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Modelado en dinámica de fluidos computacional (CFD) de transporte de masa en materiales porosos

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TÍTULO: **CFD modeling of mass transport in porous materials**

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Resumen

La difusión y la adsorción son fenómenos complejos que ocurren durante las reacciones catalíticas de forma acoplada y en función del tiempo. Estos procesos pueden ser estudiados mediante un análisis microcinético. Un método para realizar este análisis es el uso de un aparato de Respuesta por Frecuencia (FR).

El objetivo de este proyecto es la creación de un modelo, utilizando el software de simulación COMSOL Multiphysics, que recree un experimento FR en el que un gas es comprimido y expandido periódicamente para favorecer la difusión y adsorción en un material poroso.

Diferentes variables han de tenerse en cuenta, centrándose este proyecto en la simulación del material poroso – el catalizador – y los procesos de transporte de masa, además del correcto cálculo de campos de presión y velocidad, y transferencia de calor. Finalmente, se presenta un estudio de los resultados de la evolución del experimento, obtenidos del modelo computacional final.

Palabras Clave

Difusión – Adsorción – Material poroso – Respuesta por Frecuencia – COMSOL Multiphysics

Abstract

Diffusion and adsorption are complex phenomena which occur during catalytic reactions as coupled and time dependent processes. These processes can be studied by realizing a microkinetic analysis. One method to achieve this is by using a Frequency Response (FR) apparatus.

The objective of this project is the creation of a model – using the simulation software COMSOL Multiphysics – which recreates a FR experiment in which a gas is periodically compressed and expanded to favor diffusion and adsorption in a porous material.

Several variables are to be taken into account, being this project focused on the simulation of the porous material – the catalyst – and the processes of mass transport, as well as on the correct calculation of pressure and velocity fields, and heat transfer. To conclude, a study of the results of the evolution of the experiment, obtained from the final computational model, is presented.

Keywords

Diffusion – Adsorption – Porous material – Frequency Response – COMSOL Multiphysics

CFD modeling of mass transport in porous materials

Bachelor Thesis

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Abbreviations and Symbols

FR	Frequency Response
spf	Laminar Flow
ale	Moving Mesh
ht	Heat Transfer in Solids
tds	Transport of Diluted Species in Porous Media

$c_c \left[\frac{mol}{m^3}\right]$	species inflow of gas into the reactor
$c_i \left[\frac{mol}{m^3}\right]$	concentration of species i in the liquid phase
$c_{G,i} \left[\frac{mol}{m^3}\right]$	concentration of species i in the gas phase
$c_{P,i} \left[\frac{mol}{m^3}\right]$	amount of species i adsorbed or desorbed from the solid particles
$c_{Pmax} \left[\frac{mol}{Kg}\right]$	adsorption maximum
$c_0 \left[\frac{mol}{m^3}\right]$	initial concentration of fluid in the porous material
$C_p \left[\frac{J}{(Kg \cdot K)}\right]$	specific heat capacity at constant pressure
$D \left[\frac{m^2}{s}\right]$	Diffusion coefficient
$\mathbf{F} \left[\frac{N}{m^3}\right]$	volume force vector
$K_L \left[\frac{m^3}{mol}\right]$	Langmuir constant
p [Pa]	pressure
p_A [Pa]	absolute pressure of the spf interface
P_{spf} [Pa]	pressure of the spf interface
P_0 [Pa]	initial pressure in the reactor
$\mathbf{q} \left[\frac{W}{m^2}\right]$	heat flux vector
$\mathbf{q_r} \left[\frac{W}{m^2}\right]$	heat flux by radiation
$Q \left[\frac{W}{m^3}\right]$	heat sources
$Q_p \left[\frac{W}{m^3}\right]$	work done by pressure changes

$Q_{vd} \left[\frac{W}{m^3}\right]$ viscous dissipation in the fluid

$R \left[\frac{J}{Kg \cdot K}\right]$ universal gas constant

$R_i \left[\frac{mol}{m^3 \cdot s}\right]$ reaction rate expression for the species i

$S_i \left[\frac{mol}{m^3 \cdot s}\right]$ arbitrary source term for the mass balance equation

t [s]   time

T [K]   temperature

T_0 [K]   initial temperature of gas in the reactor

$\mathbf{u} \left[\frac{m}{s}\right]$ velocity vector

$\alpha_p \left[\frac{1}{K}\right]$ coefficient of thermal expansion

ε_p [-]   porosity

Θ [-]   liquid volume fraction

μ [Pa·s]   dynamic viscosity

1 Introduction

Adsorption and diffusion are two complex phenomena which occur during catalytic reactions as coupled and time dependent processes. A catalyst is a substance which, when added to a reaction, increases the rate of the reaction without being consumed or produced in it. Catalysts can be homogeneous – they operate in the same phase which reactants and products have, – and heterogeneous – they operate in a different phase, usually solid [1].

Zeolites are one special type of heterogeneous catalyst. A zeolite is a porous crystalline aluminosilicate. It consists of regular arrangements of SiO_4 and AlO_4 tetrahedra, which form a crystal structure through shared oxygen atoms [2].

Although zeolites can be found in nature, it was not until the synthetic zeolites appeared that these porous materials started having an important role as catalysts. The molecular dimensions size of the pores of a zeolite presents a range 0.3 to 2.0 nm, being thus considered microporous materials [3].

In order to characterize zeolites, a microkinetic analysis can be made. In this microkinetic analysis, the conditions of diffusion and adsorption in catalytic reactions are studied. One of the methods to achieve this is by using a Frequency Response (FR) apparatus.

The FR experiment consists of varying the volume of the system and measuring and studying the pressure response. This volume modulation compresses and expands the inner fluid towards the porous material, and favors the sorption and diffusion processes [4].

During the FR experiment many variables are to be taken into account. The main focus is to study the adsorption and diffusion processes, but other aspects such as the behavior of the fluid, the materials of which the setup is made of, or the outer gas, have an influence due to the variation of pressure, velocity fields, temperature or mass transport.

In order to perform and evaluate a FR experiment, computer simulations can be used. They present several advantages, such as a significant saving of time and resources, and the possibility to recreate quite exactly the conditions of the experiment and the laboratory. It is possible to describe the experiment in this way, and in addition, this description can be later modified in order to repeat the experiment with different settings.

For this project, the used simulation tool is the software COMSOL Multiphysics 5.2a.

2 Objectives

The main aim of the experiment using the FR apparatus is to study the time dependent processes of adsorption and diffusion, and this study can be made recreating the real experiment with a simulation tool.

Therefore, the principal objective of this project is the creation of a model using the software COMSOL Multiphysics 5.2a to simulate those coupled processes of adsorption/desorption and diffusion. This will facilitate the study and characterization of zeolites to know more about the kinetics of adsorption and diffusion, using a simulation software to reduce the study time.

An existing model based on the real FR experiment was taken as a starting point for this project [5]. The goals of this current project consist of improving the previous model and implementing the interfaces and settings needed to simulate the mass transport in porous materials. It is intended for the model to become a more complete and optimized simulation, so that results can be more accurately and rapidly obtained with the computational model, and so that they can be later compared with the real experimental results.

This way, one major aim is to make the model become more complete regarding the description of the porous material and the mass transport. It is also intended to make the model result in a more detailed recreation of the real experiment. This will provide the possibility to help future projects – both focused on this topic or not – as the settings of the model can be changed to have more possible uses in the future.

3 Theory

In this chapter, the different equations which the software COMOSL Multiphysics solves for the simulation of this project will be discussed. The model describes the conditions of the experiment, and several interfaces need to be implemented to recreate the real processes which affect the porous material, the inner fluid, and the environment.

3.1 Laminar Flow

This interface, as well as the rest of the Single Phase Fluid Flow ones, is based on the Navier-Stokes equations, which in their general form are:

The continuity equation, which represents the conservation of mass:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0 \tag{Eq. 1}$$

The equation for conservation of momentum, which is a vector equation:

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho\,(\mathbf{u} \cdot \nabla)\mathbf{u} = \nabla \cdot [-p\mathbf{I} + \boldsymbol{\tau}] + \mathbf{F} \tag{Eq. 2}$$

And the equation for conservation of energy:

$$\rho C_p \left(\frac{\partial T}{\partial t} + (\mathbf{u} \cdot \nabla)T \right) = -(\nabla \cdot \mathbf{q}) + \boldsymbol{\tau}{:}\mathbf{S} - \frac{T}{\rho}\frac{\partial \rho}{\partial T}\bigg|_p \left(\frac{\partial p}{\partial t} + (\mathbf{u} \cdot \nabla)p \right) + Q \tag{Eq. 3}$$

Being **S** the strain rate tensor:

$$\mathbf{S} = \frac{1}{2}(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) \tag{Eq. 4}$$

A Newtonian fluid presents a linear relation between stress and strain [6]. In this case, the viscous stress tensor adopts the following expression:

$$\boldsymbol{\tau} = 2\mu\mathbf{S} - \frac{2}{3}\mu(\nabla \cdot \mathbf{u})\mathbf{I} \tag{Eq. 5}$$

And more specifically, the motion equations for a single-phase fluid in the case of compressible flow are:

The continuity equation for conservation of mass:

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho \mathbf{u}) = 0$$

And the equation for conservation of momentum:

$$\rho \frac{\partial \mathbf{u}}{\partial t} + \rho \mathbf{u} \cdot \nabla \mathbf{u} = -\nabla p + \nabla \cdot (\mu(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3}\mu((\nabla \cdot \mathbf{u})\mathbf{I}) + \mathbf{F} \qquad \text{(Eq. 6)}$$

These equations can be applied to incompressible flow and compressible flow when there are variations of density and viscosity.

3.2 Heat Transfer

The interface responsible for heat transfer is based on the heat equation, which in the case of heat transfer in fluids has the following form [7]:

$$\rho C_p \left(\frac{\partial T}{\partial t} + \mathbf{u} \cdot \nabla T \right) + \nabla \cdot (\mathbf{q} + \mathbf{q_r}) = \alpha_p T \left(\frac{\partial p}{\partial t} + \mathbf{u} \cdot \nabla p \right) + \tau : \nabla \mathbf{u} + Q \qquad \text{(Eq. 7)}$$

Being the coefficient of thermal expansion:

$$\alpha_p = -\frac{1}{\rho}\frac{\partial \rho}{\partial T} \qquad \text{(Eq. 8)}$$

The terms at the right side of the equation represent the different heat sources, which are:

The work done by changes of pressure which affects the temperature of the fluid:

$$Q_p = \alpha_p T \left(\frac{\partial p}{\partial t} + \mathbf{u} \cdot \nabla p \right) = -\frac{T}{\rho}\frac{\partial \rho}{\partial T}\left(\frac{\partial p}{\partial t} + \mathbf{u} \cdot \nabla p \right) \qquad \text{(Eq. 9)}$$

The viscous dissipation in the fluid, representing the heat source coming from the transformation of kinetic energy into internal energy due to viscous stresses:

$$Q_{vd} = \tau : \nabla\mathbf{u} = \mu\left(\nabla\mathbf{u} + (\nabla\mathbf{u})^T - \frac{2}{3}(\nabla\cdot\mathbf{u})\mathbf{I}\right):\nabla\mathbf{u} \qquad \text{(Eq. 10)}$$

And finally, the last term (Q) represents the external heat source. In this experiment, there is no external heat source, nor difference between the initial temperature of the interior and exterior fluids. Therefore, all the generated heat appears as a consequence of the movement of the fluid, and this las term $Q = 0$.

3.3 Transport of Diluted Species in Porous Media

This interface solves the following equation for concentrations to describe the transport of solutes in a variably saturated porous medium, for the most general case:

$$\frac{\partial}{\partial t}(\theta c_i) + \frac{\partial}{\partial t}(\rho_b c_{P,i}) + \frac{\partial}{\partial t}(\alpha_v c_{G,i}) + \mathbf{u}\cdot\nabla c_i = \nabla\cdot\left[(D_{D,i} + D_{e,i})\nabla c_i\right] + R_i + S_i \qquad \text{(Eq. 11)}$$

The first three terms at the left side of the equation represent the accumulation of species within the liquid, solid and gas phases respectively. The forth term at the left side represents the mass transport due to convection, caused by the velocity field $\mathbf{u}$.

In this general form of the equation:

c_i describes the concentration of species i in the liquid phase.

$c_{P,i}$ represents the amount of species i adsorbed or desorbed from the solid particles.

$c_{G,i}$ describes the concentration of species i in the gas phase.

The mass transport is balanced by the equation using the porosity ε_p, the liquid volume fraction θ, the bulk density ρ_b and the solid phase density ρ.

In the current experiment, only adsorption of the inner gas on the solid particles of the porous material takes place, as these are the two materials present. Hence, only the term $c_{P,i}$ is used.

At the right side of the equation, the first term describes the spreading of the species caused by the mechanical mixing and diffusion. The second term is a reaction rate expression, which in this experiment will be $R_i = 0$, as no reaction takes place. Finally, the third term, S_i is an arbitrary source term.

To solve the diffusion process – the movement of molecules down a concentration gradient – the equation used is Fick's diffusion equation:

$$\frac{\partial c}{\partial t} = \nabla \cdot (D\nabla c) + R_i \qquad \text{(Eq. 12)}$$

As no reaction takes place ($R = 0$), and the Diffusion coefficient D is a constant, it can be expressed as the following:

$$\frac{\partial c}{\partial t} = D \, \nabla^2 c \qquad \text{(Eq. 13)}$$

To describe the adsorption and desorption processes, adsorption isotherms are used. This process of adsorption consists of the adhesion of molecules from the inner gas to the surface of the porous material. Desorption is the opposite process. Adsorption decreases the concentration of the species in the fluid, while desorption increases it.

In this project, the Langmuir isotherm is chosen to describe the amount of species sorbed, being the relation between the solid concentration, c_P and the concentration in the fluid phase, c expressed by the following equations:

$$c_P = c_{Pmax} \frac{K_L c}{1 + K_L c} \qquad \text{(Eq. 14)}$$

$$\frac{\partial c_P}{\partial c} = \frac{K_L c_{Pmax}}{(1 + K_L c)^2} \qquad \text{(Eq. 15)}$$

The number of molecules of the species which are being adsorbed, n^+ in a differential time interval, dt are directly proportional to the pressure, p and the number of empty sites, $(N - n)$ which the adsorbent presents:

$$\frac{dn^+}{dt} = k^+ p(N - n) \qquad \text{(Eq. 16)}$$

While the number of molecules which are being desorbed, n^- in this differential time interval, dt is proportional to the number of molecules which have been already adsorbed, n:

$$\frac{dn^-}{dt} = k^- n \qquad \text{(Eq. 17)}$$

Both k^+ and k^- are positive constants.

Therefore, the concentration of the species being adsorbed and desorbed suffers a variation which can be expressed as the following [8]:

$$\frac{dn}{dt} = k^+p(N-n) - k^-n \qquad \text{(Eq. 18)}$$

Finally, diffusion and adsorption can occur, not only independently, but also as coupled processes. This is the case studied in this project. The porous material is affected by the process of diffusion in the pore voids, and the process of adsorption on the surface. When the rates of both processes are comparable, the equations which describe the coupled processes are the following [9]:

$$\frac{\partial c}{\partial t} + \rho_P \frac{\partial n}{\partial t} = D\,\nabla^2 c \qquad \text{(Eq. 19)}$$

$$\frac{\partial n}{\partial t} = k^+p(N-n) - k^-n \qquad \text{(Eq. 20)}$$

4 Frequency Response Method

The Frequency Response (FR) method was originally developed by Polinski and Naphtali in 1963 [10]. Since then, this method has been used to study and measure kinetic parameters corresponding to diffusion and sorption processes occurring in chemical reactions in porous materials, such as microporous solids. The Frequency Response method permits to study coupled adsorption and diffusion processes in catalytic reactions [9].

