Delta L$ is a characteristic length of the problem (e.g. washcoat thickness). As far as $\mathcal{D}_{k,mix}$ is concerned, different models can be chosen to describe it, e.g. a Chapman-Enskog model or a simplified constant diffusivity. Future developments shall implement a code which permits to evaluate diffusivity in different micro structures, extracting an adimensional parameter which correlates diffusivity, foam properties, fluid regimes for each chemical specie. In this way a general formulation based on Buckingham theorem can be implemented for fluid-dynamics, thermophysics and chemistry, obtaining a macro-model which can be applied to an wide number of cases.
Chapter 4

Micro-Scale Simulations

This chapter will deal with the settings used in the micro-scale models and will discuss the result obtained. Micro-scale simulations consist in the detailed analysis of all phenomena which take place in the micro-structure. It provides a deep understanding of the conversion mechanisms. The results will be used to set macro-scale simulations, whose target is the complete analysis of a part or of the entire 3-way catalyst.

4.1 Mesh Generation

The mesh is generated using the OpenFOAM® utility \textit{snappyHexMesh}. It is a mesh generator which can create 3-dimensional and hex-dominated meshes automatically from triangulated surface geometries in Stereolithography (STL) format. The STL file in Fig. 4.1 represents the structure of a square block $15 \times 15 \times 15 \text{ mm}$ of a silicon carbide foam, whose properties will be investigated in the following sections. The digital structure is obtained due to a micro-CT technique. It uses X-rays to create cross sections of the physical foam that can be used to create a virtual model (3D model) without destroying the original object.

The first step is the creation and discretization of the domain with \textit{blockMesh}, which allows to create parametric hexahedral meshes with grading and curved edges. The domain generated will be a rectangular box $21 \times 15 \times 15 \text{ mm}$; on the $x$-axis the length of the domain is bigger than the length of the STL file. This is why, in foam analysis, it is important to well define the inlet and outlet regions where the Darcy velocity $U_D$ is computed. It permits to calculate the right $Re_c$ and to make comparisons between different foam structures. Starting from the hex mesh generated by \textit{blockMesh}, \textit{snappyHexMesh} splits the domain on the basis of intersection between the background mesh and STL file, removes external or internal cells, and generates the final mesh.

At this point, it is essential to fix the level of spatial discretization. A sensi-
Figure 4.1: Foam structure

Table 4.1: Properties of meshes without boundary layer

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<th>CoarseMesh</th>
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<th>UltraFineMesh</th>
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</tbody>
</table>

vity analysis will be made in order to find a reasonable compromise between accuracy and computational effort. At first three meshes without boundary layer and with a significant increase of elements are compared. Their main properties are indicated in Tab. 4.1. For this analysis incompressible steady simulations will be done under different Reynolds numbers using the OpenFOAM® solver `simpleFoam`.

Because of the lack of experimental data about the foam in exam, a comparison with numerical results provided by Bologna’s University is done.

Fig. 4.2 shows the numerical results of simulations: it is interesting to point up that all those without boundary layers tend to underrate the pressure drop calculated by Bologna. The opposite behaviour is expected, as Bologna pressure drop is calculated without considering inlet and an outlet region but an extrusion of the fluid domain on the foam inlet and outlet surfaces. In this way the fluid results well oriented and all aligned when it enters the foam structure. It is reasonable to believe that under these conditions the
pressure loss will be smaller than the one obtained with a domain structured as the one set in this work. In fact, in the domain in exam, the fluid needs to decelerate and deviate its trajectory when entering the foam structure. It represents an important contribution to the complex pressure drop and it is absent in Bologna’s configuration, as the fluid has already the correct orientation.

It seems that there is not a relevant effect of the number of cells in the result. It is caused by the fact that the coarser mesh has a number of elements that is sufficient to guarantee the independence of the solution from the discretization level of the mesh.

In the following, the effect of the boundary layer is investigated. Indelicato [16] has pointed out that the effect of boundary layers on the analysis of an idealized foam model is marginal. These considerations are valid only for cubic cell geometries, whose orderliness permits to make simulations without boundary layers. In any case, the results obtained with this model will lack accuracy. More complex idealized structures, like Kelvin Cell (KC), need a boundary layer to be well simulated. It has been proven by this work that...
the adding of a boundary layer in a KC permits to obtain an increase in the pressure drop of the $15 \div 20\%$, getting results much more accurate and closer to the reality.

For the real foam many simulations has to be done in order to set the correct parameters for the best generation of the boundary layers, i.e. the minimum number of layer added with the best mesh quality and the highest accuracy.

The main problem in the generation of the boundary layer is that *snappyHexMesh* fails in the adding layers because of the progressive worsening of mesh quality. It is necessary to relax the quality controls and to investigate different methods of adding layers. Two techniques are identified. The first one consists of the contemporary adding of all layers: it evinces that for an high number of layers the adding law is not linear anymore (see Fig. 4.4).

In the second method layer addition is done step-by-step and it permits to maintain the adding law linear. It means that all layers have approximately the same number of cells. In other words, the second algorithm forces *snappyHexMesh* to add the same number of cells at each step generating a more homogeneous boundary layer.

![Figure 4.3: Percentage variation of pressure drop compared to the $N_{Layers} - 1$ mesh](image1)

![Figure 4.4: Layer addition law](image2)

The lowest number of layers required to have a stabilization of the results is four or five for both these techniques. In fact, the progressive variation of results for higher number of layer is less than 1%. It means that five layer are enough to guarantee the complete independence of the solution from the mesh.

The layer addition is done in two steps (Fig. 4.5) starting from a mesh without boundary layer. The first boundary layer added (Step 1) consists of three
layers with relative size and without grading. This is the farthest layer from the STL surface. The nearest consists of five layers added (Step 2) with grading and with an absolute size of 25 µm. These are finer than the previous generated as they must reproduce as better as possible the washcoat surface deposited on the solid matrix.

<table>
<thead>
<tr>
<th>Cells</th>
<th>CheckMesh</th>
<th>Algorithm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 0</td>
<td>824228</td>
<td>OK</td>
</tr>
<tr>
<td>Step 1</td>
<td>1074678</td>
<td>83 Cell High SKEW</td>
</tr>
<tr>
<td>Step 2</td>
<td>1424055</td>
<td>224 Cell High SKEW</td>
</tr>
<tr>
<td>Step 1</td>
<td>1250299</td>
<td>28 Cell High SKEW</td>
</tr>
<tr>
<td>Step 2</td>
<td>1767839</td>
<td>165 Cell High SKEW</td>
</tr>
</tbody>
</table>

Table 4.2: Comparison between quality characteristics of the two algorithm for layer addition

As Tab. 4.2 shows, the second algorithm provides a mesh with an higher quality than the first one. For the best one, the max value of skewness is reached by 165 cells and it reaches 7.88814. It is higher than the limit suggested for internal boundaries ($Max Skew = 4$). However, experience points out that if a low percentage of cell has an higher value, the mesh can be globally considered valid. In this case, the percentage of elements is about 0.01% and so the mesh can be retained valid. However, many controls for each simulation will be done in order to verify if these few cells would create unboundedness in the entire domain.

Figure 4.5: Structure of the boundary layer
**Final Mesh**

The final mesh adopted in the following simulations is the one represented in Fig. 4.6. It is obtained dividing the block domain provided by `blockMesh` into $21 \times 15 \times 15$ cells. In `snappyHexMesh` three refinement levels are set with four cells between each level and the method used for the generation of the boundary layers is the second one because of the previous considerations. In this mesh, the fluid domain is the only defined. As a consequence, it can be used only in single-region simulations (see section 3).

![Figure 4.6: Final mesh for Single-Region simulations](image)

For the generation of the multi-regions mesh the same settings adopted for the single-region one are used. This second mesh is generated using `snappyHexMesh` too, which creates a mesh of the entire domain, both solid and fluid. Then the fluid and solid zones are splitted into two different
domains, obtaining the final multi-regions model. The multi-regions mesh is represented in Fig. 4.7.

Figure 4.7: Final mesh for Multi-Regions simulations
4.2 Geometrical Characterisation

Once mesh is generated, the first step in the micro-analysis of a porous media consists of the evaluation of its geometrical properties [28], [29]. These can be classified as follows:

- **Porosity** $\Phi$: it represents the ratio between the volume of the fluid phase $V_f$ and the total volume of the sample $V$.

$$\Phi = \frac{V_f}{V}$$

This ratio ranges between 0 and 1 and can be expressed in percentage.

- **Specific Surface** $S_v$: it is defined as the ratio between the surface at fluid-solid interface $S$ and the total volume of the porous media.

$$S_v = \frac{S}{V}$$

- **Cell Size** $d_c$: this parameter is defined exclusively in open-cell foam and represents the average cell diameter of the sample.

- **Pore Size** $d_p$: it is the average pore diameter in a porous media. It can be expressed by using length unit or ppi (pores per inch); the bigger it is, the smaller the pore is.

- **Strut Size** $d_s$: this parameter is the average size of the solid structure.

![Distinction between cell and pore in an open-cell foam](image)

Figure 4.8: Distinction between cell and pore in an open-cell foam

The evaluation of these properties is not simple and immediate, since there are different approaches to identify them. In this work, an approach based on Vogel’s work [30] is used. The first step of the algorithm implemented consists in associating at every point in the space the diameter of the largest
sphere that includes the point and fits completely the void space. Then, the void space is reconstructed by means of regular spherical elements obtained assigning to each computational cell the diameter value of the largest sphere. This method, shown in Fig. 4.9, allows to obtain the average cell and pore sizes.

![Cell size evaluation](image1)

(a) Cell size evaluation

![Pore size evaluation](image2)

(b) Pore size evaluation

Figure 4.9: Reconstruction of the void space by means of regular spheres

The same considerations can be done by considering the solid volume instead of the void one. In this way, the algorithm will provide information about the strut diameter as shown in Fig. 4.10.

![Strut size evaluation](image3)

Figure 4.10: Reconstruction of the solid strut by means of regular spheres

A statistical analysis has been done for both the void volume (Fig. 4.11(a)) and the solid one (Fig. 4.11(b)). For a typical open-cell foam, the size
distribution of the spherical elements in the void volume exhibits distinct maxima in correspondence of the characteristic dimension of the pores and cells. As far as the solid strut is concerned a single higher maximum can be seen in correspondence of the characteristic strut size. However, it is interesting to observe a dispersion for bigger values than \( d_s \). It is caused by the intersection between different struts that generates zones where the material is thickened (nodes).

(a) Cell and pore size evaluation

(b) Strut size evaluation

Figure 4.11: Statistical analysis of the size distributions
Both the curves are interpolated by gaussian distributions, plotted in red in Fig. 4.11. This permits to estimate the effective average size value with its standard deviation. The geometrical properties calculated are reported in Tab. 4.3; these information will be used to characterise the porous models implemented in macro simulations.

\begin{table}[h]
\centering
\begin{tabular}{llll}
\hline
 & Mean & St. Dev. \\
\hline
\(\Phi\) [\%] & 82.4318 & \\
\(S_V\) [m\(^2\)/m\(^3\)] & 586.385 & \\
\(d_c\) [mm] & 3.76315 & 0.55981 & \\
\(d_p\) [mm] & 1.89878 & 0.53684 & \\
\(d_s\) [mm] & 0.30869 & 0.07374 & \\
\hline
\end{tabular}
\caption{Geometrical properties}
\end{table}
4.3 Fluid-Dynamic Characterisation

In this section, many simulations are carried out in order to identify the main parameters which characterise the sample. These simulations are all implemented with a single-region approach, as there is no need to consider at this step thermal exchange phenomena. The range of analysis is more or less the one interesting 3-way catalyst application with $Re_c = 1 \div 750$, and all of these simulations are carried out at a fixed $T$ ($T = 20^\circ C$).

First of all, it is important to set the model and choose the level of approximation for the analysis. For this reason, it has been decided to compare a compressible model and an incompressible one. It is expected that the results obtained by the different simulations are similar, as no-evident density variation are expected and the maximum Mach number reached is 0.008. This value is much smaller than the limit ($M = 0.3$) from which compressibility effects become significant.

![Figure 4.12: Comparison between compressible and incompressible models](image)

These considerations are clearly shown in Fig. 4.12 where the results of three different simulations are plotted. For the incompressible simulation, the solver used is *simpleFoam*, while for the compressible ones is *rhoSimpleFoam*. As it can be seen, two compressible simulations are carried out: these have exactly the same parameters apart from the boundary condition used for temperature. In SIM1 the boundary condition used at the interface solid-fluid is *zeroGradient*, and in SIM2 is *fixedValue*. In the first case the thermal flux equal to zero is imposed, while in the second one temperature
is set equal to the inlet temperature. Even if the boundary conditions are formally different, their effects should be exactly the same, as evinced in Fig. 4.12. The two models provide the same results. The biggest difference between a compressible and incompressible model is less than 1.6\% when $Re_c = 100$ and rapidly decreased (under 0.1\%) with an increasing $Re_c$. This is caused by the approximation level of pressure value which is not the same for two solvers. For low Reynolds, when pressure drops are low, the main difference between the results is given by the truncation error, while at high $Re_c$ this contribution gradually becomes negligible. In conclusion, the model chosen for the next simulations is the incompressible one as it reaches the same level of approximation of a compressible one, but with a lower computational effort.

![Graph showing pressure drop across different directions](image)

**Figure 4.13: Evaluation of the isotropic behaviour of the sample**

Once the model is chosen, the actual fluid-dynamic characterisation starts. At first it has been decided to verify the isotropic behaviour of the foam in exam. To do this, meshes with inlet and outlet non-disturbed regions are generated for the $y$-and $z$-directions. The results show that the foam has an orthotropic behaviour, as the pressure drop along the $y$-axis is a little bit bigger (Fig. 4.13) than the others. It is probably related to the manufacturing process: in fact, even if the process will theoretically produce isotropic foam, evidence shows that the gravitational force tends to distort the structure when it is not completely solidified. In this way, the two horizontal directions maintain the same characteristics, but the vertical one shows elongated cells and pores. This is the reason why the $y$-axis pressure drop is
Taking in consideration this behaviour, all analysis will be carried out using the x-axis as the main direction.

### Table 4.4: Pressure-drop and fluid-dynamic parameters

The results of the simulations can be analysed in terms of non-dimensional coefficients $\Pi_1$ and $\Pi_2$. They are defined as follows:

\[
\Pi_1 = \frac{\Delta p d_c}{L U_D \mu} = f_1 (Re_c)
\]

(4.1)

\[
\Pi_2 = \frac{\Delta p d_c}{L \rho U_D^2} = f_2 (Re_c^{-1})
\]

(4.2)

where $d_c$ is the characteristic dimension of the foam microstructure, like the cell diameter and $L$ is the main length of the domain in exam ($L = 15 \text{mm}$). If the Darcy-Forchheimer regime is considered ($Re_c < 150$), the Darcy-Forchheimer law (2.40) can be recovered by expressing the functional dependency $f_1 (Re_c)$ as:

\[
f_1 (Re_c) = A + B (Re_c)
\]

(4.3)

where $A = d_c^2/K$, $B = d_c C$, $K$ is the permeability and $C$ the form coefficient.

If turbulent regimes are considered the functional dependency becomes:

\[
f_1 (Re_c) = A_{turb} + B_{turb} (Re_c)
\]

(4.4)

In Fig. 4.14(a) it is possible to distinguish the different regimes analysing the different slopes that the curve adopts.

The same considerations can be done by analysing $\Pi_2$ in 4.14(b). The function that interpolates the curve is not linear but potential. It can be expressed as follows:

\[
f_2 (Re_c^{-1}) = C Re_c^D
\]

(4.5)
this is valid if the Darcy-Forchheimer regime is considered. While for the fully-turbulent regimes the law can be expressed:

$$f_2 \left( Re_c^{-1} \right) = C_{turb} Re_c D_{turb}$$

(4.6)

By interpolating the curves, it is possible to obtain the constants that had to be used in the previous equations. Their values are reported in Tab. 4.5. The calibration curves are calculated using the least square method. The reliability of the model used and the level of approximation are very high, as the minimum value of $R^2$ is 0.9925. $R^2$ is the coefficient of determination, i.e. a number that indicates how well data fit a statistical model. The coefficient ranges from 0 to 1. The higher the coefficient, the better the model.

By an interpolation, it is also possible to obtain the constant $d$ and $f$ that had to be inserted in Eq. 2.40. It permits to introduce a model that

Figure 4.14: Fluid-dynamic characterisation with $\Pi_1$ (a) and $\Pi_2$ (b)
can be used in macro simulations.
The Darcy-Forchheimer equation is rigorously valid only for $Re_c < 150$ and theoretically its law cannot be used to describe the entire range of $Re_c$ analysed. However, the error committed is negligible ($R^2 = 0.999$) as seen in Fig. 4.15 and it is reasonable to apply this model for the entire range. It permits to set the constants for the macro simulations reproducing the average behaviour of the foam in exam for a wide range of $Re_c$.

![Figure 4.15: Comparison between calculated pressure drops and interpolated ones](image)

The values of the two constant are:

$$d = 5.74 \times 10^6 \text{ m}^{-2} \text{s}^{-1}$$

$$f = 705.029 \text{ m}^{-1}$$
4.4 Thermal Characterisation

In this section the thermal properties of the sample will be investigated. In particular, two different kind of simulations will be carried out in order to identify the main parameters characterising the heat-transfer process. These parameters are the effective conductivity and the Nusselt number evaluated for different Reynolds.

4.4.1 Conductive heat-transfer

In order to investigate the conductivity properties of the porous matrix, simulations of the heat-transfer in the solid phase are done. The computational model is based on the solution of the Fourier Law (see Eq. 2.31) for the solid matrix.

These simulation are run imposing an hot and cold temperature at the boundary of the sample. Three orthogonal directions are considered, in order to investigate the isotropic behaviour of the foam. As a result, a temperature $T_c = 400\ K$ is fixed at the cold side, $T_h = 800\ K$ at the hot side and an adiabatic boundary condition is set at the other boundaries.

Considering the x-axis, the temperature field obtained is the one in Fig. 4.17.

Once the heat flux exchanged $\dot{Q}_{\text{cond}}$ is calculated by the utility $\text{wallHeatFlux}$,
the effective conductivity in each direction is computed in the following way:

$$\kappa_{\text{eff}} = \frac{Q_{\text{cond}} L}{S (T_h - T_c)}$$

where $L$ is the main dimension ($L = 0.015 \text{ m}$) and $S$ is the cross section of the sample. The following values of $\kappa_{\text{eff}}$ are obtained:

<table>
<thead>
<tr>
<th>$\kappa_{\text{eff}}$</th>
<th>$16.04 \text{ W/(mK)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\kappa_{\text{eff}}^y$</td>
<td>$18.25 \text{ W/(mK)}$</td>
</tr>
<tr>
<td>$\kappa_{\text{eff}}^z$</td>
<td>$16.10 \text{ W/(mK)}$</td>
</tr>
</tbody>
</table>

Table 4.6: Effective conductivity

The effective conductivity is an average parameter which characterises the heat transferred by conduction in a porous media. It is always lower than the solid conductivity as it considers the effective presence of pores, cells and discontinuities inside the solid matrix. In the case in exam, the average $\kappa_{\text{eff}}$ is more or less the 7% of the solid one ($\kappa_s = 270 \text{ W/(mK)}$), aligning with data found in literature [28].