The basic principle of the FR method consists of applying a periodic perturbation of a physical variable, for example in the form of a sine or square function, to a system in equilibrium. The response to this input is a periodic output which presents the same frequency as the input, but different amplitude and a phase shift [4] .
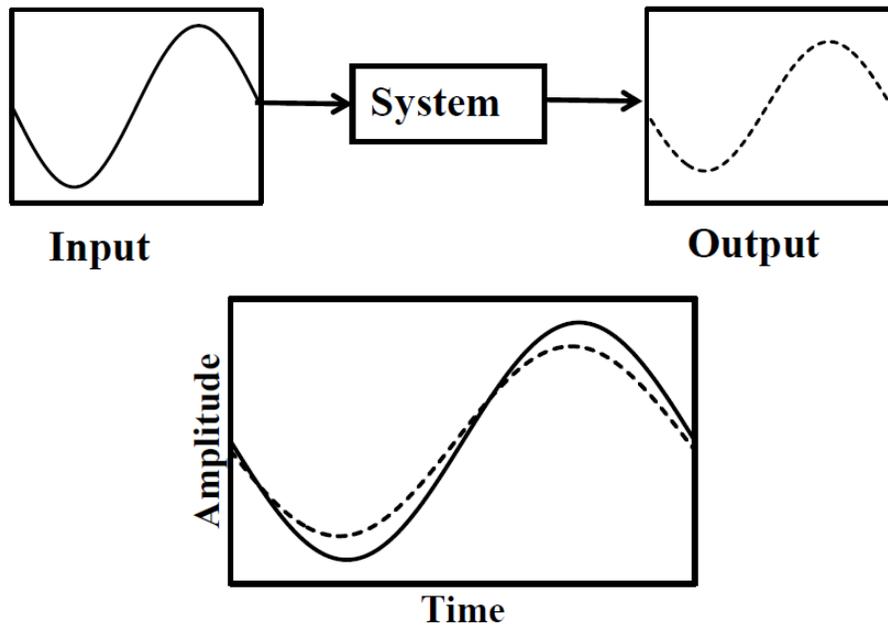
Figure 1: Fundamental concept of frequency response analysis. Taken from [4].

The amplitude and the phase lag of the response have a direct relation with the thermodynamic and kinetic characteristics of the system. The system could be open or closed [4]. The experiment studied in this project corresponds to the second case, a closed system. The volume modulation is the periodic input, and the studied output is the resulting variation of the pressure.

When a closed system containing porous solids experiments a small fluctuation in its volume, the pressure response of the closed system offers information about the rate processes which take place in the porous materials within the system. If the volume fluctuations are small, the interpretation of the response is simpler, as the equilibrium of the system does not suffer significant perturbations [9].

The calculation of the relevant constants of the studied processes is possible due to the measurement of the phase shift between the input and the output, as well as to the measurement of the amplitude of the output with respect to the amplitude of the input [11].

The results obtained with the FR method – amplitude change and phase shift – have their origin in the dynamics and capacities of the processes which make the system return to its equilibrium point. When diffusion occurs, the effective diffusivity (dynamics) and the pore volume within the porous material (capacity) are responsible for the amplitude change and phase shift of the pressure response.

As it was mentioned before, the FR method allows to determine adsorption-desorption and diffusion constants simultaneously. When not only diffusion, but also the adsorption-desorption process occur, the kinetics of adsorption (dynamics) and the surface coverage changes due to the applied perturbation (capacity) have also an influence on the pressure response obtained as the output [9].

5 Experimental Setup

The major components of which the experimental setup consists of are: A vacuum pump, a vacuum-measuring unit, a pressure-measuring unit, a glass reactor, a volume-modulation unit and two electromagnets. There are blocking valves, which permit to realize the volume modulation in a relatively small volume, consisting of the reactor and the pressure measuring unit.
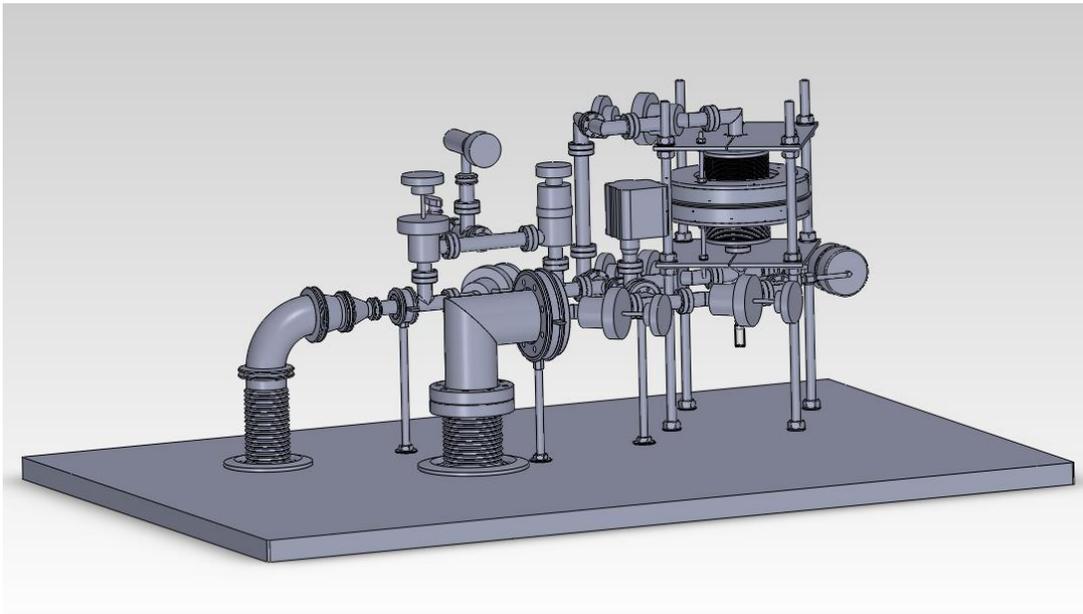
Figure 2: Experimental setup for Frequency Response

Two of the main parts of the setup will be described and analyzed in this project: The glass reactor and the volume-modulation unit. The inner fluid flows through metal pipes which connect these two parts.

The reactor is made of glass and is situated at the bottom part of the setup. It has the same diameter as the connecting tubes. It is isolated to reduce heat losses within it, and it is the part which the gas reaches the last.

The volume-modulation unit consists of a magnetic travel plate moved by two identical electromagnets. The travel plate contracts and expands two bellows which move up and down, compressing and expanding the gas towards the reactor. The electromagnets permit to establish a volume modulation closely resembling a square function. The electromagnets are not included in this study because they are not in contact with the other solid parts, and thus have no direct effect on the model.

Some other parts of the experiment, which are not included in this model, however play an important role in the experiment, are the following:

The pressure-measuring unit measures the absolute pressure. A very exact measurement is required, as the changes in pressure are relatively small, and it must also have a high measuring frequency, due to the rapid movement of the bellows.

The vacuum pump is a device used to evacuate the container before introducing the gas in it. Another function is avoiding the gas reaching its saturation pressure, once the setup is filled.

Finally, the vacuum tubes and blocking valves permit to isolate specific parts of the experiment.
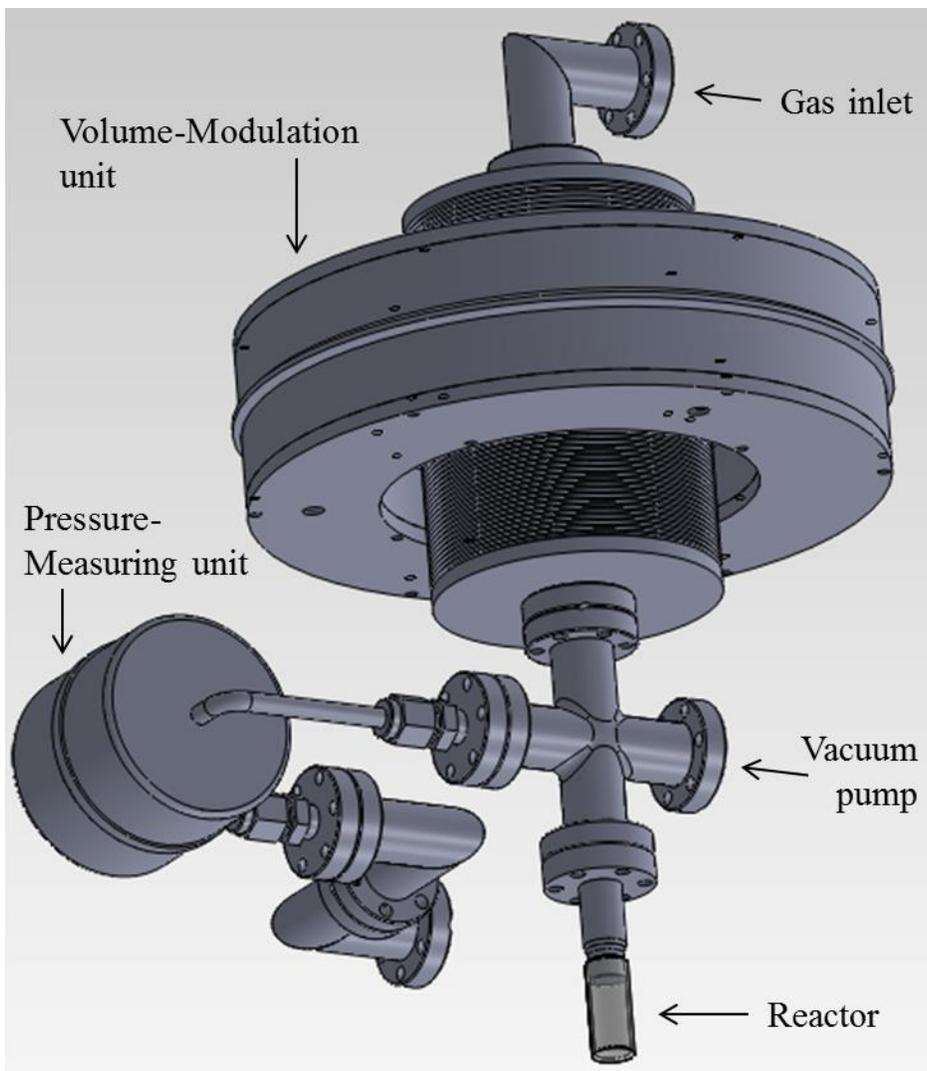
Figure 3: Detailed view to volume modulation unit of FR

Once the cell is evacuated, the gas is inserted and the investigation starts. The gas inlet is found at the top of the experimental setup. The gas is introduced in the system and suffers periodical compressions and expansions provoked by the bellows. The processes of diffusion and adsorption-desorption occur in the reactor situated at the lower part, where the catalyst is placed. The coefficients of the processes of diffusion and adsorption-desorption can be determined then by analyzing the changes in pressure, using the pressure-measuring unit.

6 Computational Setup using COMSOL Multiphysics

The experiment requires the analysis of the behavior of fluids, when compression and expansion processes occur. This includes the heat exchange between these fluids and their surroundings [5].

Moreover, the main objective for this project consists of studying the mass transport of the inner fluid in a porous material, in this case, the zeolite. Hence, it requires the measurement of several variables like pressure, velocity, temperature or concentration.

Additionally, the Frequency Response generates a volume modulation as the input for the study, which needs to be introduced into the model. This is achieved by applying a vertical movement like the one generated by the FR apparatus.

The software COMOSL Multiphysics 5.2a is used to create a model in which this experiment can be simulated. The processes which occur during the experiment can be recreated using this simulation tool.

The interfaces that will be used to describe the experiment as accurately as possible are: Laminar Flow, Moving Mesh, Heat Transfer and Transport of Diluted Species in Porous Media.

6.1 Definition of Parameters

The software COMSOL Multiphysics offers the possibility to parameterize variables. These parameters can be later introduced in the settings of the different interfaces, and it is also possible to change their value at any time without changing the settings of the whole model.

As the measurements of every part of the experiment are available in the SolidWorks file, the measurements can be straightforward introduced as parameters to create the COMOSL model. Thus, all the geometrical dimensions and the initial conditions of the system are parameterized. This is achieved by clicking in 'Parameters' and introducing the information. This facilitates the creation and modification of the model.

The measurements and initial conditions that are defined as parameters in the model can be seen in the next table:

Table 1: Parameterized variables in COMSOL Multiphysics

Parameter	Value	Description
w_glass	1[mm]	Wall width of glass reactor
d_in1	11[mm]	Internal diameter of reactor
d_in2	10.4[mm]	Internal diameter of first pipe and ring
w_pipe1	1.3[mm]	Wall width first pipe
len1	30[mm]	Length of glass reactor
len2	24.1[mm]	Length of first pipe
hei_ring	7.6[mm]	Height of every ring
w_ring1	11.8[mm]	Wall width of ring 1
d_in3	16[mm]	Internal diameter of ring 2
w_ring2	9[mm]	Wall width of ring 2
w_balg1	36[mm]	Wall width of top part of bellow
balg_in	46[mm]	Internal diameter bellow
len4	6[mm]	Length solid part of bellow
len5	8[mm]	Length joining part of bellow
d_in_balg	16[mm]	Internal diameter starting point of bellow
len3	60.8[mm]	Length of bigger pipe
num_fin	27	Number of fins per bellow
len_balg_tot	99[mm]	Maximum length of bellow
len_comp	3[mm]	Length of compression
w_pipe2	1.5[mm]	Wall width of bigger pipe
len6	2[mm]	Length of the joining plate
len_balg	40.5[mm]	Height of each bellow
len_fin	21[mm]	Length of each fin
w_joiner	46[mm]	Width of joining plate
max_mov	3[mm]	Maximum movement of the bellow
freq	10[Hz]	Frequency of square waves
t_step	0.01/freq [s]	Step time
P_amb	101325[Pa]	Pressure
T_amb	298.15[K]	Temperature
rho_factor	1	Factor for density
P_N2	133[Pa]	Pressure nitrogen or carbon dioxide

6.2 Simulation of the Frequency Response Input

The Frequency Response apparatus provokes a volume modulation –the input– which has an effect on the pressure –the output–, and this permits the simultaneous study of several coefficients. The FR system way to function needs, therefore, to be represented in the model.

In order to achieve this, a periodical function is created to generate the volume modulation. For this study, there are two options: sinusoidal function or square function.

It should be preferred to use the sinusoidal function as it is managed by the simulation tool with less convergence problems, due to the slow growth of its velocity. The program is capable of working with it having fewer errors, and in addition, the simulations using this function need less time to be completed.

However, the square function implies a more accurate representation of the real movement of the bellows and the travel plate, as it is the function used by the FR system in reality. The results have in this case higher long term reliability, and can also be more easily compared to the results of the real experiment.

In spite of the square function being more similar to the actual experiment, the sinusoidal function is the chosen one to work with and create the model, due to the program managing the sinusoidal function with less convergence problems, and the need of less time to run the simulations, which implies more available time to study and improve the different model settings.

This input function can, nonetheless, be changed at any time. So the square function can be used to test the model, once the simulation presents good results when using the sinusoidal function.

In both cases, the function is created by right clicking on 'Definition', found under 'Component', and then selecting 'Functions' and 'Waveform'. The label and name can then be modified, and the type of the waveform function can be chosen.

For the sinusoidal function, having selected the 'sine' type, the parameters are the following:
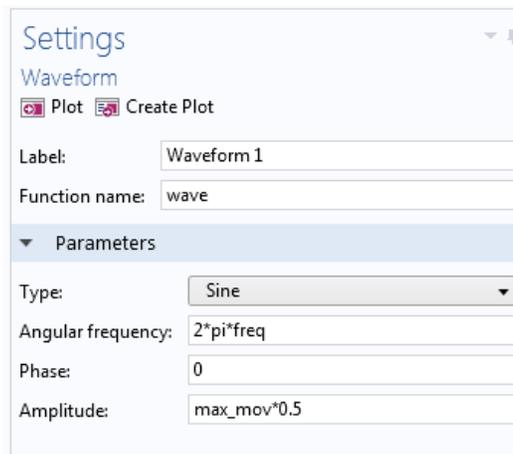
Figure 4: Main parameters of the sinusoidal function of displacement

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The angular frequency of the wave is introduced as $2*\pi*freq$, having the parameter *freq* the value of 10 Hz. The real experiment presents a range 0.001 to 10 Hz, and the latter value is selected as it implies the shortest simulation time with acceptable results.

The amplitude consists of the distance between the middle point of the function and the lowest or highest point. The parameter *max_move* is defined as the total displacement of the bellow, due to this, the amplitude is introduced as half of this value (*max_move**0.5).