It can be noticed by looking Tab. 4.6 that the effective conductivity is higher along the y-axis while similar values are computed in the other two. This orthotropous behaviour is very similar to the one identified in the fluid-dynamic analysis and, in the same way, it can be explained as a consequence of the manufacture process, which determines a slightly different cell geometry in one direction.

### 4.4.2 Conjugate heat-transfer

As final step, simulations of the heat transfer process between the fluid and solid phases are addressed under different $Re_c$. These are run in a multi-region framework (see Fig. 4.7). The computational model is based on the coupled solution of the equations governing the flow of a compressible fluid and the heat-conduction in a solid. The energy equations, solved on both the fluid and on the solid computational domains, are coupled by means of the heat flux at the interface of the two phases.

The steady-state simulations are carried out by a SIMPLE solver implemented in OpenFOAM®, setting the inlet fluid temperature equal to 500 $K$ and the solid boundary one equal to 300 $K$. The principal target of these simulations is to extract a law correlating $Nu$ and $Re_c$ that can be used in the macro-scale simulations.

The definition of $Nu$ considered in this research is based on the average quantities. It implies that the effects connected with the thermal conductivity are
considered, since it influences the difference of temperature between the bulk and the external surface of the solid matrix. \( Nu \) is so computed:

\[
Nu = \frac{hd_c}{\kappa_{fluid}}
\]

(4.7)

where \( \kappa_{fluid} \) is the washcoat surface averaged fluid conductivity and \( h \) is the inter-phase heat transfer coefficient. It can be evaluated as follow:

\[
h = \frac{Q^{\rightarrow vw}}{S_v V (\hat{T}_f - \hat{T}_s)}
\]

(4.8)

\( \hat{T}_f \) is the volume average fluid temperature and \( \hat{T}_s \) is the solid one. By interpolating the numerical results (Fig. 4.18) it is possible to extract the coefficients which correlates \( Nu \) and other adimensional groups. In particular, the classical thermodynamic theory provides a correlation between \( Nu \), \( Re \) and \( Pr \) \((Pr = \frac{\mu c_p}{k})\):

\[
Nu = CRe^m Pr^n
\]

(4.9)

However, the simulations are all run maintaining \( Pr \) constant in order to investigate the only dependence on \( Re \). In fact, as the fluid considered is
exactly the same in all simulations and the variation of its properties ($\mu$, $c_p$, $k$) with temperature is negligible, it is reasonable to analyse the variation of $Nu$ under different $Re$. In this way, Eq. 4.11 can be written as follow:

$$Nu = DRe^b$$

(4.10)

For the case in exam, the following law is obtained:

$$Nu = 2.6017Re^{0.4267}$$

(4.11)

$R^2$ is equal to 0.9975.

Figure 4.18: Dependence of Nu coefficient on Re number
4.5 Chemical Characterisation

In this section the performances regarding the pollutant abatement will be investigated. To validate the model, the $CO$ reaction is the only one considered. As previously pointed out, two different models will be analyzed. Both of them are used in steady-simulations under a variation of the fluid inlet temperature $T_{in}$. In this way, it will be possible to determine the effects of $T$ in $CO$ abatement, identifying operating curve of the foam and the light-off temperature.

4.5.1 Single-Region Simulations

In the single-region simulations, the fluid domain is the only analyzed. The temperature at the interface solid-fluid is set equal to $T_{in}$. This implies that it has been assumed that the solid guarantees an infinite heat exchange, as all thermal power generated by chemical reactions on the washcoat surface is exchanged. Consequently, there is no accumulation of heat in the solid domain and the washcoat temperature is maintained constant.

The complete set of boundary condition is reported in Fig. 4.19: $p_{in}$ is $1.001 \times 10^5 \ Pa$, $T_{in}$ varies in a range between $450 \ K$ and $700 \ K$ and the mass
Table 4.7: Mass fractions at inlet

<table>
<thead>
<tr>
<th>Species</th>
<th>Mass Fractions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>0.626</td>
</tr>
<tr>
<td>$O_2$</td>
<td>0.201</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>0.145</td>
</tr>
<tr>
<td>$CO$</td>
<td>0.028</td>
</tr>
</tbody>
</table>

The principle target of these simulations is the identification of the abatement efficiency, computed as follows:

$$
\eta_{CO} = \left( \frac{Y_{CO}^{out} - Y_{CO}^{in}}{Y_{CO}^{in}} \right) \times 100
$$

(4.12)
(a) Langmuir-Hinshelwood Constants

\[
A_1 \, [mol K/(m^2 s)] = 5.0 \times 10^9 \\
E_1 \, [J/mol] = 95000
\]

(b) Arrhenius Constants

\[
A \, [mol K/(m^3 s)] = 2.239 \times 10^{12} \\
E_{att} \, [J/mol] = 20446.3
\]

Table 4.8: Chemical constants

In Fig. 4.20 the results obtained from single-region simulations are plotted and a comparison between three different models is done.

As explained in section 2.4, the pressure drops obtained with or without a turbulent model should be more or less the same. These considerations are also valid in the analysis of chemical reaction as it can be clearly seen in Fig. 4.20. The turbulent model used is a \( k - \omega_{SST} \), i.e. a Low Reynolds Number (LNR) method. It is obtained by coupling two different models: \( k - \epsilon \) and \( k - \omega \). The first one is an High Reynolds Number (HRN) method; it well describes the shear flow, but is not able to give a strong characterisation of the wall flux. On the contrary, the second one, which is a LRN method, well describes the wall flux, but it is not accurated in the characterisation of the
shear flow. This last model needs a fine boundary layer near the wall, as it require a $y^+ < 1$. The $k - \omega$ SST model is the one that characterise at best the turbulence in all fluid regions, both close to and away from the wall. The value of $y^+$ in the simulations is always lower than 1. It suggests that the model is properly working. However, its contribution is correctly negligible, as the max difference between turbulent and laminar results is lower than 0.03%.

In Fig. 4.20 it is possible to identify the light-off temperature for this model. This is the temperature where the abatement efficiency is $0.5 \cdot \eta_{CO}^{max}$. In this case, the maximum efficiency is approximately equal to 50% and the $T_L$ seems to be between 325°C and 350°C. This value is aligned with the ones investigated by other authors ([16], [3]). The most interesting thing is that the maximum efficiency reached by this foam is about 50%, resulting lower than those investigated for other foams. This is essentially caused by the fact that this foam has a lower porosity and surface volume ratio. This last parameter is the one that mostly influences the maximum efficiency, as it determines the availability of reacting surface per unit volume. The bigger it is, the higher the pollutant abatement would be. The specific surface of the foam analyzed by [16] is about 1827.4 m$^2$/m$^3$, and it is about three times the specific surface of the foam in exam. This explains why their $\eta_{CO}^{max}$ is more or less the double of the one in Fig. 4.20.

It is also possible to observe that the results provided by a classical single region simulation and an infinitely fast one are exactly the same at an high temperature. The main difference between a traditional simulation and the infinitely fast one is that, in the first one, the reaction speed $\Omega_k$ is computed and, to provide $R_{f \rightarrow w}$, the minimum between $\Omega_k$ and $\rho \cdot D_{k,mix} \frac{(Y_{k,f} - Y_{k,w})}{\Delta L}$ is evaluated. In the second case, as $\Omega_k$ is assumed equal to infinity, $R_{f \rightarrow w}$ is set automatically equal to $\rho \cdot D_{k,mix} \frac{(Y_{k,f} - Y_{k,w})}{\Delta L}$. This means that all reactants react in contact with the washcoat surface and the bottleneck of the process is exclusively given by their diffusion in the homogeneous phase. An infinitely fast simulation always considers the conversion process diffusion-limited; consequently, it is physically significant only if $T >> T_L$. This implies that, if the comparison between these two reaction models is done when $T > T_L$, the conversion process is naturally diffusion-limited and the two model are expected to provide the same results. It is correctly shown in Fig. 4.20 and means that the single-region model is properly working.

Once the model is rightly set, the analysis of the morphological effects on mass transportation is prominent. Indeed, it allows to estimate those coefficients that would be used in a macro simulation. The approach used is the lumped element model proposed by Giani et al. [3]. They have defined a
mass-transfer coefficient by the integration of a 1D molar balance equation:

\[
\frac{d\dot{n}_{CO}}{dV} = Q \frac{dc_{CO}}{dV}
\]  

(4.13)

where  \( \dot{n}_{CO} \) is the molar flow rate,  \( c_{CO} \) is the concentration,  \( Q \) is the volumetric flow rate.