The resulting sinusoidal function of displacement is shown on the following image:
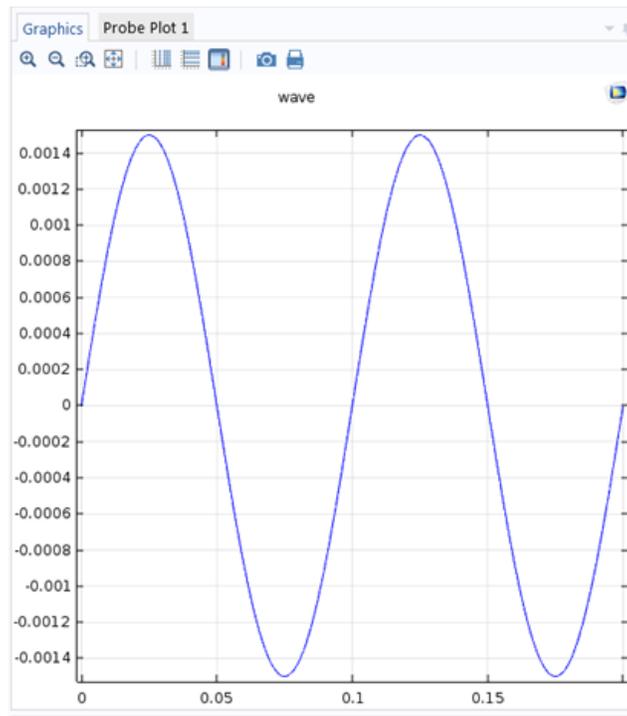

Figure 5: Sinusoidal function of displacement, wave (x)

To use a square function instead of a sinusoidal one, only the type of the waveform needs to be selected as 'square' instead of as 'sine'. The parameters in this case are the following:

To define the square function, some other values need to be introduced. A transition zone is necessary to avoid the square function leading to infinite values. Therefore, the 'Smoothing' is selected, with a transition zone size of 25*t_step. The parameter *t_step* depends on the frequency according to the expression *t_step = 0.01/freq* [s]. If the value of the frequency changes, so will the values of the time step and of the transition zone.

The resulting square function of displacement is shown on the following image:

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7 Geometry

To create the geometry of the model, the 2D axisymmetric option is selected as Space Dimension. This increases significantly the solver speed compared to a full three dimensional model. The model itself is axisymmetric, as it can be seen in the CAD model created using the software SolidWorks.

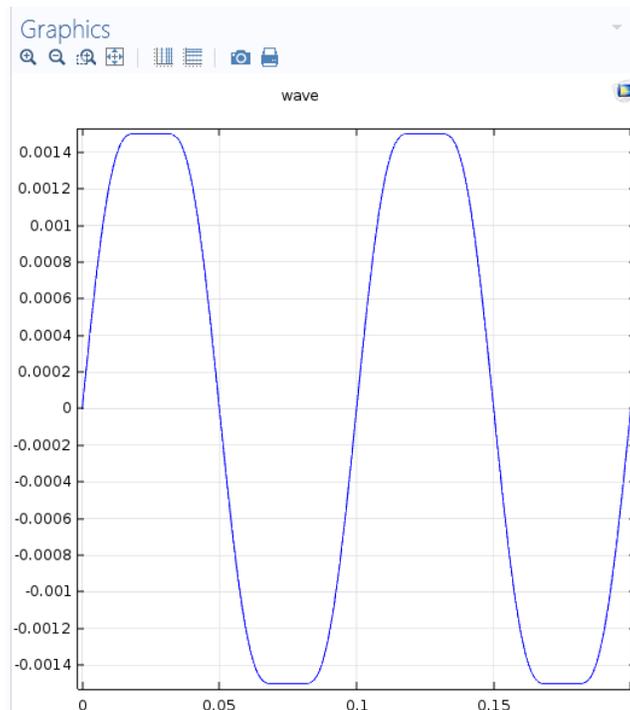The geometry from the SolidWorks file cannot be directly imported to COMSOL so it is necessary to build the geometry in COMSOL too. In order to do this, the measurements of the parts which are relevant to the simulation are taken from a section done to the SolidWorks model.

As the model is axisymmetric, the geometry in COMSOL is built in the 2D layout representing the right half and having the z axis on the left side.

The parts of the experiment which do not need to be represented in the model, as they do not have an influence in the results of the process, are: The pressure measuring unit; the cross joint, that connects it to the rest of the system; the electromagnetic plates, responsible for moving the plate to provoke the volume modulation; and the top pipe, which is the inner fluid inlet, as the model simulates the experiment when this fluid is already filling the interior and starts getting compressed and expanded.

The steps to create this geometry in COMOSL consist of the following:

In the Geometry node several geometrical shapes are available. The first one used is 'Rectangle', by clicking the right button on 'Geometry' and selecting the 'Rectangle' option. The coordinates and dimensions of the different rectangles can be introduced and this way most of the geometry of the model is created.

The domains under the volume modulation unit are divided into several rectangles, being some of them very small, for meshing purposes. The objective is not to have rectangle vertexes inside the geometry, so that a more regular mesh can be achieved and convergence problems can be avoided.

The original model had also the bellows as part of the geometry. In order to do that, the 'Polygon' option of 'Geometry' was used. After introducing at least three coordinates of the first fin in the 'Polygon' settings, the option 'Array' can be chosen to create copies of the selected geometry. The total number of fins per bellow is 27. The number of copies, the array type (linear or rectangular) and the total displacement can be selected. Both the upper and lower bellow were created following this procedure.

The current geometry presents a simplified version of the bellows, as it was proven that there is not a big difference regarding temperature and pressure evolution. In addition, the simulation time is reduced, so this previous detailed bellow geometry is not necessary. The new geometry will be further discussed.
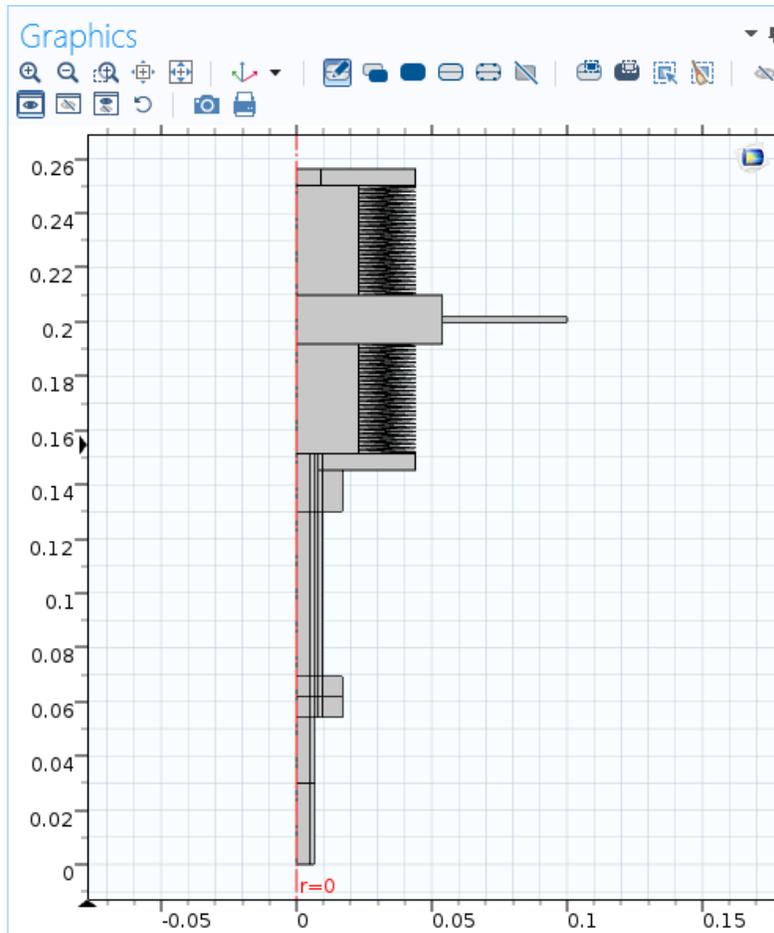
Figure 8: Interior geometry of the model

As the inner gas experiments a heat exchange with the outer fluid, in this case air, the outer fluid needs to be taken into account in the model. Hence, more geometry elements are added to represent the air surrounding the system. These elements are created using the option 'Polygon'.

This air domain is an auxiliary one, which means that its size is not important as long as there is enough space for the fluid properties to develop. It is built around the outer boundaries of the experiment and covers both the lower part that remains still and the upper part, which is in contact with the volume modulation unit – the moving part of the setup.

Figure 9: Complete previous geometry of the model
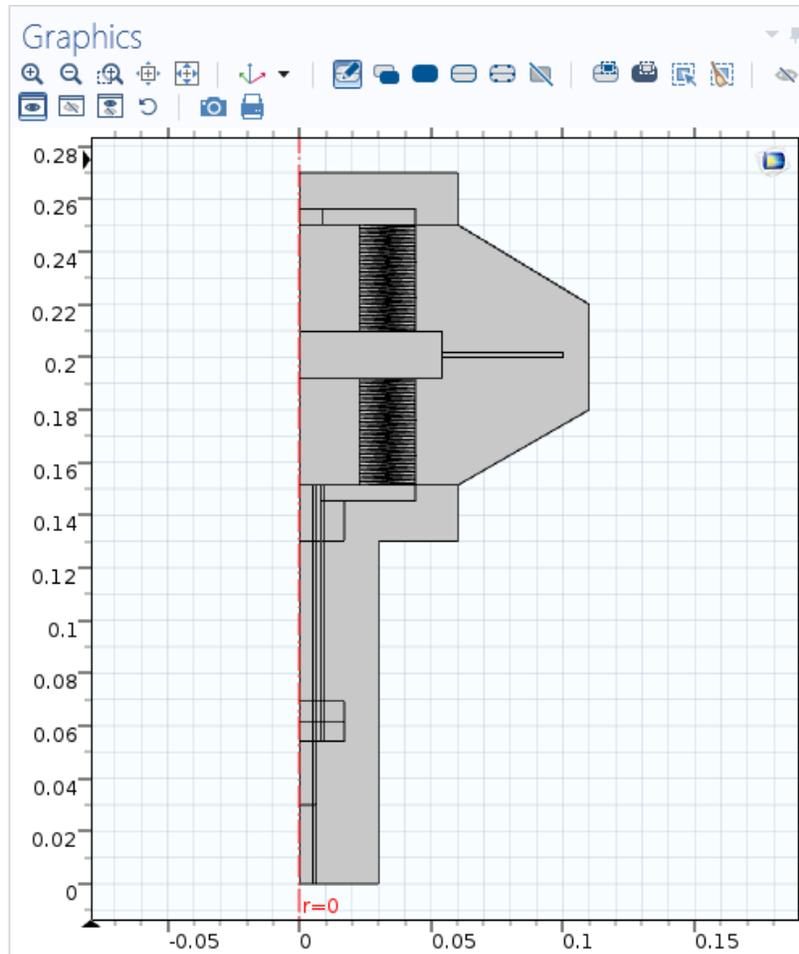
Once all the geometry elements have been designed, the last step is to select the option 'Form Union' in the 'Geometry' menu. It joins all the parts, so that more interfaces and simulation settings can be applied to them.

As it was commented before, the current model does not have the bellows represented like that anymore. A simplification was made to test if there were significant differences regarding the temperature and heat transfer evolution, as that area is where the main heat transfer takes place. In order to do so, instead of the detailed representation of the bellows, just a vertical line indicates the separation between the inner and outer gases. This is possible because, even though the bellows are represented in the previous model geometry, those geometrical elements do not have a physical meaning representing a material part, but just have the function to represent the separation of the fluids.

To study the heat transfer with more detail, four new rectangles are created using the 'Rectangle' option and placed in the space formerly occupied by the bellows, so that the area remains the same.

Having two rectangles at each side of the border where the main heat transfer occurs, a finer mesh can be applied in all of them, and thus have more precise results on this area.
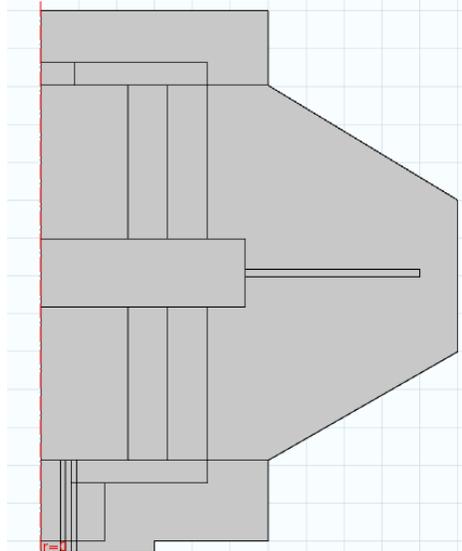
Figure 10: Detail of the new geometry
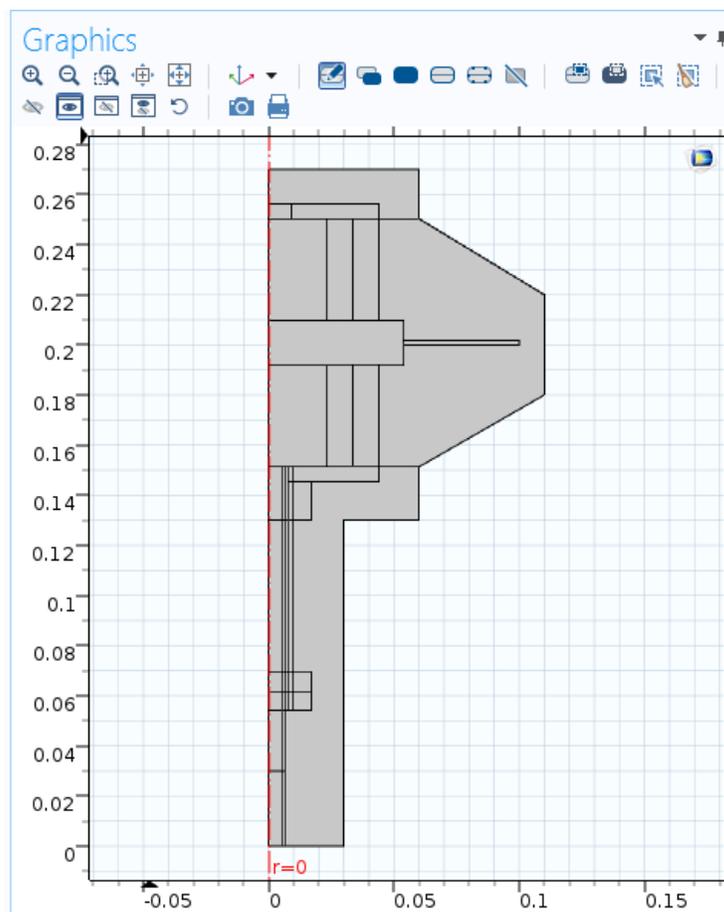
Figure 11: Complete current geometry of the model

It was confirmed that the temperature evolution does not present significant changes, and reaches its peak at the same time, and physical point, using the simplified geometry, as using the former one. Furthermore, it could be seen that the pressure evolution does not suffer changes because of this modification.

Not only does this new geometry allow a finer mesh for the study, but also reduces the simulation time considerably. Due to this reason, this is the geometry which is used from now on to work on the simulation.

8 Materials

The 'Materials' node in COMSOL Multiphysics allows to add predefined or user-defined materials, to specify material properties using model inputs, functions, values, and expressions as needed.

Figure 12: 'Add Material' window
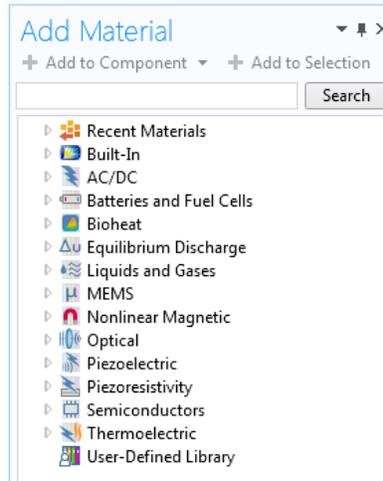
The materials for each domain of the model, as well as their properties, need to be defined in order for the software to run the simulation and calculate the different variables which take part in the process. In this model, five materials are defined:

The inner fluid of the experiment is Carbon dioxide. It can be selected by right clicking on the 'Materials' node and selecting 'Add Material'. The 'Add Material' window is now open and Carbon Dioxide can be found under 'Liquids and gases' > 'Gases' > 'Carbon dioxide'.

Another possible gas to be used as the inner fluid is Nitrogen. In this case, Nitrogen would be selected following the same procedure as to select the Carbon Dioxide. This change in COMSOL Multiphysics is very easily made, and the inner fluid can be thus changed at any time if necessary.

The domains corresponding to the inner fluid (Carbon dioxide) are the following:
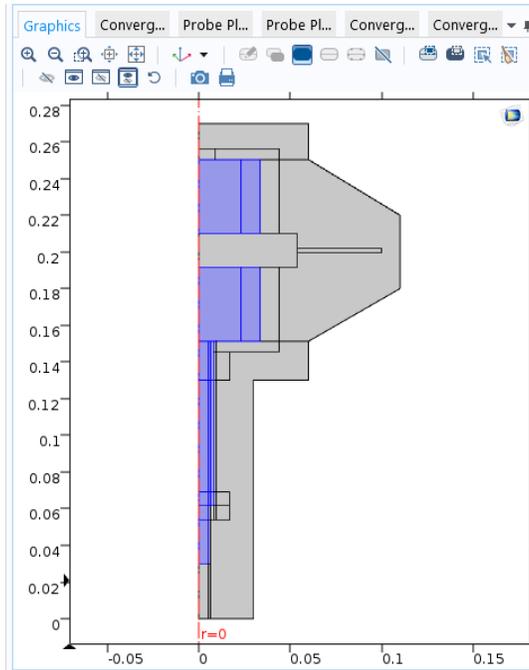
Figure 13: Carbon dioxide domains

The outer fluid is air. It can be found under 'Add Material'>'Liquids and gases' > 'Gases' > 'Air'.