As explained in section 3.1.2, when the process is diffusion-limited, it is possible to express 4.13 in the following way:

\[
Q \frac{dc_{CO}}{dV} = -k_{m}S_{v}c_{CO}
\]  

(4.14)

where  \( k_{m} \) is the mass-transfer coefficient. By integrating 4.14,  \( k_{m} \) can be written as follows:

\[
k_{m} = -\frac{ln(1 - \eta_{CO}^{\text{max}})}{S_{v}V/Q}
\]  

(4.15)

Figure 4.21: Mass transfer coefficient

In Fig. 4.21 the values of  \( k_{m} \) computed under different mass flow rates are plotted. It can be seen that  \( k_{m} \) increases its value under mounting
effective flow rate. The range of mass flow analysed is more or less the same that is generally investigated in experimental simulations \(Q_{EX} = 1000 \div 10000 \text{ Ncm}^3/\text{min}\). For the given foam it is possible to interpolate the numerical data obtaining a general law which can express the mass-transfer coefficient as a function of the effective volume flow rate only:

\[
k_m = 3.9002Q^{0.4164}
\]  \hspace{1cm} (4.16)

Eq. 4.16 is obtained by a potential regression with \(R^2 = 0.9993\).

Another interesting effect that can be seen is that \(\eta_{CO}\) decreases when \(Q\) augments. These considerations are all done at 700 \(K\), so that it is sure that the process is exclusively diffusion-dominated. This behaviour is justified by the fact that an higher velocity inside the structure does not gives enough time to reactants to diffuse over washcoat surface. As results, the \(CO\) conversion decreases (see Tab. 4.9).

<table>
<thead>
<tr>
<th>(Q_{EX}[\text{Ncm}^3/\text{min}])</th>
<th>(\eta_{max}^{CO})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1500</td>
<td>65.42 %</td>
</tr>
<tr>
<td>3000</td>
<td>50.08 %</td>
</tr>
<tr>
<td>6000</td>
<td>37.43 %</td>
</tr>
<tr>
<td>9000</td>
<td>31.09 %</td>
</tr>
</tbody>
</table>

Table 4.9: Conversion under different mass flow rates

### 4.5.2 Multi-Regions Simulations

Single-region simulations demonstrate some limitations as far as the heat transfer is concerned. It has been proven that this kind of simulation can well describe the region where \(T > T_L\). However, if the target is the analysis of the transition from kinetics-dominated to diffusion-dominated process, this method is not really accurate. In fact, in this region small variation in temperature could create big changes in the reaction rate. As the temperature that mostly influences the kinetic is the one close to washcoat, a model with an infinite conductivity does not reproduce at best the actual phenomenon. All comparison between conversion experimental data and numerical ones show that, during transition, the experimental ones are always higher than the numerical ones. Furthermore, the experimental \(T_L\) is always lower than numerical one. This is why the effective foam conductivity is not infinite, but has a real value \((\kappa_s = 270 \text{ W/(mK)})\). This means that in an experimental test-bench, where temperature is imposed at side boundaries, there is a little heat accumulation, due to the generation of thermal power.
by reactions and, for this reason, the washcoat temperature is not exactly equal to the inlet one, like in a single-region model, but it is higher. This behaviour can be well reproduced through a multi-regions modelling of the problem. The entire domain is split into two different regions, the solid and the fluid one. For both of them the complete balance equation set is solved. The fluid one has the same set up used in single-region simulations: the boundary conditions are exactly the same apart from the one at the solid-fluid interface, which would be discussed later. To definite properly the solid domain, it is important to know its properties. The foam in exam is made up of silicon carbide (SiC). This is a material which shows a strong dependence of its thermal properties from its structure and temperature. However, the implementation of a dedicated utility which can describe as best this behaviour is not justified by a relevant increasing of accuracy. This explains the reason why, for this work, constant value are assumed on the basis of experimental analysis provided by literature [32], [33] and [34]. In particular, the following values are adopted: \( \kappa_s = 270 \, \text{W/(mK)} \), \( c_p = 750 \, \text{J/(kgK)} \) and \( \rho = 3100 \, \text{kg/m}^3 \).

Figure 4.22: Comparison between multi and single-region simulations
For the solid region, temperature is fixed at $I_{nY}$, $O_{utY}$, $I_{nZ}$, $O_{utZ}$ equal to the fluid inlet one. As far as the fluid-solid interface is concerned, a mapped-Wall boundary condition is used; it permits to couple the two domains after solving their balance equations.

The main disadvantage of this kind of simulation is the computational burden, which is higher than the single-region one. Indeed, it is observed that a multi-regions analysis lasts approximatively three times more than a single-region one.

As expected, the results plotted in Fig. 4.22 show a reduction of $T_L$ passing from single to multi-regions model. Numerical results show that the light-off temperature is reduced by $\sim 25^\circ C$.

![Figure 4.23: Percentage differences between multi and single-region simulations](image)

(a) Percentage Variation of $\eta_{CO}$  
(b) Percentage Variation of $T_{out}$

In Fig. 4.23(a) the percentage difference, $\left(\frac{\eta_{CO}^{Multi} - \eta_{CO}^{Single}}{\eta_{CO}^{Single}}\right)$, is plotted. The maximum difference is reached when $T_{in}$ is equal to 325$^\circ C K$, that is in the transition zone. When temperature is low, the two models give the same results. This depends on the fact that chemistry is not activated and so no thermal power is generated. The same considerations can be done for the diffusion-limited region, as washcoat temperature does not influence the reaction rate anymore.

Regarding $T_{out}$, Fig. 4.23(b) shows that at low temperatures there are no differences between the two models, as reactions are not activated. The biggest differences are marked when the reactions start to generate thermal power ($T_{in} = 250^\circ C$). In fact a single-region model maintains an outlet temperature more or less equal to the inlet one, while the multi-regions one has a $T_{out} > T_{in}$ because the whole thermal power generated cannot be exchanged.
by the solid matrix. These considerations are further highlighted in Fig. 4.24.

Figure 4.24: Percentage $\eta_{CO}$ variation VS percentage $T_{out}$ variation

In conclusion, single-region simulations allows to obtain an accurate estimation of $\eta_{CO}^{max}$ with a lower computational effort. However, to identify the right abatement curve, a multi-regions simulation is required at the cost of an higher computational effort.
Chapter 5

Macro-Scale Simulations

This chapter presents the validation and the application of the macro-scale model based on the equations already exposed in section 3.2. As previously explained, in a macro-scale simulation there is no need to reproduce exactly the sample micro-structure to investigate its properties. Indeed, the addition of extra terms in the averaged Navier-Stokes equations permits to describe the average phenomena that take place inside the REV. Different simulations are carried out in order to verify if the model implemented fits well the results extracted from micro-scale analysis. The same simulations performed at the micro scale are now up-scaled.

5.1 Mesh Generation

For the validation a domain with the same dimensions of the micro-sample is used (21 × 15 × 15 mm). It is divided into hexahedral regular cell without skewness and non-orthogonality (see Fig. 5.1 e 5.2). Two different meshes are used. The first one is a 1D mesh: it allows to characterise all simulations carried out without thermal exchange. As Fig. 5.1 shows, there is no growth of elements along the transversal directions. The 1D scheme provides data only along the main direction considering an average behaviour along the other two. This condition is guaranteed by the boundary condition set at the external surfaces (empty). The second mesh is a 3D mesh used for all simulations which consider heat transfer processes. More detailed considerations of the usage of these meshes are reported in the following chapters. In any way, the computational effort will be very low, due to the reduced number of cell. Both these mesh are generated using the OpenFOAM®utility blockMesh. The number of cell is chosen after a sensitivity analysis. It has been verified that by a comparison between meshes with different numbers of cells that the solution is independent from the spatial discretization.
Figure 5.1: Mesh 1D used in macro-scale simulations without heat exchange

Figure 5.2: Mesh 3D used in macro-scale simulations with heat exchange
5.2 Fluid-Dynamic Validation

In this section many simulations are performed considering a problem without heat transfer. In this way, it is possible to evaluate the performances of the macro-model in the estimation of the pressure drop. The set of boundary conditions is exactly the same of the simulations described in section 4.3. Fig. 5.4(a) and 5.4(b) show the up-scaling process: in the same image the micro and the macro geometry are represented and the average process of the pressure gradient can be clearly seen. The simulations are carried out by using a SIMPLE solver and considering a compressible gas model, using a Sutherlad transport model for the calculus of the dynamic viscosity and a Janaf model for the calculus of the specific heat.

![Graphs showing pressure drop and Π₁](image)

(a) Comparison between pressure drop per unit length (b) Comparison between Π₁ computed by a micro-model and by macro-one

Figure 5.3: Fluid-dynamic validation

A comparison between dimensional (Δp/L) and non-dimensional (Π₁) parameters which describe the pressure gradient is achieved. As reported in Fig. 5.3(a) and 5.3(b), the two different simulations provide more or less the same results under different $Re_c$. It is interesting to observe that the macro-model tends to slightly underrate the effective value of Π₁. However, this difference is always less than 2.5% and, as it is almost constant for all $Re_c$, it suggests that this systematic error is principally given by the truncation used to approximate the values obtained by micro-simulations and involved in the macro-model setting.

In conclusion, this difference can be considered reasonable and, as results, the model is valid for the rating of the correct pressure drop.

As far, the computational time for macro simulation is about thousand times less than the one required for the correspondent micro simulation. It evinces
the power of this approach.

Figure 5.4: Comparison of the pressure fields computed in micro and macro simulations
5.3 Thermal Validation

In order to consider the correct thermal behaviour of the sample, it is important to adopt a multi-region 3D mesh. The heat transfer process inside the solid matrix is governed by Eq. 3.52. It shows that an important contribution is given by the diffusion term. Since the strongest temperature gradients are evident along transversal directions and not along the axial one, a 1D schematization is not reasonable. Indeed, this introduces an error that is not negligible underrating the effective heat exchange process. Therefore, a 3D model is considered.