Its corresponding domains are the following:
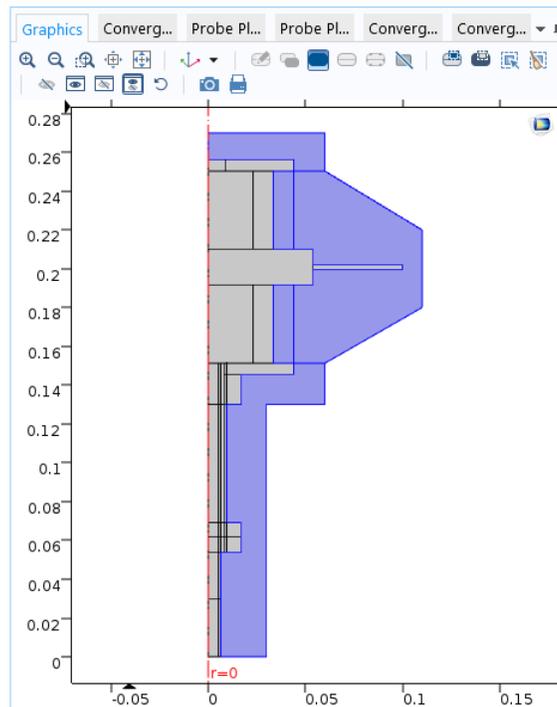
Figure 14: Air domains

The solid parts of the experiment, like the pipes or rings, are made of steel. The selected material for these domains is steel AISI 4340, found under 'Add Material' > 'Liquids and gases' > 'Build in' > 'Steel AISI 4340':

Figure 15: Steel AISI 4340 domains

The reactor wall is made of glass. It can be found under 'Add Material' > 'Liquids and gases' > 'Build in' > 'Glass (quartz)'.
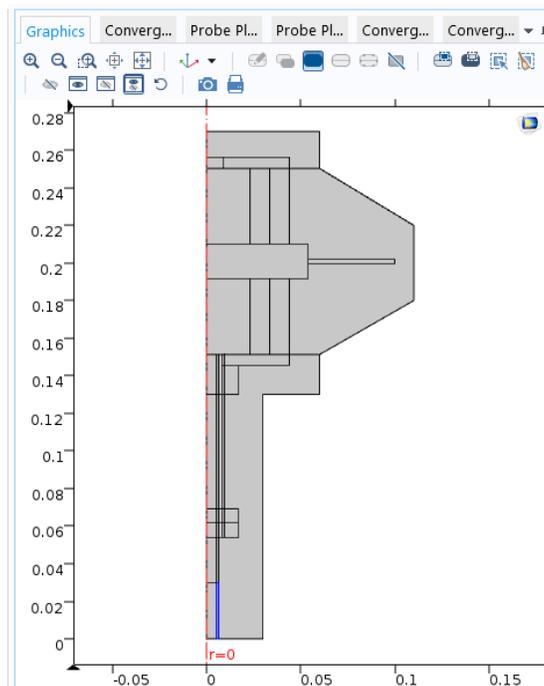
Figure 16: Glass domain

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Finally, the last material to be added is the Zeolite 5A, the porous material. It cannot be found in COMSOL's Materials Library, so in this case the steps to follow are right clicking on 'Geometry' and se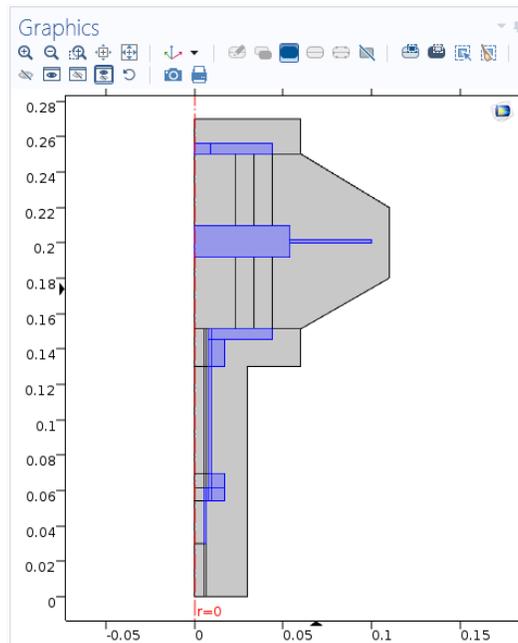lecting 'Blank Material'. This option allows the user to define the properties for the new material as needed. In this case, the properties that the applied interfaces need, as well as the density and porosity of the zeolite, are manually introduced, either taken from experimental data, or from bibliography [12].

	Property	Name	Value	Unit	Property group
☑	Density	rho	689	kg/m³	Basic
☑	Porosity	epsilon	0.66	1	Basic
☑	Heat capacity at constant pres...	Cp	783	J/(kg·K)	Basic
☑	Thermal conductivity	k	0.02596	W/(m·...	Basic

Figure 17: Material Contents table for the Zeolite 5A

This option will facilitate the selection and use of the zeolite properties when applying several interfaces. The domain corresponding to the porous material can be seen in the following image:

Figure 18: Zeolite 5A domain

9 Interfaces

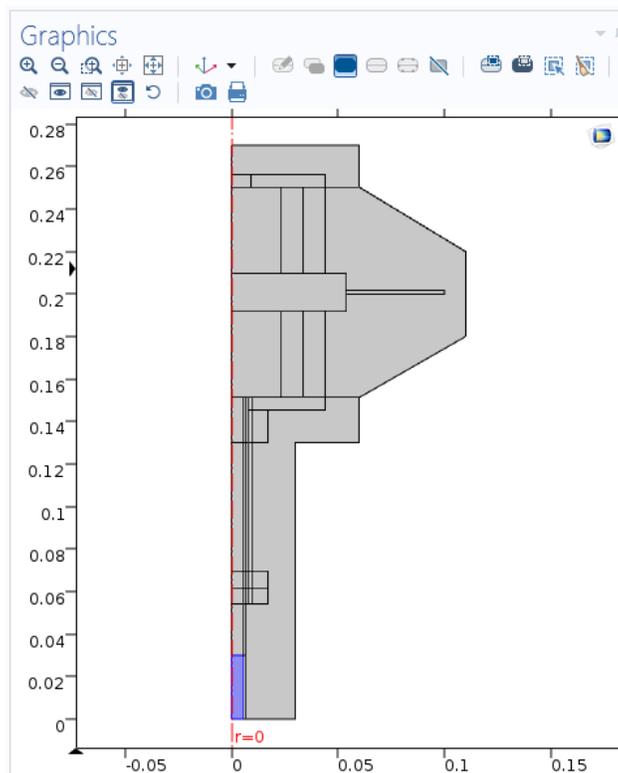To incorporate the different interfaces, which COMSOL Multiphysics offers, the 'Add Physics' window is used. It can be opened by right clicking on 'Component' in the Model Builder tree and then clicking on 'Add Physics'. Another possibility is to click directly on 'Add Physics' in the 'Physics' section of the main toolbar. The different interfaces are organized according to their scientific field.
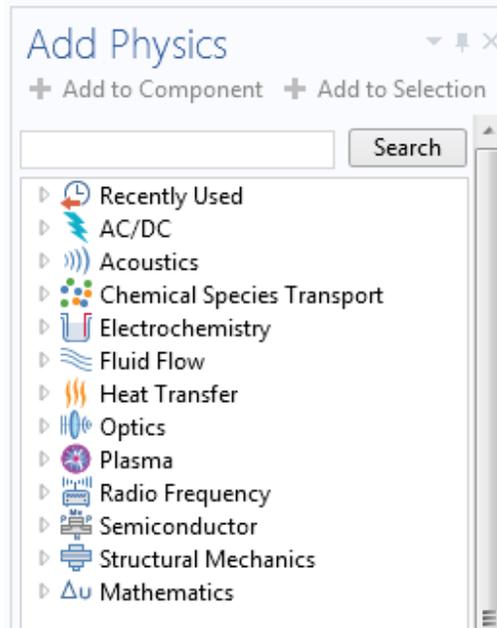
Figure 19: 'Add Physics' window

The interfaces used in this model to simulate the real experiment are discussed next. These interfaces are: Laminar Flow, Moving Mesh, Heat Transfer in Solids, and Transport of Diluted Species in Porous Media.

9.1 Laminar Flow 1

The function of the Laminar Flow (spf) interface is to compute the velocity and pressure fields for the flow of a single-phase fluid in the laminar flow regime. This interface is used twice in this model. In this first case, it is used to compute the pressure and velocity fields of the inner fluid. As it was commented in chapter 3, the laminar Flow interface solves the Navier-Stokes equations for conservation of mass (Eq. 1) and conservation of momentum (Eq. 6) [13].

This interface can be found in the 'Add Physics window' under 'Fluid Flow' > 'Single-Phase Flow' > 'Laminar Flow (spf)'. It is applied to all the domains corresponding to the inner fluid, in this case, Carbon Dioxide.
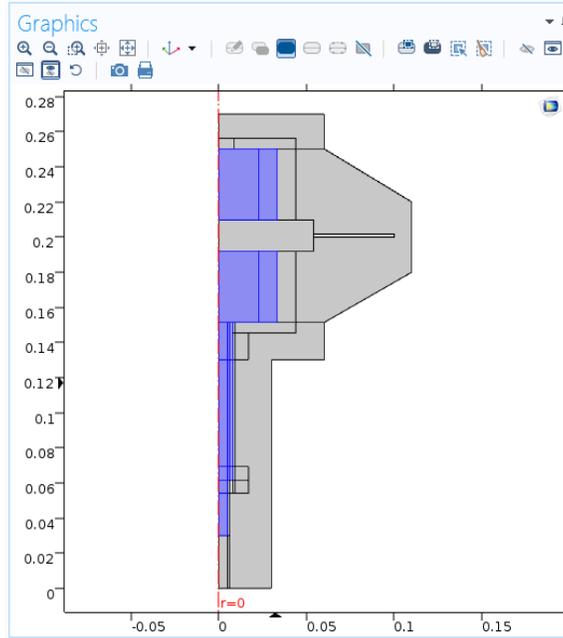
Figure 20: Laminar Flow 1 domains

When the 'Laminar Flow' interface is added, the following nodes appear by default in the Model Builder: Fluid Properties, Wall (whose default boundary condition is 'No slip'), Initial Values, and Axial Symmetry.

In the 'Laminar Flow' settings, the option 'Compressible Flow (Ma<0.3)' is selected, and the reference values for temperature and pressure are introduced. Although initially COMSOL expects certain units, it is possible to introduce a numeric value in a different unit, as long as the used unit is specified using square brackets:
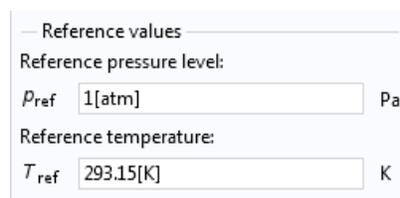
Figure 21: Laminar Flow 1 reference values

In the 'Fluid Properties' settings, the model inputs are introduced as 'User defined'. The temperature corresponds to the initial temperature of the experiment, 298.15 K. The absolute pressure, p_A is expressed by adding 1 atm to the gauge pressure obtained by the simulation, *root.comp1.p*. The fluid properties, such as density or dynamic viscosity, are selected to be obtained 'From material', which means using the properties of the material defined in the corresponding domains.

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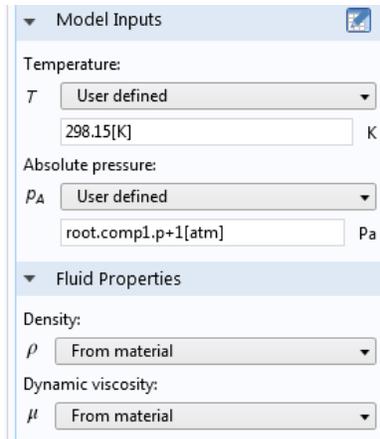
Figure 22: Laminar Flow 1 model inputs and fluid properties

For the 'Initial values' settings, the velocity field is set up as 0, as there is no movement until the experiment starts. The initial pressure is introduced as gauge pressure, *P_N2-Pamb*. The initial absolute pressure of the inner gas was parameterized as *P_N2*, as the inner fluid of the experiment was originally nitrogen, but this initial pressure has the same value when using carbon dioxide, so the defined parameter can be used in the same way without being changed.

The 'Wall' node permits to add several boundary conditions to describe the fluid-flow behavior. The default boundary condition is 'No slip', which prescribes $\mathbf{u} = 0$, meaning that the fluid is not moving at the wall. This condition applies to the separation between the inner and outer fluid – the bellows in the real experiment – as well as to the limits of the inner fluid with the not moving materials.

Figure 23: 'No Slip Wall' boundaries

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The other boundary condition used is 'Moving wall', applied to the boundaries corresponding to the surface of the travel plate in contact with the inner fluid. This boundary condition permits to assign a velocity to the moving wall. The recreation of the movement of the travel plate, by using another interface – Moving Mesh –, will be further described in this chapter.
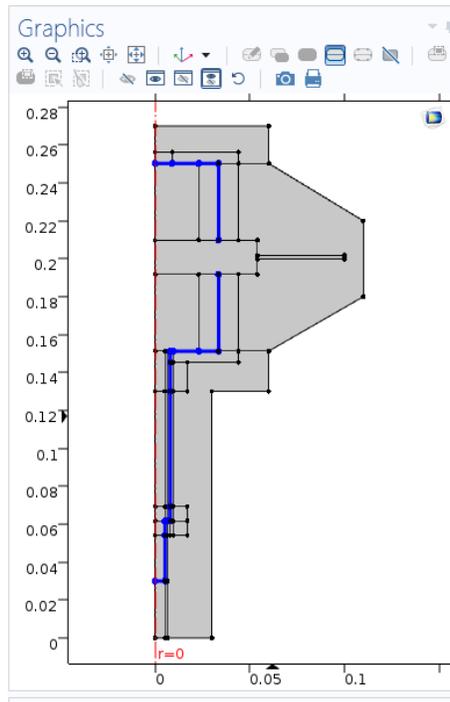
In order to assign a velocity to these boundaries affected by the 'Moving wall' condition, and to represent the movement of the fluid in contact with them, it is necessary to create first 'Linear Extrusion' coupling operators. They can be created by right clicking on 'Definitions' and then selecting 'Component Couplings' > 'Linear Extrusion'. One Linear Extrusion needs to be created for every boundary belonging to the volume-modulation unit representing the separation between each fluid and the solid materials. Both the boundary and its two vertexes need to be selected for each coupling.
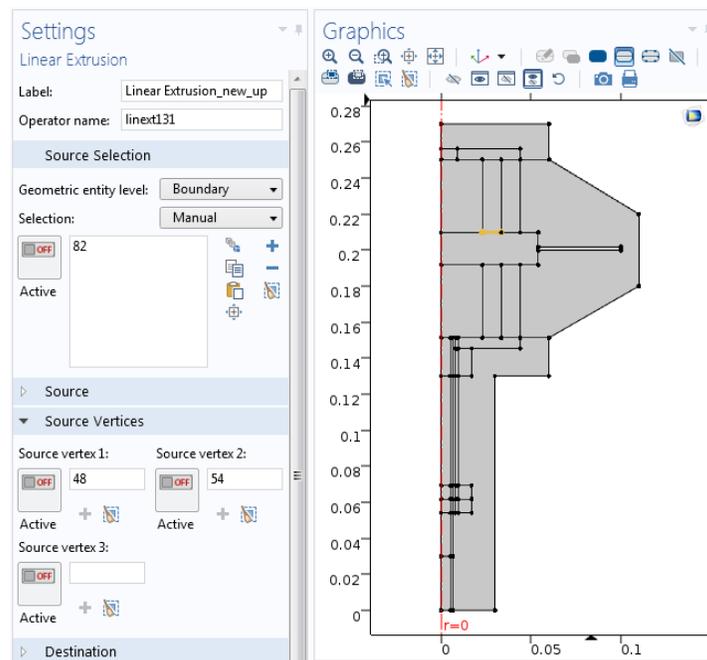
Figure 24: Example of the settings of a Linear Extrusion

Once the Linear Extrusions are created, and back in the 'Laminar Flow' interface, the velocity of the travel plate can be coupled with the fluid in contact with it. To achieve this, the z axis velocity needs to be introduced for the boundaries of the travel plate with 'Moving wall' condition. For each of them, the velocity will be their corresponding 'Linear extrusion' – written as the shortcut *linext* – followed by '*(zt)*' to indicate that the complete expression is a velocity:
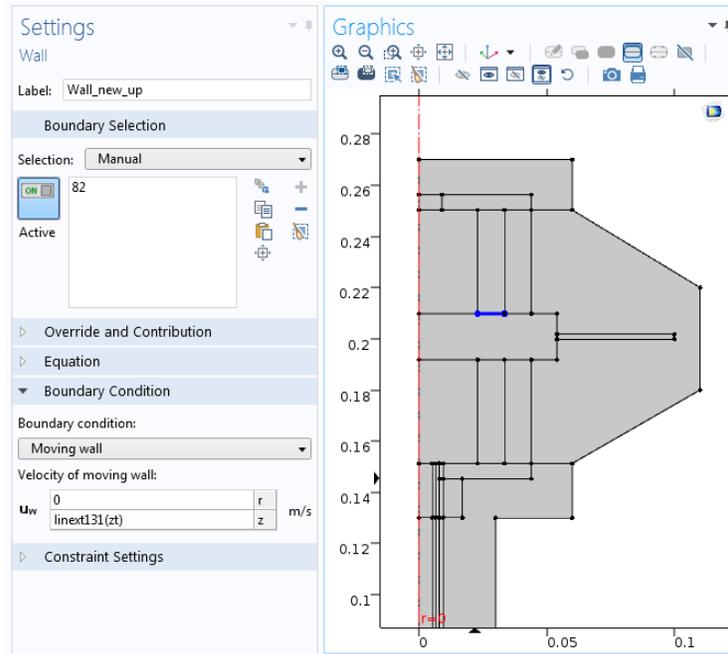
Figure 25: Example of the settings of a 'Moving Wall' in Laminar Flow 1

Finally, the last main node used in this interface is a 'Pointwise Constraint'. The steps to select it consist of clicking in 'Show' at the top of the Model Builder tree and then on 'Advanced Physic Options'. This permits to find the 'Pointwise Constraint' by right clicking on 'Laminar Flow' and then selecting 'Points' > 'Pointwise Constraint'.

The 'Pointwise Constraint' is applied on the boundary which represents the separation between the inner fluid and the porous material, in the reactor. As it will be discussed later in this chapter, the variation of the pressure, as a result of the inner gas being compressed and expanded, favors the adsorption and desorption of the inner fluid in the porous material. As a consequence, the variation of the concentration of the inner fluid in the porous material has also an influence in the pressure of the inner gas: When the porous material adsorbs gas, the pressure in the reactor decreases, whereas when desorption occurs, the pressure in the reactor increases.

In order to recreate this relation in the model, the Ideal Gas law is used to express the inner gas pressure as a function of the gas concentration in the porous material:

$$P = \frac{n}{V} R T = c R T \tag{Eq. 21}$$

The 'Pointwise Constraint' sets equal to zero the introduced constraint expression. Therefore, to introduce as a condition that the pressure at the boundary separating the fluid and the porous material suffers a change due to the variation of concentration, the pressure of the inner fluid minus the pressure expressed as a function of the concentration is written as the constraint expression – this is the same as equalizing both expressions of the pressure, establishing that the pressure at that boundary will depend on the concentration changes.

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In terms of the model variables, this constraint expression is written as:

$$root.comp1.p + 1[atm] - (R\_const * root.comp1.T) * root.comp1.c$$
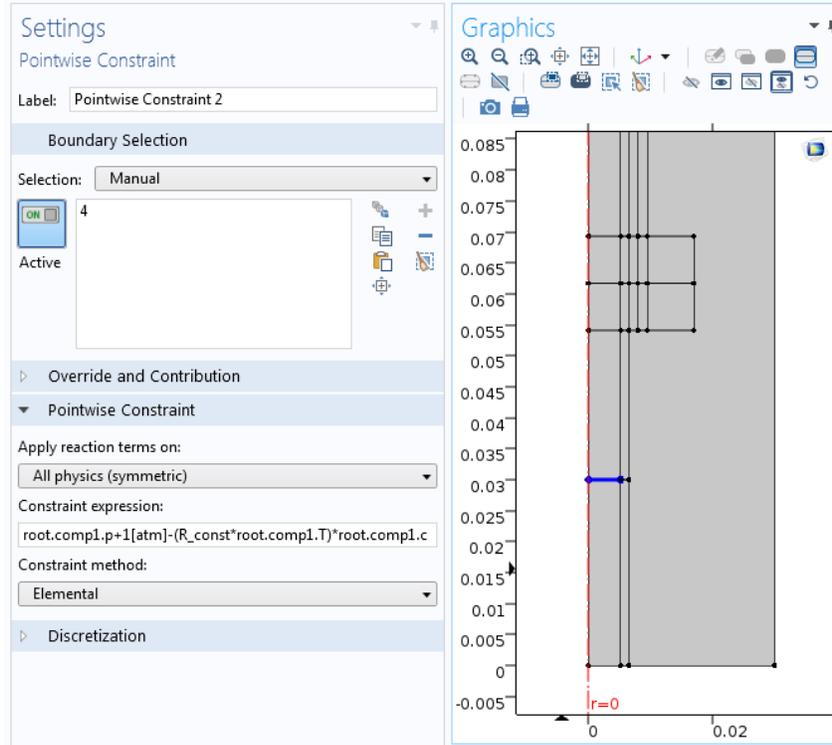
Figure 26: Settings and selected boundary of the 'Pointwise Constraint'

Being $root.comp1.p + 1[atm]$ the expression of the pressure of the inner fluid with which the program works, and $(R\_const * root.comp1.T) * root.comp1.c$ the pressure expressed as a function of the concentration variation of the gas in the porous material.

9.2 Laminar Flow 2

A second 'Laminar Flow' interface is applied to the outer fluid to calculate its velocity and pressure fields during the experiment. In this case, the outer fluid is the air of the environment. The second 'Laminar Flow' is then applied to every domain corresponding to air:

Figure 27: 'Laminar Flow 2' domains

The reference values and 'Compressible Flow' option are the same as for the inner fluid. The model inputs are also introduced in the same way, and the fluid properties are taken 'From material'.
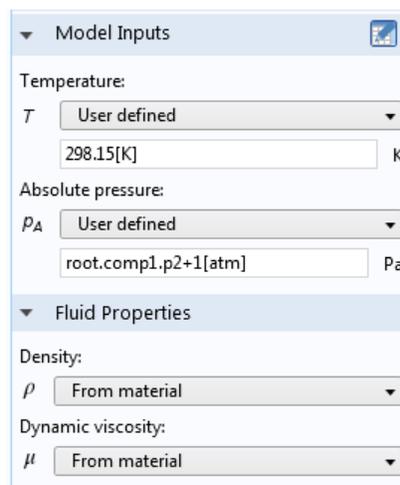
Figure 28: Laminar Flow 2 model inputs and fluid properties

The 'No Slip Wall' boundary condition which appears by default has the same effect as in the previous 'Laminar Flow' interface, but this time form the other side. Likewise, to match the movement of the travel plate and its effect on the air, the 'Moving Wall' nodes are needed. The steps to 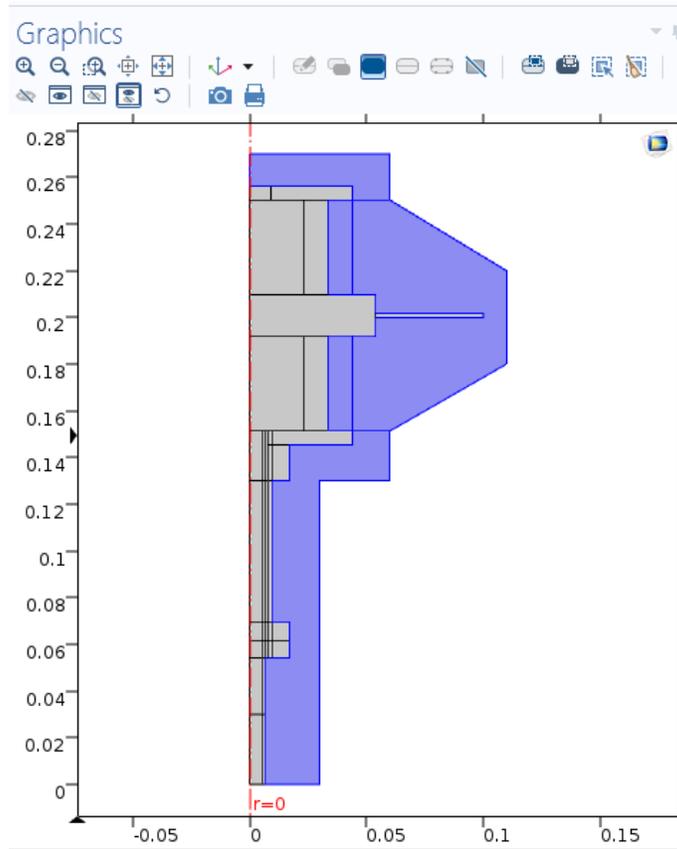couple the 'Laminar Extrusion' functions created under 'Definitions' with the 'Moving Wall' nodes are the same as in the first 'Laminar Flow' interface. The expression of velocity in the z axis is also the shortcut for the corresponding Laminar Extrusion followed by *(zt)*:
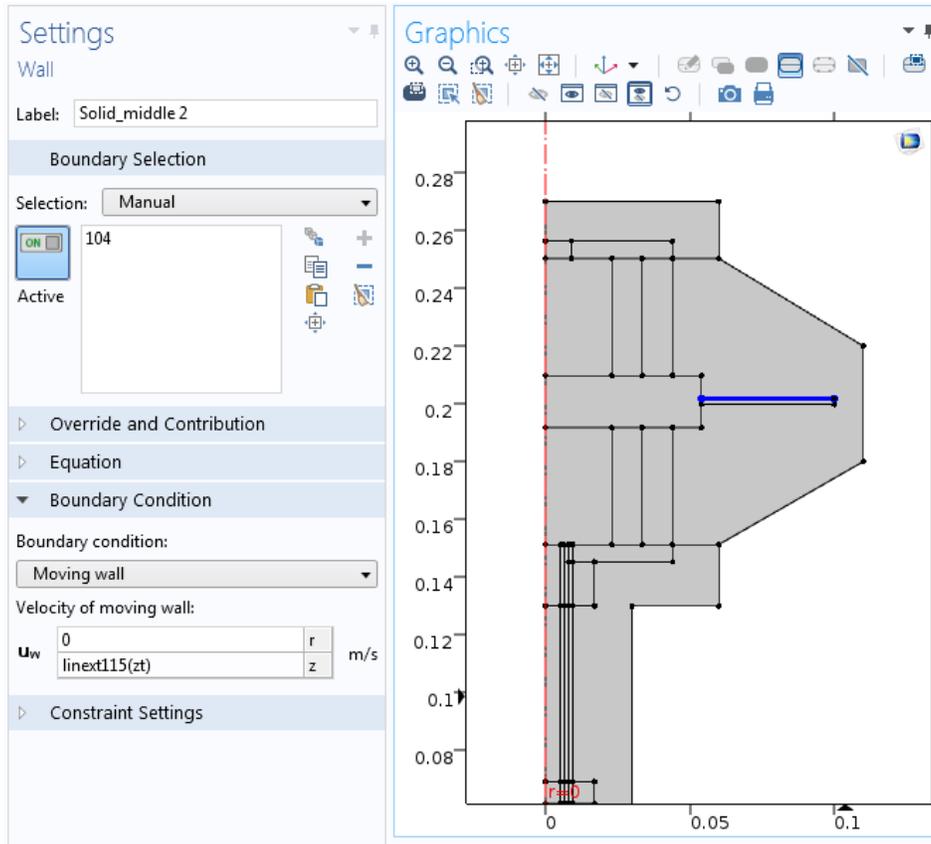
Figure 29: Example of the settings of a 'Moving Wall' in Laminar Flow 2

Another boundary condition used in this interface is 'Open Boundary', which can be found by right clicking on 'Fluid Flow 2'. The 'Open Boundary' condition describes boundaries in contact with a large volume of fluid, in this case, the air of the environment surrounding the experiment. Fluid can both enter and leave the domain on boundaries with this type of condition.

All the outer boundaries of the outer fluid are selected. The boundary condition is selected as 'Normal stress' with a value of 0 N/m^2.
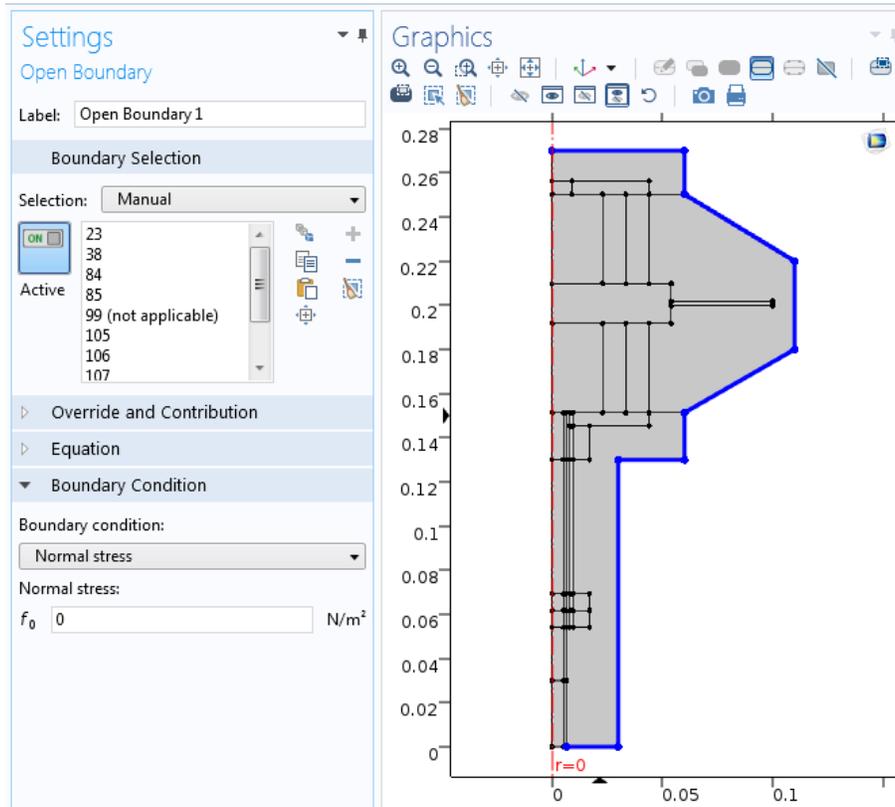
Figure 30: Settings and selected boundaries of 'Open Boundary' in Laminar Flow 2

9.3 Moving Mesh

The Moving Mesh (ale) interface can be used to create models where the geometry experiments shape changes provoked by physical phenomena without material being removed or added. When using this interface, the changing geometry is represented by the mesh.

The Moving Mesh interface can be found in the 'Add Physics' window under 'Mathematics' > 'Deformed Mesh' > 'Moving Mesh'.

There is another interface under the same branch, called 'Deformed Geometry'. This other interface is not used, as it defines a deformation of the material frame relative to the geometry frame, rather than a displacement of the spatial frame relative to the material frame. The second option is what can be applied to simulate the experiment, and it is what 'Moving Mesh' defines [14].