Many simulations are performed, setting the same boundary conditions of those presented in section 4.4. Two different quantities are analysed in order to evaluate the macro-model behaviour in thermal simulations. These are the temperature difference between the inlet and the outlet and the correspondent pressure drop.

![Graphs showing comparison between ΔT and pressure drop per unit length](image)

(a) Comparison between ΔT  
(b) Comparison between pressure drop per unit length

Figure 5.5: Thermal validation

As it can be seen in Fig. 5.3, for both temperature and consequently heat exchanged, and for pressure drop there is a good rating. The results computed by the macro-model fit well those obtained by micro-simulations. There is a faint underrating in the evaluation of both quantities, always smaller than 3.5%. This behaviour is analogous to the one showed in the previous section, and the causes are probably the same.

There is also a good estimation of the temperature field inside the solid matrix, as it can be seen in Fig. 5.7. For these simulations the value of the conductivity used for the solid domain is not $\kappa_s$ but $\kappa_{eff}$, since it describes the global behaviour of the foam. Indeed, the solid domain is representative of the average foam domain.
In conclusion, all these considerations suggest that the 3D macro-scale model has correctly evaluated the thermal performances of the sample. Also for these simulations, there is a remarkable saving of the computational resources, as the main computational time is more or less the 1% of the correspondent micro-simulation.

![Figure 5.6: Temperature fields in micro and macro simulations](image1)

![Figure 5.7: Temperature field in the solid matrix evaluated by micro and macro simulations](image2)
5.4 Chemical Validation

At this point, it is possible to introduce chemistry in the problem. Indeed, it is proved that the macro model has good behaviour in simulations both with and without thermal exchange.

In the micro-model, the catalytic reactions are solved by a FA solver. It means that these are considered as surface reactions. On the contrary, in a macro-model, chemistry is implemented using volume reactions. In the first case, catalytic conversion occurs exclusively on washcoat surface. In reality, reactions are promoted inside the whole washcoat layer and not only over the surface. In the macro-model, as there is not the solid matrix, the conversion is promoted inside the whole sample and an average behaviour is estimated. It means that the pre-exponential coefficients used in a Langmuir-Hinshelwood micro-schematization need to be rescaled by a factor that is exactly the washcoat thickness. This is the parameter which permits to compute the correct coefficients per unit volume from those computed per unit washcoat surface. As a result, the correct pre-exponential coefficient used in these simulations is \( A = 1.3 \times 10^{15} \text{ molK}/(m^3s) \). \( E_{att} \) and \( K_i \) do not change as these are not directly related to the washcoat volume.

5.4.1 Single-Region Simulations

As already done in micro simulations, two different models are compared. The first one is a single-region schematization of the problem. This model requires a less computational burden but lacks accuracy especially in the identification of the light-off temperature. This model in macro-simulation
can be analysed by using a 1D geometry, since all heat generated by reaction is immediately exchanged by the solid matrix. Therefore, it is as if there is no heat generated by reactions and all temperatures inside the sample are more or less constant. Fig. 5.8(a) shows the comparison between the micro and macro model in a single-region schematizations. There is a good estimation of the reaction rate and of the light-off temperature. For temperatures lower than $T_L$, there is slightly overrating of CO abatement (lower than 3%). However the model globally fits micro-data.

The macro-model implemented for chemistry does not consider, in these simulations, the diffusion-limit area, as the aim of these simulation is the prediction of the light-off temperature. It implies that, for $T > T_L$, it overrates the effective $\eta_{CO}$, as it still considers the kinetic-dominated problem. As a consequence, CO abatement law is an exponential one (Langmuir-Hinshellwood). This law is plotted in Fig. 5.8(b) and it remarks a good fitting between the two models.

5.4.2 Multi-Regions Simulations

![Figure 5.9: CO abatement in multi-region simulations](image)

Multi-regions simulations are performed by using the 3D mesh. Indeed, in these analysis the heat exchanged between the different phases is considered. To reproduce the correct behaviour, it is important to set the correct parameters regarding the interface surface. As the reaction occurs inside the washcoat that has a porous structure too, the heat transfer surface considered is the one of the washcoat. This results bigger that the one provided by $S_v$, that permits to compute the surface of the only foam. Therefore, it is necessary to multiply $S_v$ computed for the foam by $S^w_v$ evaluated for the
washcoat:

\[ S^w_w = \frac{S^w}{V^w} \]  \hspace{1cm} (5.1)

where \( S^w \) is the surface and \( V^w \) is the volume of the entire washcoat.

In Fig. 5.9(a) and 5.9(b) the comparison between the two models is plotted. At low temperatures the macro model tends to overrate the reaction rate. It is probably related to the performances of the model in thermal evaluation. Indeed, it has been shown that it tends to underrate the heat transferred from fluid to solid. As a result, the fluid close to the solid domain exhibits an higher temperature in macro simulations than micro ones. This behaviour has a relevant meaning in the kinetic-dominated region, as low variations of temperature determine variations in the reaction rate. However, the over-ratings are restrained and the global abatement is fitted. In conclusion, it is possible to consider valid the model implemented.

As far as the redistribution of the enthalpy generated by the reactions is concerned, \( \Delta T \) between inlet and outlet are plotted in Fig. 5.10(a) and 5.10(b). This is an effective parameter that permits to estimate the generation, distribution and disposal of heat power inside the sample. Once again, these results prove that the macro model fits well the micro simulations.

![Figure 5.10: Absolute and relative difference between inlet and outlet temperatures](image)

Finally, Fig. 5.11 shows a comparison between single and multi-region schematization. It is clear that, like in the micro-scale analysis, the multi-region model provides a lower light-off temperature.
Figure 5.11: Comparison between multi and single-region using micro and macro-model

Figure 5.12: CO abatement in micro and macro simulations
5.4.3 The Diffusive Control

Once verified that the macro-model implemented in this work is able to estimate with an high accuracy and reliability the light-off temperature, the diffusive-control is set. As explained in section 3.2, this is necessary to reproduce the correct behaviour during the catalytic conversion, and it permits to compute the effective reaction rate.

The sub-model implemented requires three different parameters as input: the value of the real foam interface surface $S$, the diffusive constant $D_{k,mix}$ and a characteristic length $l$. It provides the diffusion term in the following way:

$$J = \rho S D_{k,mix} \frac{c_{k,f}}{l}$$

(5.2)

where $c_{k,f}$ is the concentration of the $k$-th specie inside the fluid. The concentration in the solid phase is assumed to be equal to zero, as proposed by Baruah [20]. $D_{k,mix}$ can be computed by using the assumption of $Sc = 1$ or by using a detailed model like Chapman-Enskog. $l$ is a parameter which describes the diffusion process inside the micro-structure. It is strictly related to the cell dimension as it represents that distance through which the gradient concentration is developed. The aim of the implemented sub-model is to reproduce the behaviour shown in Fig. 5.13.

To validate the sub-model, many simulations are promoted evaluated the reaction rate under different inlet temperatures. The audits are done for both single and multi regions schematizations, using the same settings of previous analysis.
The results plotted in Fig. 5.14 show a good rating of the maximum abatement efficiency. These are referred to a multi-regions modelling, but the same is obtained for the analogous single-region one. It is interesting to observe that there is not a smooth transition like in micro simulations. It is principally related to the limitations of the sub-model implemented.

As far as the thermal performances are concerned, the global behaviour is rightly as shown in Fig. 5.15.
5.5 Multi Reactions Model

Once the macro model is validated for only one reaction, a multi reactions scheme is implemented. Many simulations are performed in order to evaluate the behaviour of the model under different conditions and considering multi reactions. The scheme implemented aims to reproduce the simplified catalytic conversion of pollutants.

The species considered represents those involved in an effective catalytic conversion; the reactions are the following:

1. $R_1$: $NO_x$ reduction
   \[ CO + NO \rightarrow CO_2 + 0.5N_2 \] (5.3)

2. $R_2$: $CO$ oxidation
   \[ CO + \frac{1}{2}O_2 \rightarrow CO_2 \] (5.4)

3. $R_3$: $H_2$ oxidation
   \[ H_2 + \frac{1}{2}O_2 \rightarrow H_2O \] (5.5)

The reaction model used is a Langmuir-Hishelwood one. It permits to compute the reaction velocity as follows:

\[
\dot{\Omega}_1 = \frac{A_1 e^{-E_1} c_{CO} c_{NO_x}}{G_1} \quad (5.6)
\]
\[
\dot{\Omega}_2 = \frac{A_2 e^{-E_3} c_{CO} c_{O_2}}{G_2} \quad (5.7)
\]
\[
\dot{\Omega}_3 = \frac{A_3 e^{-E_3} c_{H_2} c_{O_2}}{G_3} \quad (5.8)
\]

where:

\[
G_1 = (1 + K_1 c_{CO})^2 (1 + K_2 c_{NO_x}^{0.7}) \quad (5.9)
\]
\[
G_2 = (1 + K_3 c_{CO})^2 (1 + K_4 c_{NO_x}^{0.7}) \quad (5.10)
\]
\[
G_3 = (1 + K_5 c_{CO})^2 (1 + K_6 c_{NO_x}^{0.7}) \quad (5.11)
\]

with:

\[
K_i = A_i e^{-\frac{E_i}{RT}} \quad (5.12)
\]
The reaction rate constants are the following:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A$ [mol/(m$^3$s)]</th>
<th>$E$ [J/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_1$</td>
<td>$1.2 \times 10^{20}$</td>
<td>80000</td>
</tr>
<tr>
<td>$R_2$</td>
<td>$1.3 \times 10^{15}$</td>
<td>95000</td>
</tr>
<tr>
<td>$R_3$</td>
<td>$4 \times 10^{15}$</td>
<td>100000</td>
</tr>
</tbody>
</table>