The selected domains for the 'Moving Mesh' interface are those which represent the moving part of the model, in other words, the domains corresponding to the volume-modulation unit: The travel plate, and the domains of inner and outer fluids which are affected – compressed and expanded – by this movement in the top part:
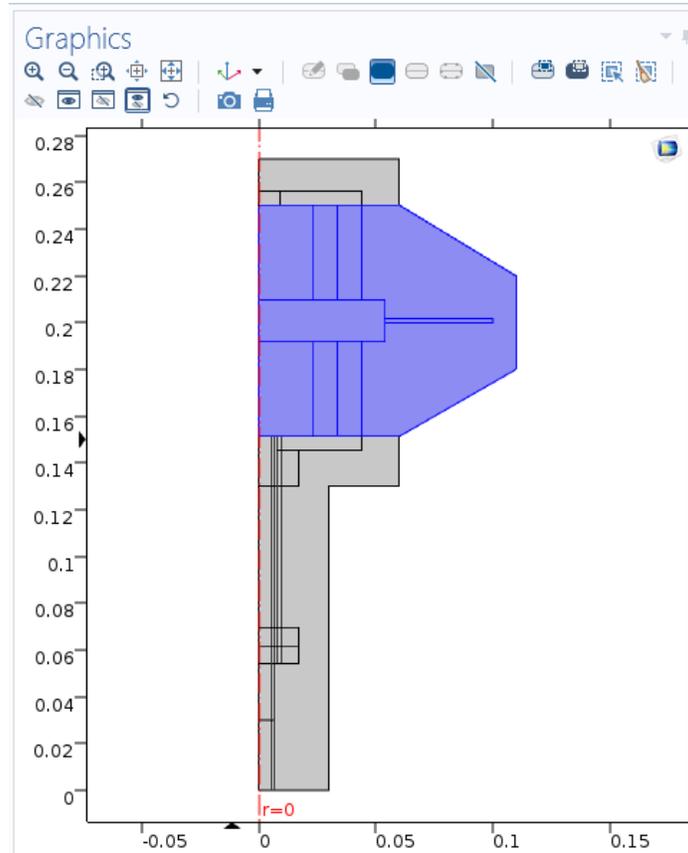
Figure 31: 'Moving Mesh' domains

The default nodes which are added to the Model Builder together with the 'Moving Mesh' interface are: Fixed Mesh, and Prescribed Mesh Displacement. In order to add more nodes representing the different conditions, it is necessary to right click on 'Moving Mesh' and then select 'Free Deformation'. The Free Deformation node constrains the mesh displacement only by the boundary conditions on the surrounding boundaries. The initial mesh displacement can be introduced, which in this case is 0 m both in the z and r directions, since there is no movement until the experiment begins. The selected domains are the same as for the 'Moving Mesh' interface – the moving parts.

Finally, by right clicking again in 'Moving Mesh', the node 'Prescribed Mesh Displacement' can be selected. This node is used three times in this model. The 'Prescribed Mesh Displacement' node permits to specify the displacement of the boundaries of domains with free deformation. The spatial frame in the adjacent domain moves in accordance with the displacement.

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The first 'Prescribed Mesh Displacement' is used to represent the vertical movement of the travel plate, which is what causes the volume modulation. In order to achieve this, the wave function created in 'Definitions' is used. The selected boundaries are the ones representing the travel plate. The travel plate only moves in the z axis, so the prescribed z displacement is set as *wave(t[1/s])* m, which means that the z displacement will behave over time following the periodic function. As the units of the displacement must be length units, the [1/s] is multiplied to the expression of time [s].
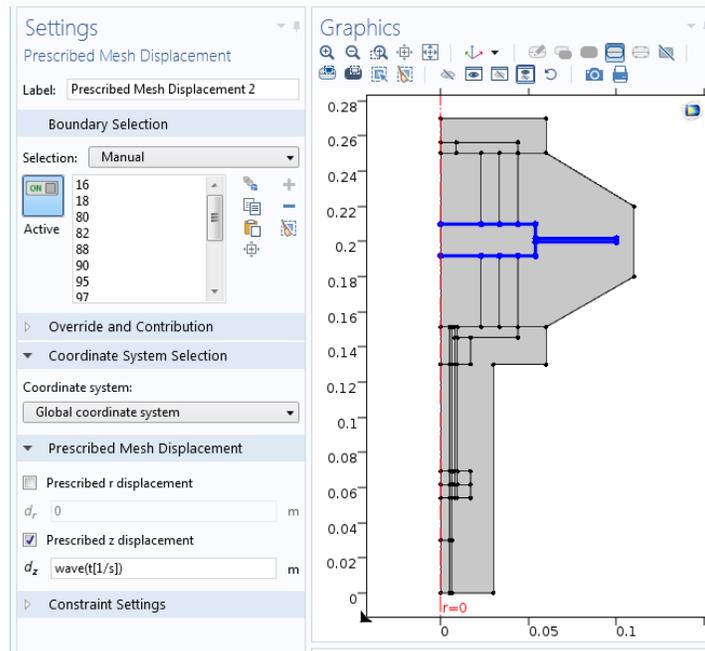
Figure 32: Settings and selected boundaries of Prescribed Mesh Displacement 1

The second 'Prescribed Mesh Displacement' is applied to the boundaries belonging to the symmetry axis and its function is to restrict the horizontal movement of these boundaries, having 0 m as the value of the prescribed r displacement.

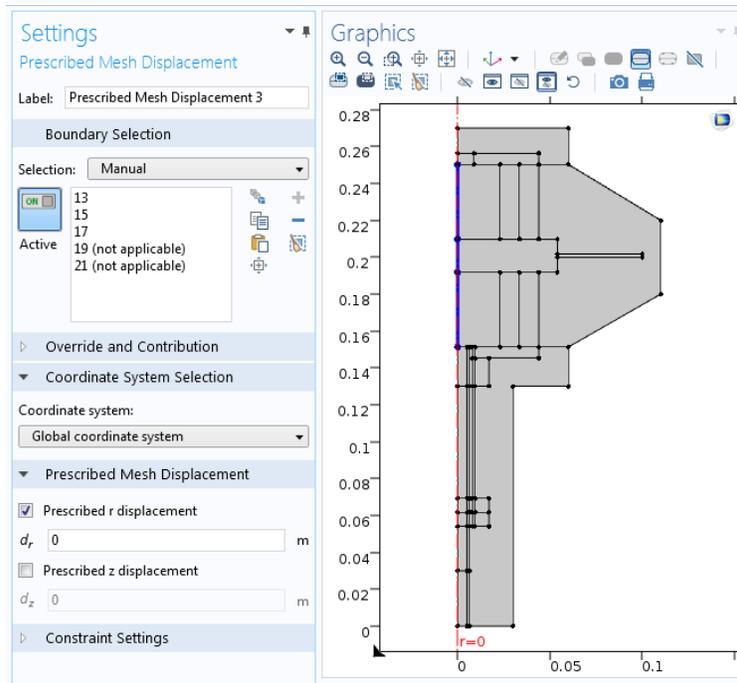Figure 33: Settings and selected boundaries of Prescribed Mesh Displacement 2

To conclude, the third and last 'Prescribed Mesh Displacement' is applied to the outer boundaries of the volume-modulation unit to indicate that these boundaries do not have any movement. Both prescribed r and z displacements are selected as 0 m.
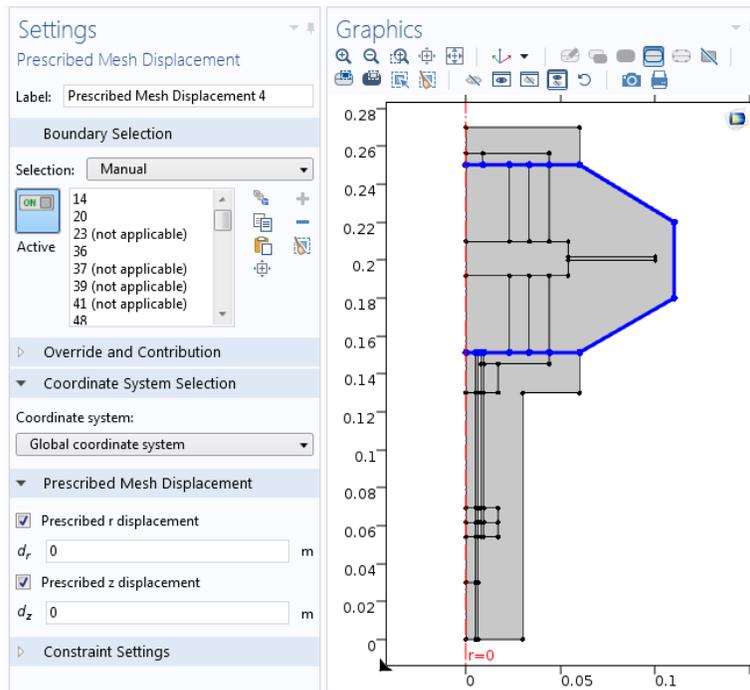

Figure 34: Settings and selected boundaries of Prescribed Mesh Displacement 3

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9.4 Heat Transfer in Solids

The Heat Transfer in Solids (ht) interface can be used to model heat transfer in solids by conduction, convection, and radiation. It can be found in the 'Add Physics' window under 'Heat Transfer' > 'Heat Transfer in Solids'. The name of the interface is 'Heat Transfer in Solids', however, it can also be applied to fluids using specific nodes. The equation that this interface solves is the differential form of the Fourier's Law (Eq. 7), and it is possible to add heat sources to represent additional contributions.

The default nodes which are added to the Model Builder when 'Heat Transfer in Solids' is incorporated are: Solid, Thermal Insulation (the default boundary condition), Initial Values, and Axial Symmetry. Then, by right clicking on the node in the Model Builder tree or directly from the 'Physics' toolbar, other nodes to implement physic features, boundary conditions or heat sources can be added [15].

All the domains are selected for the 'Heat Transfer in Solids' interface, and the ambient temperature and ambient pressure are introduced as 293.15 K and 1 atm, respectively. The temperature at the 'Initial Values' node is introduced as 'User defined', using the already defined parameter T_amb.

Then, for the 'Solid' node – which is renamed as 'Heat Transfer in Solids' – the domains corresponding to the glass reactor, the steel parts, and the porous material are selected. The absolute pressure is set as 1 atm, and the option 'From material' is chosen for the program to obtain the properties such as thermal conductivity, density and heat capacity at constant pressure from the information of the material defined in each of the selected domains.
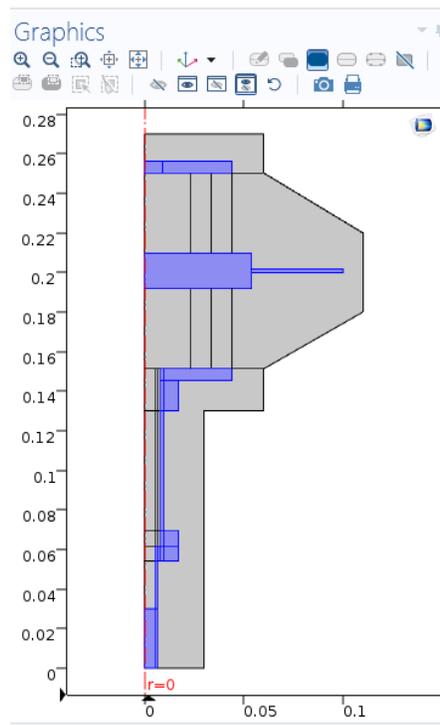
Figure 35: 'Solid' node domains

The 'Thermal Insulation' node indicates that there is no heat flux across the selected boundary, $\mathbf{n} \cdot \mathbf{q} = 0$, and hence, establishes where the domain is insulated. The 'Thermal Insulation' node is applied at the left bottom boundary of the model, to insulate the reactor, where the porous material is placed.
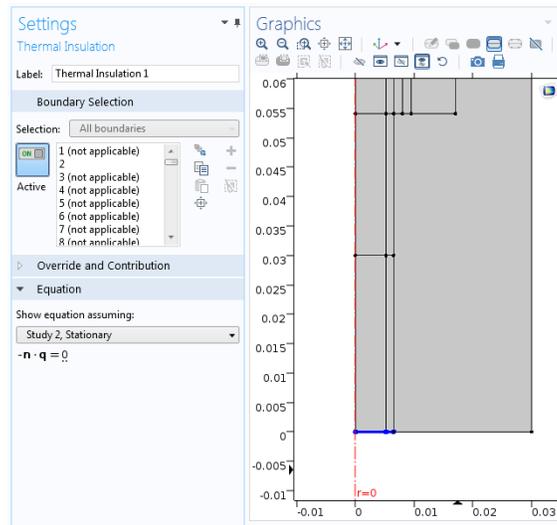
Figure 36: 'Thermal Insulation' boundary

For the rest of the boundaries, the node 'Open Boundary' is used. It works in the same way as in the 'Laminar Flow' interface, except that in this case the boundary condition is established as temperature, being *T_amb* the parameter introduced.
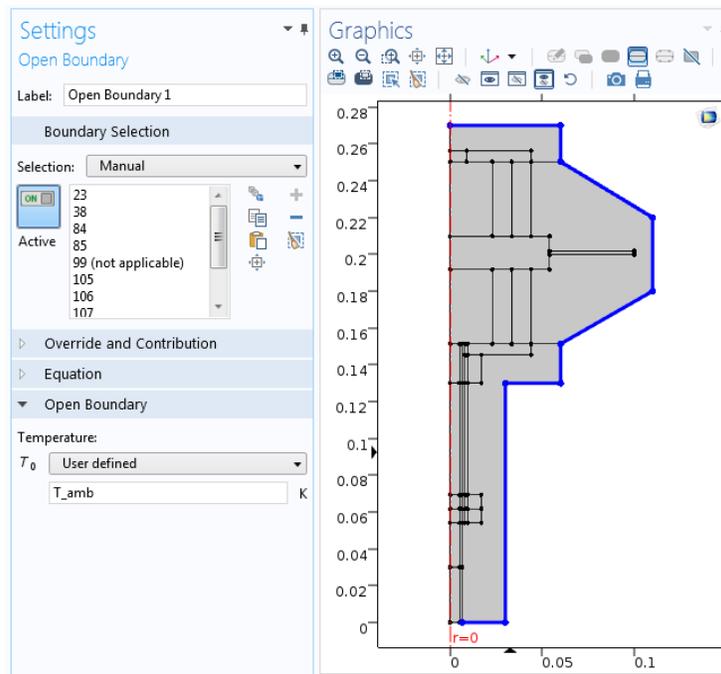
Figure 37: Settings and selected boundaries of 'Open Boundary' in Heat Transfer

In order to simulate the heat transfer in fluids, another node is selected by right clicking on 'Heat Transfer in Solids' and then selecting 'Fluid'. This node is used twice – one time for each fluid – and renamed as 'Heat Transfer in Fluids 1' and 'Heat Transfer in Fluids 2'.

For 'Heat Transfer in Fluids 1', the domains corresponding to the inner gas are selected. The absolute pressure is defined as *root.comp1.p+1[atm]* and the velocity field is coupled with the 'Laminar Flow 1' node by selecting 'Velocity field (spf)'. The fluid properties used by the interface are introduced as 'From material' so that the program takes the properties values form the material defined in those domains.

As it was commented in chapter 3, all the generated heat appears as a consequence of the movement of the fluid, so the two terms representing the heat origin are: The work done by changes of pressure which affects the temperature of the fluid (Eq. 9), and the viscous dissipation in the fluid (Eq. 10). To incorporate these effects to the model, the nodes 'Pressure Work' and 'Viscous Heating' are selected respectively. They can be found by right clicking on 'Heat Transfer in Fluids 1'. The absolute pressure in the 'Viscous Heating' settings is also introduced as *root.comp1.p+1[atm]*, and the dynamic viscosity is taken 'From material'.

For 'Heat Transfer in Fluids 2', the domains corresponding to the outer gas are selected. The steps to follow are the same as for the 'Heat Transfer in Fluids 1' node. The absolute pressure in this case is introduced as 1[atm], which is the ambient pressure, and the properties are also taken 'From material'. The nodes 'Pressure Work' and 'Viscous Heating' are also applied here, being the absolute pressure in the 'viscous Heating' settings expressed as *root.comp1.p2+1[atm]*.

Finally, the node 'Thin Thermally Resistive Layer' is selected under 'Heat Transfer in Solids', to be applied in the boundaries where the inner and outer fluids are in contact. There is a line indicating the separation of the fluids where the bellows are placed in the real experiment. This permits to divide the space in several domains, but it is not enough to represent the resistive material between the fluids. This 'Thin Thermally Resistive Layer' is applied to complete it by introducing the thickness and thermal conductivity of this material, which are defined as 0.2 mm and 16 W/(mK) respectively [16].
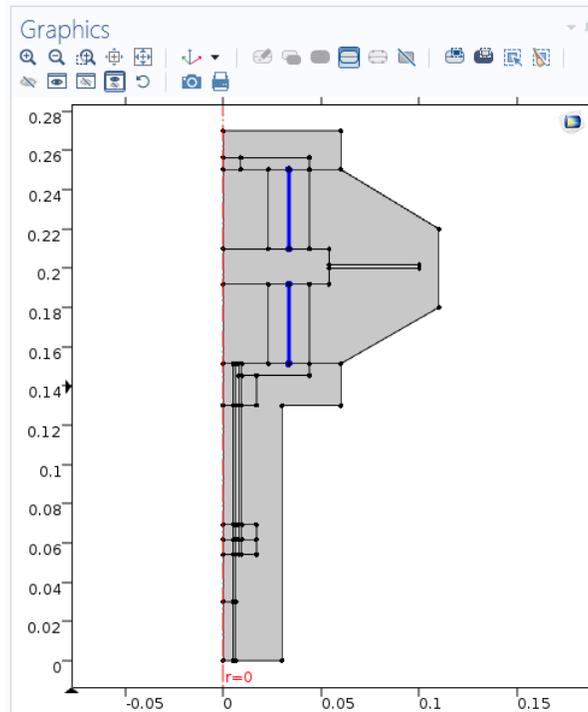
Figure 38: 'Thin Thermally Resistive Layer' boundaries

9.5 Transport of Diluted Species in Porous Media

The Transport of Diluted Species in Porous Media (tds) interface is used to simulate the mass transport in the porous material. The function of this interface is to calculate the species concentration and transport in free and porous media. It is the same interface as Transport of Diluted Species but presents other default nodes, such as the 'Porous Media Transport Properties' node. The rest of the default nodes that appear when the 'Transport of Diluted Species in Porous Media' interface is selected are: Axial Symmetry, No Flux, and Initial Values. More nodes can be added by right clicking on the interface in the Model Builder tree.

The 'Transport of Diluted Species in Porous Media' interface can simulate free and porous media flow with immobile and mobile phases, and supports several processes such as diffusion, convection, dispersion, adsorption, and volatilization in porous media. It can be applied to cases in which the solid phase substrate is immobile, as well as to cases in which a gas-filling medium is also assumed to be immobile.

The mass transport which can be defined with this interface can be applied to one or more diluted species or solutes which move within a fluid that fills (saturated) or partially fills (unsaturated) the voids in a solid porous medium. When the pore space is not filled with fluid, then the pore space contains an immobile gas phase [17].

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The domain in which this interface is applied is the domain corresponding to the porous material. Diffusion is included in the study, but to include also the adsorption and desorption processes, the option 'Adsorption in porous media' needs to be selected in the 'Additional transport mechanisms'.
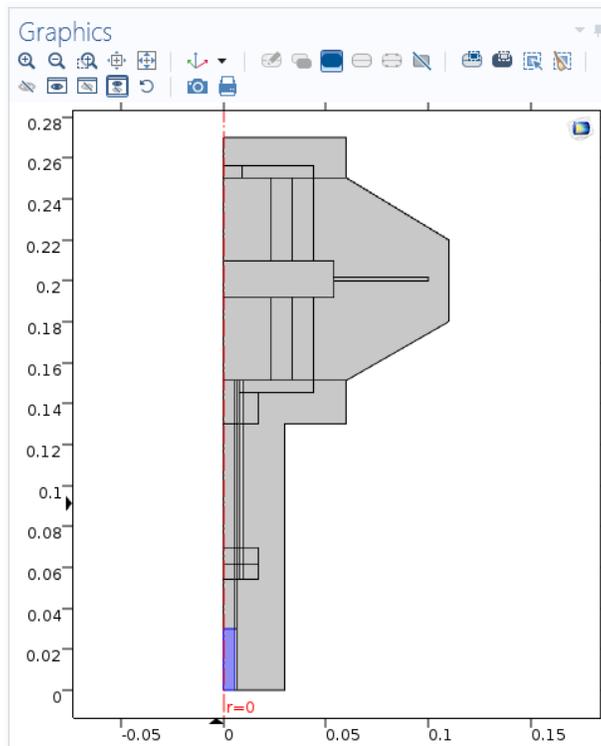
Figure 39: 'Transport of Diluted Species' domain
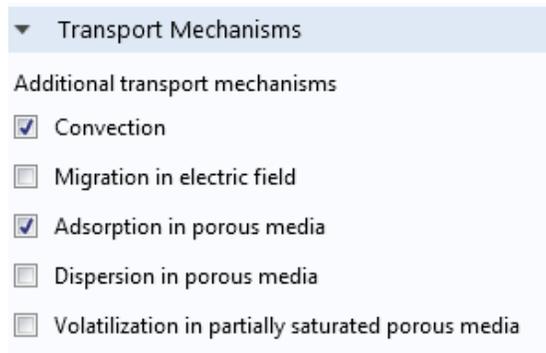
Figure 40: Selection of 'Adsorption' in the Transport Mechanisms section

The main node of the 'Transport of Diluted Species in Porous Media' interface is 'Porous Media Transport Properties'. In the Settings of this node, the model inputs are defined. The velocity field is introduced as 0, as the porous material is an immobile solid, and the absolute pressure is coupled with the 'Laminar Flow 1' interface by selecting 'Absolute pressure (spf)'.

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In the 'Matrix Properties' section of the settings, for the Porous material the selected option is 'Domain material', as the porous solid – the Zeolite 5A – was already defined in that domain. The properties such as density and porosity are obtained using the 'From material' option, once the material has been specified.
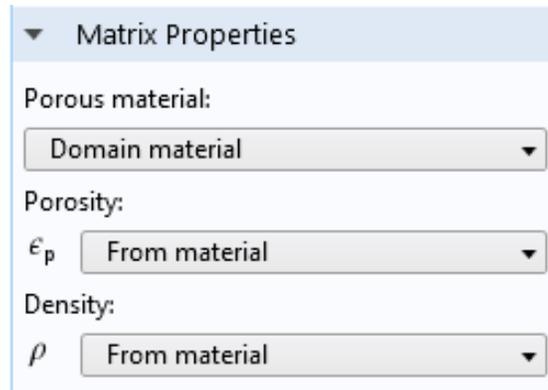
Figure 41: 'Matrix properties' settings

In the 'Diffusion' section, carbon dioxide is selected as the fluid material, and the experimental data such as the fluid diffusion coefficient $D_{F,c}$ is introduced as $5 \cdot 10^{-5} \, \text{m}^2/\text{s}$.

Figure 42: 'Diffusion' settings

In the 'Adsorption' section of the settings, the Langmuir sorption type is used, and the Langmuir constant $K_{L,c}$ and the adsorption maximum $c_{P,max,c}$ are given the values of 1.5 m³/mol, and 4.5 mol/kg, respectively.

Figure 43: 'Adsorption' settings

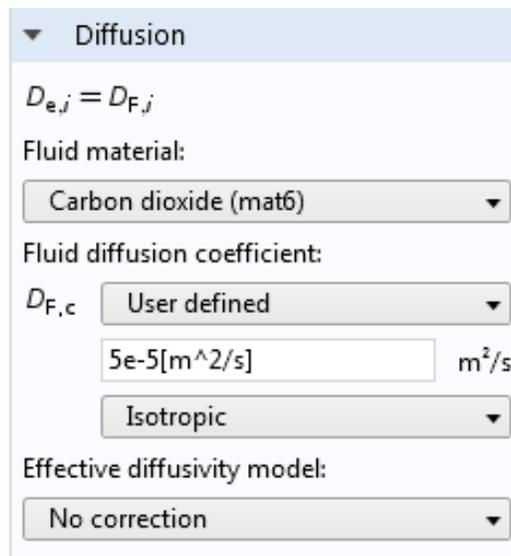In the 'Initial Values' node, the value for the initial concentration of the fluid in the porous material needs to be introduced. The Ideal Gas law (Eq. 21) is used to calculate the initial concentration, based on the initial pressure and the initial temperature of the reactor:

$$c_0 = \frac{P_o}{R \cdot T_0}$$ (Eq. 22)

Thus, being the initial absolute pressure $P_o = 133$ Pa, and the initial temperature $T_0 = 298.15$ K, the initial gas concentration in the porous material is set to be $c_0 = 0.054$ mol/m³.

Finally, to express the gas flowing into the reactor and its contact with the porous material, the 'No Flux' and 'Inflow' nodes are used.

The 'No Flux' node is the default boundary condition on exterior boundaries. It represents boundaries where there is no mass flow in or out of the selected boundaries. Hence, the total flux in these boundaries is zero. This node is used to indicate that the gas only flows in the reactor from the top part, as the rest of the reactor – sides and bottom – is closed. This can be expressed in the model by applying the 'No Flux' node to the right and bottom boundaries of the domain corresponding to the porous material.
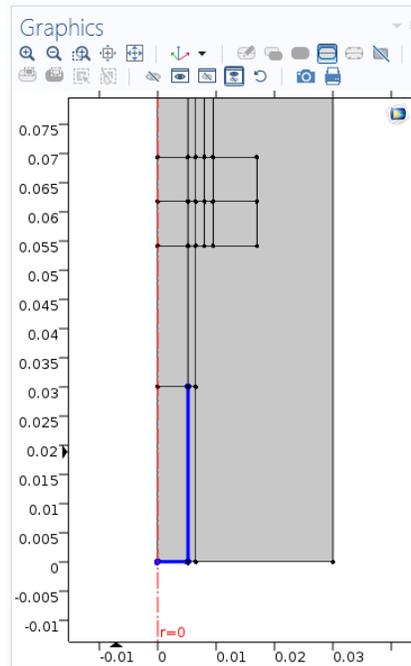
Figure 44: 'No Flux' boundaries

On the top boundary of the porous material domain, where the inner fluid gets in contact with the porous material and adsorption and desorption start occurring, the 'Inflow' node is applied. It is used to indicate the mass transport through a boundary. As the volume-modulation unit is provoking a variation in the pressure, the flux of the fluid species entering or leaving the reactor is not constant.

To establish the relation of the moles entering the reactor and the increasing or decreasing pressure, the Ideal Gas law (Eq. 21) is used, in the same way as it was previously described to make the pressure vary according to the adsorption and desorption occurring during the experiment. However, this time, this relation is used to introduce an expression in the species 'Inflow' settings, instead of a constant value for the flux. Thus, the species inflow [mol/m^3] is expressed as the following:

$$c_c = \frac{P_{spf} + P_0}{R \cdot T}$$
(Eq. 23)

Being P_{spf} the absolute pressure of the inner gas with which the simulation software works

P_0 the initial pressure in the reactor

R the universal gas constant

and T the temperature in the reactor.

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This expression is introduced in the settings as the following:

$$spf.pA/(R\_const*root.comp1.T)$$
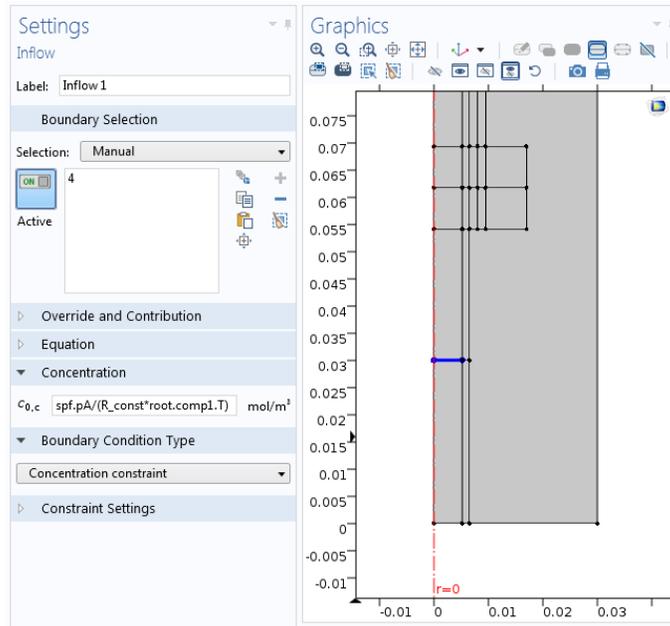
Figure 45: Settings and selected boundary of 'Inflow'

This way, the 'Transport of Diluted Species' interface can simulate the mass transport of the inner fluid in the porous material, considering the processes of diffusion and adsorption-desorption. By selecting the necessary options in the settings and using the adequate expressions, this interface can be coupled with the previous interfaces, which study the laminar flow and heat transfer of the fluids, and thus, the model can take into account the relations and influence of every interface during the whole process.

10 Mesh

Once the geometry is built, meshing is a fundamental part of the model. The 'Mesh' module enables the division of the designed geometry into mesh elements, which are small, simple shaped units. Thanks to this discretization, the software can analyze the model in a more detailed way, and the results of the simulation will be obtained with certain continuity.

The main shapes available to create the mesh, when using the 2D layout, are triangular and quadrilateral mesh elements.

As it was commented in chapter 7, the domains under the volume modulation unit are divided into several rectangles, being some of them very small, for meshing purposes. This is due to the fact that no mesh vertex can end at a mesh boundary, and hence, the geometry was built avoiding the presence of rectangle vertexes inside the geometry, especially in the lower domains of the model. This contributes to avoid meshing errors [14].

The triangular mesh elements present a smaller size than the rectangular ones. However, the rectangular mesh manages to be more consistent. For the most complicated geometrical parts, and those who are subject to a more detailed study of the processes occurring in them, the triangular mesh is used. It can be applied by right clicking the 'Mesh' module and selecting the 'Free Triangular' option. In this case, the domains selected are the ones corresponding to the main heat exchange zone, in the upper part, and the domains which represent the reactor, in the lower part. The domains where the main heat exchange occurs are the first in which the finer mesh is implemented:
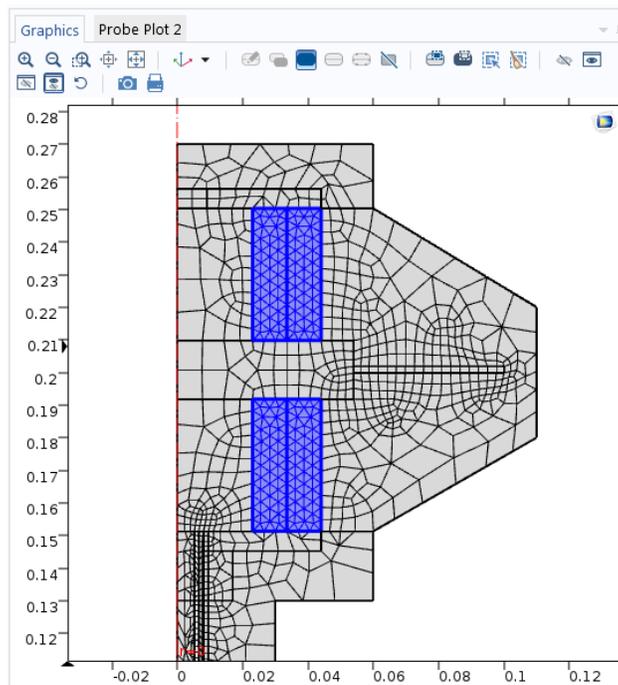
Figure 46: Free Triangular Mesh in the main heat exchange zone domains

The element size can be modified in the 'Size' settings, found in the node under 'Free Triangular' in the 'Model Builder' tree. For the element size of the triangular mesh, the option 'Fluid dynamics' is selected, as the main object of the study in those domains are the inner and outer fluids, and this allows a more precise mesh than the 'General physics' option.
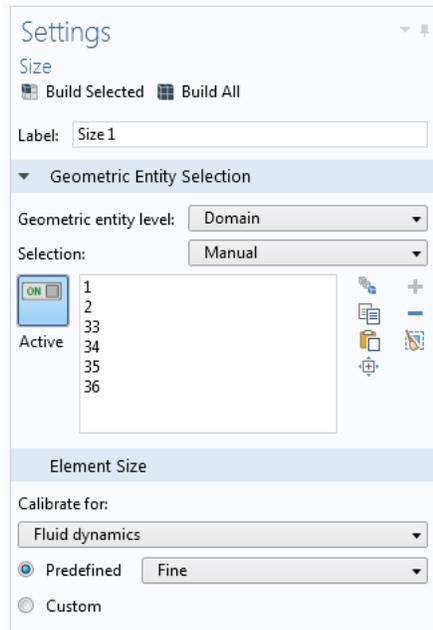
Figure 47: Free Triangular Mesh settings

The finer the mesh is, the more detailed the study will be. However, the simulation time will suffer a significant increase. Hence, for these domains the mesh is selected to be 'Fine', as it allows a balance between detailed results and a reasonable simulation time.