Table 5.1: Pre-exponential constant and activation energy

The coefficients for the calculation of $K_i$ are listed in the following table:

<table>
<thead>
<tr>
<th>$K_i$</th>
<th>$A_i$ [mol/(m$^3$s)]</th>
<th>$E_i$ [J/mol]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1$</td>
<td>400</td>
<td>$-7990$</td>
</tr>
<tr>
<td>$K_2$</td>
<td>$2 \times 10^{5}$</td>
<td>31036</td>
</tr>
<tr>
<td>$K_3$</td>
<td>65.5</td>
<td>$-7990$</td>
</tr>
<tr>
<td>$K_4$</td>
<td>$4.79 \times 10^{5}$</td>
<td>31036</td>
</tr>
<tr>
<td>$K_5$</td>
<td>400</td>
<td>$-7990$</td>
</tr>
<tr>
<td>$K_6$</td>
<td>$4.79 \times 10^{5}$</td>
<td>31036</td>
</tr>
</tbody>
</table>

Table 5.2: Pre-exponential constant and activation energy

The whole analysis is steady and reaction rates are evaluated under different inlet temperatures. The aim of this section is to assess if the model implemented can rightly estimate the diffusion limit area and the light-off temperature for a group of reactions. All simulations consider the heat exchanged between the solid and fluid phase, using a multi region models with a 3D mesh. The temperature at the external boundary of the solid domain is fixed equal to the inlet fluid temperature. The inlet composition is obtained by the one considered for previous single-reaction simulations (see Tab. 5.3).

<table>
<thead>
<tr>
<th>Species</th>
<th>Mass Fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$N_2$</td>
<td>0.7223</td>
</tr>
<tr>
<td>$O_2$</td>
<td>0.201</td>
</tr>
<tr>
<td>$CO_2$</td>
<td>0.0107</td>
</tr>
<tr>
<td>$CO$</td>
<td>0.028</td>
</tr>
<tr>
<td>$NO_x$</td>
<td>0.01</td>
</tr>
<tr>
<td>$H_2$</td>
<td>0.028</td>
</tr>
</tbody>
</table>

Table 5.3: Mass fractions at inlet
Figure 5.16: $NO_x$ reduction

Figure 5.17: $CO$ oxidation
At first, the contribution given by a single reaction at a time is considered. Fig. 5.16 shows the abatement of chemical species if only $R_1$ is considered. It can be observed that compared to the other cases it has the lowest light-off temperature. This is principally related to the fact that its activation energy, as proposed by Koltsakis [35], is significantly lower than the others.

Fig. 5.17 shows the abatement of chemical species if the only $R_2$ is considered. This curve is very similar to the one obtained by previous simulations. The light-off temperature and the slope are more or less the same. However, the maximum conversion reached is lower. It is given by the fact that the different inlet composition determines different molar fractions and different properties of the mixtures, and, as a consequence, the equilibrium changes.

In Fig. 5.18 the reaction of H$_2$ oxidation ($R_3$) is plotted. It has more or less the same light-off temperature of $R_2$, as they have similar activation energy. However, this reaction provides a great quantity of heat released. The reaction energy ($\Delta H_{\text{reac}} = 2.860 \times 10^5$ $J/mol_{H_2} = 1.418 \times 10^5$ $J/kg_{H_2}$) is the biggest one in mass term and it significantly contributes to increase the temperature inside the sample, when reaction starts. Because of the strong dependence of conversion from temperature during the transition zone, the slope of the abatement curve is very steep.
5.5.1 CO Abatement

At this point, the other reactions are added in order to consider the progressive effect provided by the new conversions. As far as the CO abatement is concerned, the progressive effects of the different contributions added are plotted in Fig. 5.19.

If the case with $R_1 + R_2$ is analysed, it is possible to notice the effect of the different activation energies and consequently of the two light-off temperatures. Indeed, at low temperatures the reaction which provides the carbon monoxide conversion is $R_1$, while at high temperatures is $R_2$. It is proven by the change of slope at $300^\circ C$: when $T < 250^\circ C$ the slope is more or less the same as the curve provided by the only $R_1$ reaction. For $250^\circ C < T < 300^\circ C$, the contribution of $R_2$ is arising, and, in the end, for $T > 300$ it becomes predominant because $R_2$ is diffusion limited. In fact, in this range of temperatures the slope is similar to the one provided by the only $R_2$ reaction. Clearly, this configuration provides the highest CO abatement efficiency, as both $R_1$ and $R_2$ contribute to reduce carbon monoxide concentration inside
the mixture. The addition of the $H_2$ oxidation ($R_2 + R_3$) determines a strong increase of the slope of the abatement curve during the transition zone if compared to the only $CO$ oxidation ($R_2$). This is caused principally by the high energy released by the hydrogen oxidation, which increases the average temperature of the sample and provides higher abatements efficiency than the case with only $R_2$. Because the activation energies of these two reactions are similar, the light-off temperature does not significantly change. The most marked consequence of the addition of $R_3$ is the reduction of the maximum $\eta_{CO}$, related principally to the strong competition between the two species in reacting with oxygen.

If all these effects are combined, the final behaviour is described by the curve $R_1 + R_2 + R_3$. The light-off temperature is imposed by $R_1$ and the slope is bigger than the simply case with $R_1 + R_2$, as the starting of the hydrogen combustion at $250^\circ C$ provides an higher temperature inside the sample.

5.5.2 $NO_x$ Abatement

By analysing results plotted in Fig. 5.20, it can be observed the effect of concentrations in chemical equilibrium. As previously pointed out, this reaction shows the lowest light-off temperature. Indeed, for all three curves the transition starts at $250^\circ C$.

When the only $R_1$ is considered, the maximum efficiency in the diffusion-limited area is more or less constant (few variations are admitted because of the weak dependence of $D_{h,mix}$ from temperature). However, when $R_2$ is added, a sensible reduction of $\eta_{CO}^{max}$ with $T$ is observed. This is given by the chemical equilibrium. This concept is essential and it was introduced in section 3.1.2. It is that condition reached by chemical species when their concentration does not change any more with time. This is the situation investigated by these steady simulations. A parameter which describes the equilibrium is the constant $K_{eq}$. For the $R_1$ this can be expressed as follows:

$$K_{eq} = \frac{c_{CO}^2 c_{N_2}}{c_{CO}^2 c_{NO_x}^2}$$  \hspace{1cm} (5.13)

This is a function of the only thermodynamic state of the system. Le Chatelier’s principle (1884) claims that if a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium moves to partially reverse the change. It means that, if $CO$ is consumed by $R_2$, $R_1$ will tend to compensate this effect reducing its globally conversion and, as a result, the new point of equilibrium in $R_1$ will be biased towards reactants. This effect seems clearly to stabilise when also $R_2$ reaches the diffusion-limitation. The
Le Chatelier’s effect is particularly evident in NO\textsubscript{x} reduction because of the markable difference of light-off temperature compared to \(R_2\) and \(R_3\). As a consequence, this effect is not gradual as for the other species, but assumes an abrupt behaviour when \(R_1\) starts to convert at \(\sim 275^\circ\text{C}\).

These considerations are not evident when all reactions are considered, because the hydrogen combustion tends to increase the temperature of the sample. This effect contrasts the reduction of NO\textsubscript{x} converted and provides a more or less constant abatement.

This behaviour is also related to the simplified diffusion model used, which does not consider the effective dependence of the diffusion coefficient from temperature and, as a consequence it does not take into account the increase of the reaction rate with temperature in the diffusion limit area.
5.5.3 \( H_2 \) Abatement

The results of \( H_2 \) abatement efficiency are plotted in Fig. 5.21. The most interesting feature shown is the changing of slope passing from the only \( R_3 \) reaction to the case with both \( R_2 + R_3 \). As it can be seen, the addition of the carbon monoxide combustion provides an higher quantity of heat released, and, as a consequence, higher temperatures inside the sample. It implies that the slope of the curve would be higher, as correctly shown.

The addition of \( R_1 \) determines a reduction in light-off temperature. It is given by the energy released by this reaction that activated \( R_3 \) at lower temperatures than other cases.
5.5.4 Final Considerations about the Macro Model

In Fig. 5.22 the conversion of the different species when \( R_1 + R_2 + R_3 \) is considered is plotted. It represents qualitatively a trend comparable to those found in three way catalyst. Indeed, it can be seen that, even if the reactions have different light-off temperature when these are considered singularly, when are in competition these manifest more or less the same behaviour.

These qualitative considerations permit to affirm that the model is able to characterise a multi-reaction system with a satisfactory accuracy and reliability. As previously pointed out, the macro-model implemented has some limitations: related to the diffusive model adopted. The one implemented is simplified (constant diffusion coefficient) with the aim to reduce the computational effort for the calculation of the reaction rate in the diffusion-limited area.
Chapter 6

Test Cases

In this chapter, a cold-start situation is considered. The fluid inlet temperature is time dependent:

- from 0s to 1s it is constant and equal to 27°C. This first steady condition is principally related to numerical problems. Indeed, transient simulations especially during the first iterations can show unboundedness and fluctuations. A good transient simulation must follow the so called Courant-Friedrichs-Lewy’s condition, i.e. that 
  \[ Co = U / (\Delta t / \Delta x) \leq 1. \]
  This permits to obtain a reasonable solution. However, especially the first iterations are problematic and so, to separate the numerical errors to the physical solution, this ploy is used.

- from 1s to 150s temperature has a linear law, and passes from 27°C to 327°C.

- from 150s temperature is constant and equal to 327°C.

6.1 Case A

The geometry analysed is the one in Fig. 6.1. There both the solid and fluid domain are plotted translated even if in simulations these are overlapped. The fluid region is the longer one, as an inlet and outlet section are reproduced and it is the one with edges.

The fluid domain is long 156 mm and it passes through a catalytic domain 150 mm long; these have a section 15 mm × 15 mm. The mass flow \( Q_{EX} = 3000 \text{Nm}^3/\text{s} \) is set at the inlet surface and, as a consequence, the pressure \( p_n = 100000 \text{Pa} \) is set at the outlet patch. The inlet concentration of the chemical species is the one in Tab. 5.3. As previously pointed out, this is not the typical concentration of ICE exhaustion gases, as the level of CO, NO and H₂ is higher. However, for consistency, it is obtained...
from experimental mixture presented in previous works [16]. This produces high temperatures in the catalyst, which are unthinkable in an automotive three-way catalyst, because the energy released by reactions, especially by the hydrogen combustion, is very high. The set of reactions used is the one described in section 5.5.

As far as the solid domain is concerned, an initial temperature equal to 27°C is set to all catalyst and external boundaries are considered adiabatic. The aim of this simulation is the evaluation of the transient behaviour of the macro-model reproducing a simplified cold start situation.

The two domains are discretized by using a 1D mesh; this means that the only axial conductivity is considered. This choice has been made in order to reduce the computational time. Nevertheless, this modelling is reasonable and close to reality, because the domain is not particularly extended along the transversal directions.

Fig. 6.2 shows the abatement efficiency versus time. It can be clearly seen that the light-off is more or less between 125 ÷ 175 s, when temperature is about 350°C. It is interesting to observe that, at about 270s, the NO abatement efficiency decreases and it seems to stabilise after 30s. This transient behaviour is principally related to the increase of velocity inside the sample. Indeed, if the mass flow is fixed, and temperature rises, due to chemical reactions, ρ is reduced and, as a consequence, ⃗U raises. This implies that the fluid has not enough time to diffuse in the washcoat. This considerably limits the maximum reaction rate. This effect is not usually shown in experimental data and it is related to the fact that a simplified model has been applied for the calculation of the diffusion coefficient. For this modelling, a constant
diffusion coefficient is considered. There is the need in future developments to implement a model based on binary coefficients, which take into account the effective diffusion properties of chemical species in a generic mixture.

Figure 6.2: Abatement efficiency in time

![Abatement efficiency](image)

Figure 6.3: Temperature fields in time

![Temperature fields](image)

Fig. 6.3 shows the trend of the temperature evaluated at different sections during time. It is interesting to observe that the temperature arises in the
middle section of the catalyst (Sec 2) much more than the inlet one (Sec 1). It is principally related to the inlet fluid, whose temperature is fixed after 150s, and it tends to cool the first sections of the solid domain.

![Temperature Field](image)

Figure 6.4: Temperature distribution in time

The temperature distribution can be clearly seen in Fig. 6.4, where the evolution of the reaction is shown. At 125s, reactions are not activated and the temperature field is principally given by the conduction in the solid phase, as no heat is released by reactions. The solid phase tends to cool the fluid that is at higher temperatures determining the given profile. At 175s, only $NO_x$ reduction is activated, it provides a less quantity of heat released. However, its contribution is appreciable in the curves plotted. At 250s, all reactions are completely activated, and the heat released determines a markable increase of temperature, heating the solid domain. At this time, the entering fluid is heated by the solid phase. Step by step this process determines a gradual progress of the catalytic reactions until the equilibrium is reached. Fig. 6.5 shows the abatement in the catalyst in the steady condition. It is interesting to observe that the $\sim 90\%$ of the abatement is performed in the first part of the solid domain. This probably means that the sample analysed is too long, determining a markable pressure drop, i.e. $\sim 1050Pa$. This causes a strong reduction of the engine performances because of the markable decrease of its efficiency.

This is the reason why three-way catalysts are generally stocky. Indeed, this permits to have bigger inlet section and, fixed the mass flow rate, lower crossing speed. This provides an important benefit for the conversion, as
the particles have more time to react on the active sites, and the inertial contribution to pressure drop is reduced.

![Abatement distribution in time](image)

**Figure 6.5: Abatement distribution in time**

### 6.1.1 Effects of Geometry

As a further step, an alternative geometry is considered: this has the same volume of the previous one, but a section that is four times bigger; it means that its length is four times smaller than the first geometry. This analysis wants to show a simplified example of what optimization is, as it shows the effective problems, that the design of a catalyst offers.

Simulations show that this stocky configuration provides a pressure drop that is the 4% of the one of the long geometry. It is a markable advantage for the engine cycle.

Fig. 6.6 shows that the maximum abatement efficiencies reached are more or less the same of the previous case. This is a positive aspect as it means that the shorter catalyst is able to convert pollutants in an efficient way when the situation is steady. However, if the transition is considered, in the shorter set up light-off occurs later. It means that the overall quantity of pollutants emitted from the cold start is higher in the second case, as the maximum efficiency is reached about 150s later than the longer catalyst. This delay is principally caused by the lower temperatures inside the catalyst during the first seconds, as Fig. 6.7 shows.

A shorter geometry has also, when the steady condition is reached, higher outlet temperatures; generally it can be a problem for all those components that are placed after the catalyst. Moreover, standards fix specific outlet
temperatures for exhaust gasses, in order to avoid effects on climate. These generally impose the usage of backward control system to monitor the temperature, determining, if it is necessary, the shut down of the entire vehicle. These considerations suggest that the correct choice of the dimensional parameter of the three-way catalyst is essential, as this influences not only the abatement efficiency but also the global performances of the all complex engine system.

Figure 6.6: Efficiency comparison between two different configurations

Figure 6.7: Temperature comparison between two different configurations
6.1.2 Effects of Foam Properties

At this point, brief considerations about the influence of the physical properties of the foams are reported. The previous analysis has shown that the shorter geometry is the one which permits to reduce the pressure drop, increasing the efficiency of the engine. However, it has a too long warm-up transition, because of the low temperatures. This problem can be solved by changing the thermal capacity. Indeed, by reducing this, a less quantity of heat is required to have the same temperature difference \( \dot{Q} = C \Delta T \). A changing of the effective density \( \rho_{\text{eff}} = \rho \Phi \) of the sample is the right way. This can be done by changing the material of the solid matrix or/and the porosity of the foam. Two more cases are considered: the geometry is exactly the shorter one and their main properties the same, however, density is gradually reduced.

![Figure 6.8: Temperature comparison between different foams](image)

Fig. 6.8 shows the considerations previously described. The sample with the minor \( \rho_{\text{eff}} \) is the one that is firstly heated. This analysis wants to define the guideline in the correct choice of the material used for a foam. Another important facet that has to be considered is that the lower the thermal capacity, the higher the temperatures. It means that the ideal material is not only able to give high performances in terms of resistance and thermal properties, but that has also an high melting point. In a real case, temperatures are sensibly lower than the ones of these cases, because of the lower concentration of pollutants. However, the highest reached in ICE catalysts are more or less 500 ÷ 600°C, which require materials with high melting point. The challenge
is the design and development of materials more performant which can be used in applications like that one. As far as the conversion is concerned, the delay is reduced, as shown by Fig. 6.9.

![Figure 6.9: CO Abatement comparison between different foams](image)

<table>
<thead>
<tr>
<th>Case</th>
<th>PressureDrop</th>
<th>PressureDrop</th>
</tr>
</thead>
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<tr>
<td>Long $\rho_{eff}$</td>
<td>1044</td>
<td>Pa</td>
</tr>
<tr>
<td>Short $\rho_{eff}$</td>
<td>30</td>
<td>Pa</td>
</tr>
<tr>
<td>Short $0.75\rho_{eff}$</td>
<td>39</td>
<td>Pa</td>
</tr>
<tr>
<td>Short $0.5\rho_{eff}$</td>
<td>44</td>
<td>Pa</td>
</tr>
</tbody>
</table>

Table 6.1: Pressure drops comparison

The increase of temperature inside the sample determines an enhancement of the volume averaged $Re_p$ which determines, in its turn, higher pressure drops. A comparison between the four cases is reported in Tab. 6.1. This show a slight increase of $\Delta p$ under a decreasing $\rho$. However, the increment is very small if compared to the case with the long duct. In conclusion, these analysis suggest that the best configuration is one realized with a low density foam and an extremely compact geometry. In this way, the right trade-off between the abatement of pollutants and performances of the engines is reached.
### 6.2 Case B

For this second case, the geometry used is the one described in section 5 (21\text{mm} \times 15\text{mm} \times 15\text{mm}).

A mixture with typical concentrations involved in after treatment systems is considered; its composition is taken from [25], and is listed in Tab 6.2.

<table>
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<tr>
<th>Species</th>
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<tr>
<td>$N_2$</td>
<td>0.769754</td>
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<tr>
<td>$O_2$</td>
<td>0.00628</td>
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<tr>
<td>$CO_2$</td>
<td>0.118221</td>
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<td>$H_2O$</td>
<td>0.08826</td>
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<tr>
<td>$C_3H_6$</td>
<td>0.0017591</td>
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<tr>
<td>$CO$</td>
<td>0.00898</td>
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<td>0.0020372</td>
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<tr>
<td>$H_2$</td>
<td>0.00471003</td>
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</table>

Table 6.2: Mass fractions at inlet

The set of reactions considered is more extended than the previous case and takes into account the six main reactions which involve all chemical species.

1. $R_1$: $CO$ oxidation

   \[ CO + \frac{1}{2}O_2 \rightarrow CO_2 \] 

   (6.1)

2. $R_2$: $H_2$ oxidation

   \[ H_2 + \frac{1}{2}O_2 \rightarrow H_2O \] 

   (6.2)

3. $R_3$: $NO_x$ reduction

   \[ CO + NO \rightarrow CO_2 + 0.5N_2 \] 

   (6.3)

4. $R_4$: $NO_x$ reduction 2

   \[ H_2 + NO \rightarrow H_2O + 0.5N_2 \] 

   (6.4)

5. $R_5$: $CO$ Steam Water Reforming

   \[ CO + H_2O \rightarrow CO_2 + H_2 \] 

   (6.5)

6. $R_6$: $C_3H_6$ Steam Water Reforming

   \[ C_3H_6 + 3H_2O \rightarrow 3CO_2 + 6H_2 \] 

   (6.6)
The reaction model used is a Langmuir-Hishelwood one. It permits to compute the reaction velocity as follows:

\[ \dot{\Omega}_1 = \frac{A_1 e^{-\frac{E_1}{RT}} c_{CO} c_{O_2}}{G_1} \]  

(6.7)

\[ \dot{\Omega}_2 = \frac{A_2 e^{-\frac{E_2}{RT}} c_{H_2} c_{CO_2}}{G_2} \]  

(6.8)

\[ \dot{\Omega}_3 = \frac{A_3 e^{-\frac{E_3}{RT}} c_{CO} c_{NO_x}}{G_3} \]  

(6.9)

\[ \dot{\Omega}_4 = \frac{A_4 e^{-\frac{E_4}{RT}} c_{H_2} c_{NO_x}}{G_3} \]  

(6.10)

\[ \dot{\Omega}_5 = \frac{A_5 e^{-\frac{E_5}{RT}} c_{CO} c_{H_2} c_{O}}{G_2} \]  

(6.11)

\[ \dot{\Omega}_6 = \frac{A_6 e^{-\frac{E_6}{RT}} c_{C_3H_6} c_{H_2} c_{O}}{G_1} \]  

(6.12)

where:

\[
G_1 = (1 + K_1 c_{CO} + K_2 c_{HC})^2 (1 + K_3 c_{CO}^2 c_{HC}^2) (1 + K_4 c_{NO_x}^0) \]  

(6.13)

\[
G_2 = (1 + K_5 c_{CO} + K_6 c_{HC})^2 (1 + K_7 c_{CO}^2 c_{HC}^2) (1 + K_8 c_{NO_x}^0) \]  

(6.14)

\[
G_3 = (1 + K_9 c_{CO} + K_{10} c_{HC})^2 (1 + K_{11} c_{CO}^2 c_{HC}^2) (1 + K_{12} c_{NO_x}^0) \]  

(6.15)

The reaction rate constants are the ones in Tab. 6.3 and constants for the calculation of \(K_i\) are listed in Tab.6.4.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(A) [mol/(m³·s)]</th>
<th>(E) [J/mol]</th>
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<tbody>
<tr>
<td>(R_1)</td>
<td>(1.3 \times 10^{17})</td>
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<tr>
<td>(R_2)</td>
<td>(4 \times 10^{14})</td>
<td>100000</td>
</tr>
<tr>
<td>(R_3)</td>
<td>(1.2 \times 10^{20})</td>
<td>80000</td>
</tr>
<tr>
<td>(R_4)</td>
<td>(5 \times 10^{17})</td>
<td>85000</td>
</tr>
<tr>
<td>(R_5)</td>
<td>(1.3 \times 10^{15})</td>
<td>50000</td>
</tr>
<tr>
<td>(R_6)</td>
<td>(2 \times 10^{24})</td>
<td>75000</td>
</tr>
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</table>

Table 6.3: Pre-exponential constant and activation energies

The coefficient in the inhibition factor are computed as follow:

\[ K_i = A_i e^{-\frac{E_i}{RT}} \]  

(6.16)
The results are plotted in Fig. 6.10. Here it is interesting to observe the effect of the different reactions. \( R_5 \) has the lowest activation energy, and, as expected, has the earlier light-off. From 100s to 175s, the production of \( H_2 \) is evident: this is promoted by \( C_3H_6 \) and \( CO \) steam water reforming reactions. These have an activation energy that is lower than \( R_2 \) and \( R_4 \). As a consequence, when in the first seconds, \( R_5 \) and \( R_6 \) produce hydrogen that is not consumed by \( R_2 \) and \( R_4 \). An analogous consideration can be done for \( H_2O \); indeed, in the first seconds, the steam water reforming reactions (\( R_5 \), and \( R_6 \)) consume the water and its concentration decreases. However, when \( R_2 \) and \( R_4 \) start, water is produced and its concentration consequently arises. Fig. 6.11 shows the outlet temperature of the fluid in time. It is interesting to observe that in this case, with realistic concentrations, the steady temperature reached is around 550°C. This value is more realistic and sensibly lower than the previous one, especially because of the smaller concentration of hydrogen.
Chapter 6

Figure 6.10: Abatement efficiency in case B

Figure 6.11: Fluid outlet temperature in case B
Conclusions and Future Developments

This work aims to investigate, by means of a CFD analysis, the possibility to apply an open-cell foam as catalytic support in three-way catalysts. Nowadays, honeycombs monolithic supports are used. Open-cell foams have all those properties required in this kind of applications: high specific surface, low density, and an enormous flexibility in terms of geometrical characterization and cost. These represent an interesting substitute of traditional structures as it has been demonstrated that they provides a significant saving in term of noble metals involved and consequently of costs.

It has been possible to analyse in details a micro-CT reconstructed foam and not an idealized structure, as previously done by several authors. This has permitted to approach the final goal, i.e. the complete design of a three-way catalyst.

The first step is the micro-characterisation of a sample. This substrate has been chosen considering its geometric properties which suggest a good application in three-way catalysts. Many facets has been considered in order to reach the best methodology in CFD analysis. Different models have been taken into account: mesh grading, boundary layer, cell number, compressible or incompressible fluid, steady or unsteady simulations, turbulence models, and so on.

Not only a fluid- and thermo-dynamical characterisation has been performed, but also a chemical one. In this context, the limitations of previous works have been understood, becoming the starting point for this kind of analysis. Single-region and multi-regions simulations are performed. Even if the first ones have been done also by previous authors, the second one are applied to an open cell foam considering a reacting model for the first time. The multi-regions simulations, much more expensive in terms of computational effort, have proved to provide a more reliable description of the thermal behaviour taking into account the effective conductivity of the solid matrix.

The results of simulations have permitted to understand some physical phenomena occurring in real foams and have explained the deviation between the experimental and numerical data already pointed out by previous works. In conclusion, a complete set of non-dimensional parameters has been ex-
tracted. This is the one which permits the up-scaling process. The passage from a micro to macro analysis is mandatory when the final aim is the analysis of the complete catalyst with a reasonable computational burden. In order to up-scale the problem, the implementation of dedicated sub-models has been necessary. Indeed, the macro model has to describe the same phenomena occurring in the micro-scale without considering the micro-geometry. It implies that macro-scale sub-models are required in order to model the permeability, conductivity, convection and conversion directly simulated with a micro-scale approach.

For the description of fluid-dynamics and thermodynamics, libraries are already available. Indeed, these fields have been largely investigated by previous authors. However, the need of simulating chemistry in a CFD code, like OpenFOAM®, has required the implementation of dedicated sub-models, which can be used to characterise the reacting problem both in single and multi-regions modelling, considering single or multi reactions. A simplified diffusion model is implemented in order to take into account all phenomena involved in a conversion process.

The chemical model is firstly validated by comparing, for the same sample, the light-off temperature and the diffusive-control computed both in micro and macro-simulations. The results obtained suggest a good behaviour in term of prediction of these parameters.

In addition, the analysis of a multi-reaction problem is considered. The group of reactions considered is extracted from chemistry models used to describe the catalyst conversion in three-way catalysts. The mixture described is similar to the one used in experimental activities. The results provided can be regarded as reasonable, suggesting the possible future application in more complex models.

Finally, more realistic cases are considered. The introduction of time dependent inlet temperature has permitted to reproduce a simplified cold-start situation, firstly considering an experimental mixture and, then, an effective ICE composition. For the first case, geometrical and physical properties are changed in order to investigate the design guidelines, that the model can provide. In the second one, a more complete set of reaction is considered.

This thesis has applied an up-scaling methodology to the modelling of reacting flows in after-treatment systems considering, in particular, open-cell substrates. Possible future developments will include the application of the model implemented in a real case which considers an effective pulsed flux and real compositions. In its turn, this will unlock the possibility to apply this model to a complete catalyst and, up-scaling it again, to analyse the entire engine scale.
# Nomenclature

## Latin Letters

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<th>Symbol</th>
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## Greek Letters

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### Nomenclature

#### Subscripts

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#### Superscripts

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#### Operators

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Bibliography


[34] Accuratus. Silicon Carbide Material Properties.