Since the simplification of the geometry was made, the improvement of the results could be noticed when applying the new mesh. In the next two images, the graphic results for the outer domain velocity are compared, and it can be seen how the results corresponding to the current geometry and mesh present more continuity, and the changes of color in the mesh elements are smoother – the simplification of the geometry also avoids the apparition of turbulences which could appear in the former representation of the bellows. In addition, the simulation time is reduced:
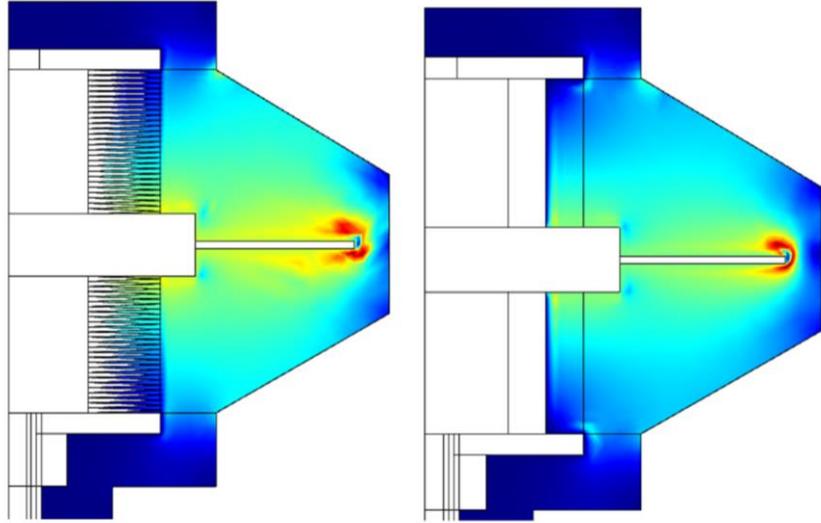
Figure 48: Results comparison for velocity of the outer fluid. Former vs. new geometry and mesh. Smoother evolution of the results in the second case.

Although by this time the porous material and its effect in the reactor had not yet been implemented, the simulation time for the model presented already a significant reduction, as it is shown in the next table:

Table 2: Simulation times comparison. Former vs. new geometry and mesh

Model	Simulation Time
Former Geometry and Mesh	4 h 38 min 30 s
New Geometry and Mesh	1 h 30 min 7 s

For the rest of the domains, in which the different processes do not need to be studied with such a high level of detail, a 'Free Quad' mesh can be used. These domains mainly represent the outer fluid – the air – and the materials of the pipes and the reactor in the lower part. The 'Free Quad' node is found as well by right clicking on 'Mesh'.
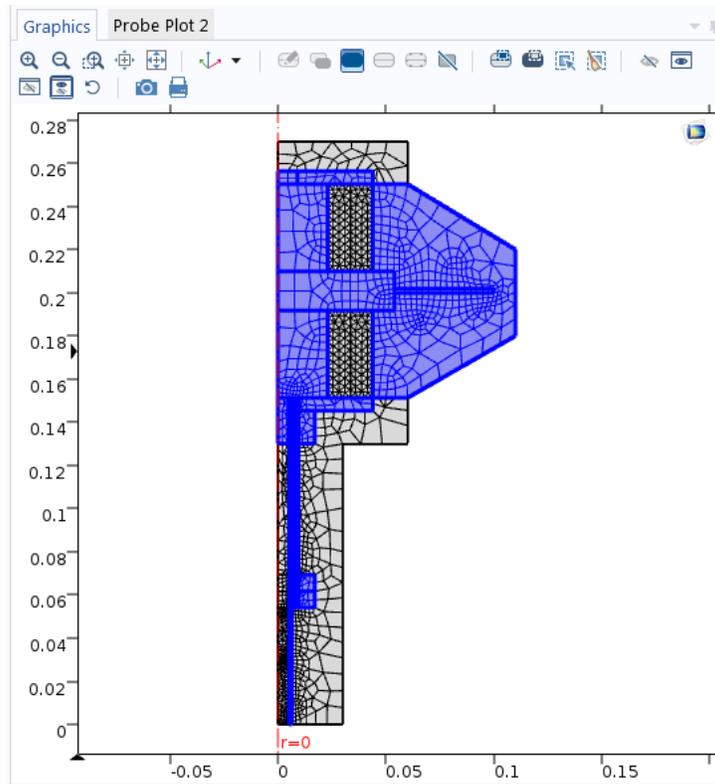
Figure 49: Free Quad Mesh domains

As it was said, for these domains the mesh can be rather large, as the detail if the study does not need to be so high, and a short simulation time is preferred. Thus, the 'General physics' option is used, and the size is selected as 'Coarse'.
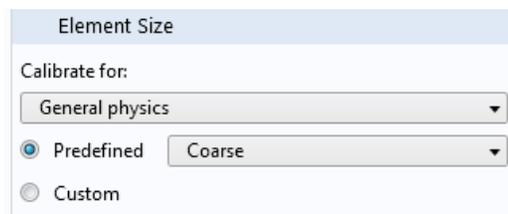
Figure 50: Free Quad Mesh settings

The main challenge when applying a large mesh next to a finer one is that the vertexes of the two meshings need to be compatible, in order for the model to be able to run the simulation successfully.

The reactor at the bottom part of the model is one of the most important parts to be meshed, as it is where the porous material is placed, and therefore, where the processes of diffusion and adsorption-desorption occur. Due to this, and as mentioned, a fine triangular mesh is applied to the reactor domains.

Additionally, to achieve a correct connection with the vertexes of the coarser mesh which does not provoke mesh errors, the adjacent domains which represent the walls of the reactor are selected too to have the triangular mesh.
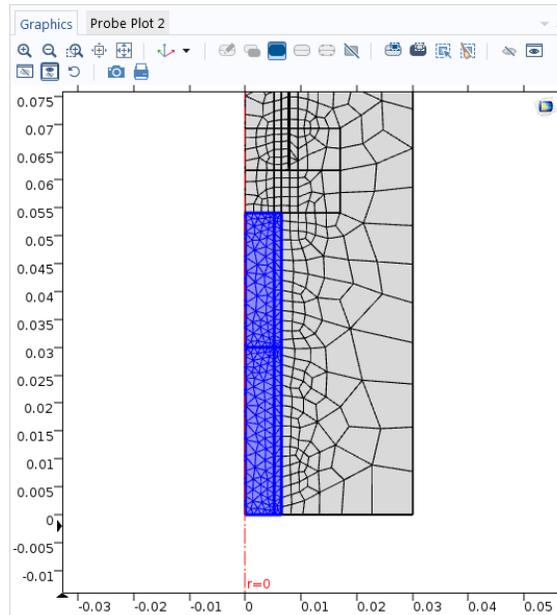
Figure 51: Free Triangular Mesh in the reactor domains

Thanks to this new meshing, the results in the reactor domains present a higher precision. The significant difference between the original mesh in the reactor domains, and the finer mesh and its adjustment to the adjacent parts, can be seen in the following images:
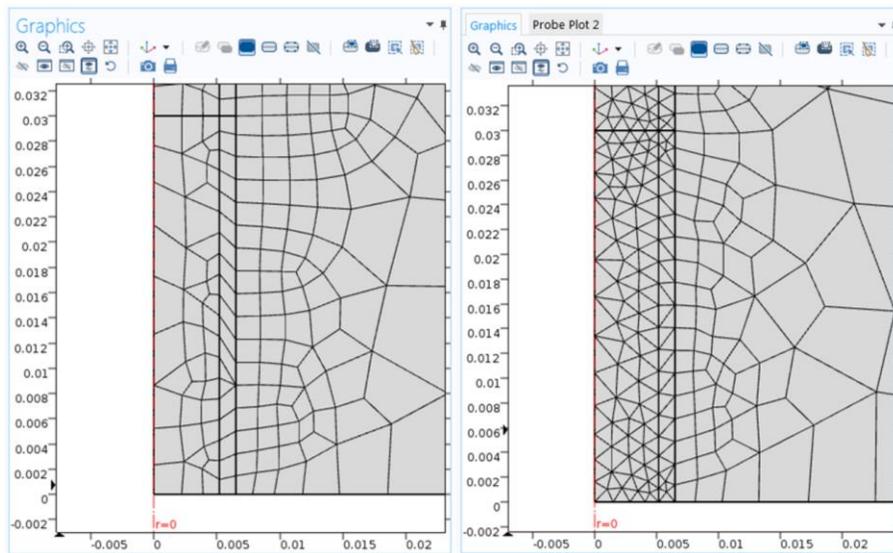
Figure 52: Former vs. new mesh comparison in the reactor
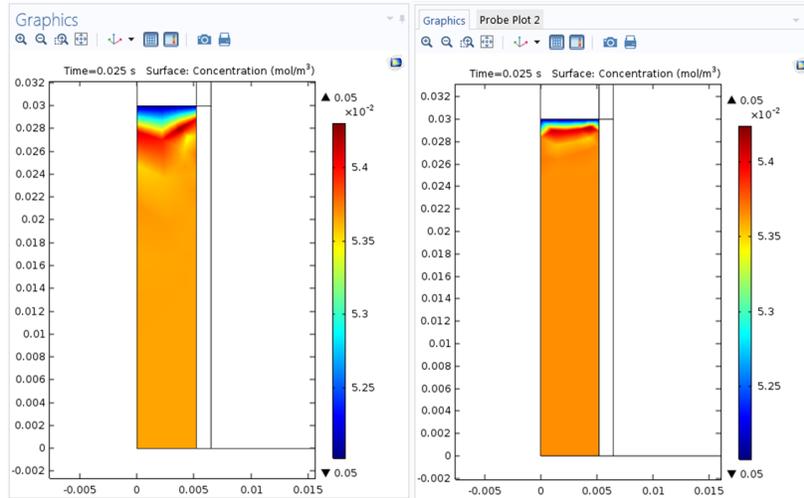
Figure 53: Concentration results comparison. Former vs. new mesh. Smoother evolution of the results in the second case.

The next node used to increase the quality of the mesh is 'Boundary Layers'. The 'Boundary Layers' node permits to implement a mesh with dense element distribution in the normal direction along specific boundaries, and it is typically used to solve thin boundary layers in fluid flow problems. The chosen number of layers is 4.
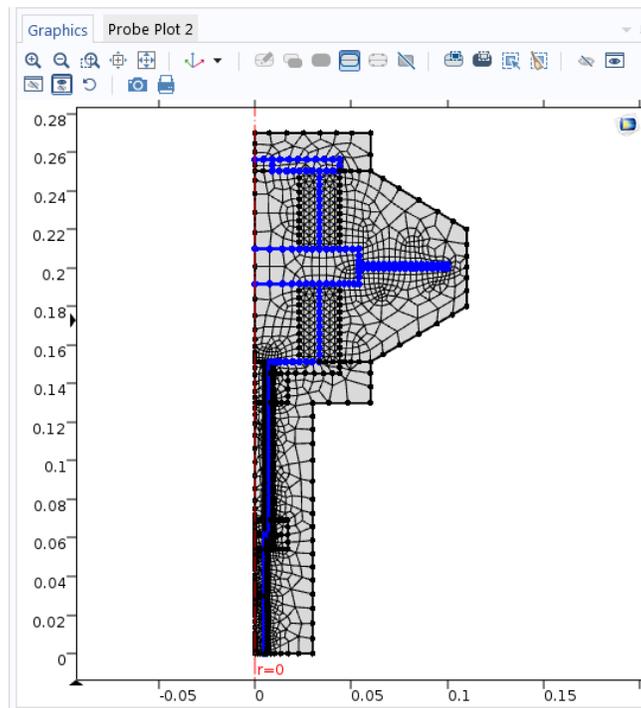
Figure 54: 'Boundary Layers' boundaries

Once the mesh settings are decided, the 'Build All' button is clicked and the whole mesh is created. The geometry is ready to be analyzed during the simulation. The settings can be changed at any time needed.

11 Simulation Study Settings

The 'Study' module contains all the nodes which are used to define and adjust how the software solves the simulation. The different categories of the available nodes in 'Study' are Study Steps, Solver Configurations, and Job Configurations.

In this simulation, two Study Steps are used: A 'Stationary Study Step', and a 'Time Dependent Study Step'. The first one, 'Stationary Study Step', is used when the studied variables do not change over time. In this model, the variables do change over time. However, this Study Step is used to obtain initial values for the mentioned variables.

These initial values are then sent to the next study step, which is the 'Time Dependent Study Step', so that the final results can be obtained faster and presenting a higher consistency and reliability. This 'Time Dependent Study Step' is used when field variables change over time [14].

As the Stationary Study is in charge of the variables which do not change over time, it is necessary to disable in this Study the nodes which depend on time. This applies to the 'Wall' nodes in the 'Laminar Flow' interfaces, as they function with expressions which contain variables such as zt. In order to do this, the 'Modify physics tree and variables for study step' option must be activated. This option can be found in the 'Stationary' settings, in the 'Physics and Variables Selection' section.

The function of the 'Time Dependent Study' is to calculate and store the results of the simulation. For this study, the time range in seconds of the simulation is (0, 0.001. 0.1), and the 'Relative tolerance' is introduced as 0.01. The value of the 'Relative tolerance' is intended to be big enough for the simulation to converge, but small enough for the results to be accurate.

In the 'Results while solving' section, the available plot groups are presented. By selecting one of them, the graphic results of the studied variable will appear in the 'Graphics' window during the running of the simulation. This option is useful, as it permits to detect unexpected or incorrect behaviors of the variable, so the simulation can be stopped at any time if considered necessary. The 'Temperature, 3D (ht)' is selected, as its evolution can be followed without major complications during the convergence process to supervise the right functioning of the simulation.

The last step is establishing the relation between the 'Stationary Study' and the 'Time Dependent Study'. This is achieved in the 'Time Dependent Study' settings, by selecting 'Study 2, Stationary' in the Study options of the 'Values of Dependent Variables' section :
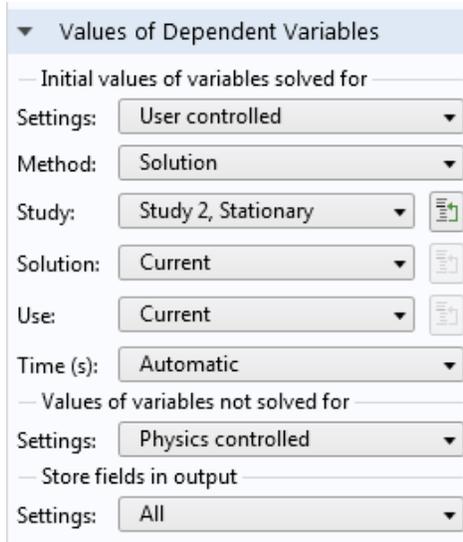
Figure 55: Selection of 'Study 2, Stationary' in the 'Time Dependent Study' settings

Finally, as the model implies the study of several variables and their relations, the software needs to calculate their values simultaneously. In the 'Solver Configurations' node, different options are available, such as using 'Segregated Steps', or a 'Fully Coupled' node.

Although 'Segregated Steps' can be used to study the variables separately and permits to see which one presents errors in a direct way, the software needs to calculate the values of each variable before applying these values to the next interface, which complicates the calculations of inter-related variables. Hence, the 'Fully Coupled' node is preferred for this study. The 'Fully Coupled' node is selected, both for 'Stationary Solver' and 'Time Dependent Solver', by right clicking on each of the nodes of the solvers. The 'Fully Coupled' node facilitates the calculation of variables which are related to one another, making the simulation capable of calculating their values simultaneously.

12 Results

In this chapter, the results achieved in several simulations aiming to optimize the model are discussed. Through the work process, different modifications in the settings of the model have been done, and the uses of different interfaces have been compared. The most significant results are shown next, after applying the settings and interfaces which manage a more accurate and complete approximation to the real experiment up to this time.

The used function for the 'Moving Mesh' interface – which causes the volume modulation – is the sinusoidal wave function defined in chapter 6, as it presents less convergence problems and permits more rapid simulations.

12.1 Simplification of the Geometry

The first results correspond to the evolution of the temperature in the system, when the geometry is simplified. As it was commented in chapter 7, the geometrical elements of the volume-modulation unit were modified to achieve a less complex model and decrease the simulation time. In order to study if this change is acceptable the variable studied is the temperature, as the modified geometry occupies the domains corresponding to the main heat exchange zone.

A 'Domain Probe' applied to every domain of the model permits the study of the temperature over time, choosing between minimum, average, or maximum temperature. The 'Domain Probe' is implemented by right clicking on 'Definitions' in the 'Model Builder' tree, and then selecting 'Probes' > 'Domain Probe'. The temperature T is selected, and the 'Probe type' is chosen to be 'Maximum', as the objective of this study is to compare the physical point and time instant in which the maximum temperature is reached in the model, for both geometries.

In this case, nitrogen is used as the inner gas. For both geometries, the temperature presents its maximum value at t=0.056 s, and at the middle part of the lower half of the volume-modulation unit. In the case of the former geometry, the temperature peak presents the value $T_{max} = 299.27$ K, whereas in the case of the simplified geometry it presents $T_{max} = 299.55$ K . Being the difference of the temperature peak of 0.28 K, - less than 0.5 K – and occurring at the same time instant and physical point, the difference is not considered significant. In addition, the simplification of the geometry permits a more uniform distribution of both fluids in the main heat transfer zone than when the bellows are represented in detail. This allows the temperature to vary in a smoother way. Due to these reasons, it is decided to continue working with the new version of the geometry

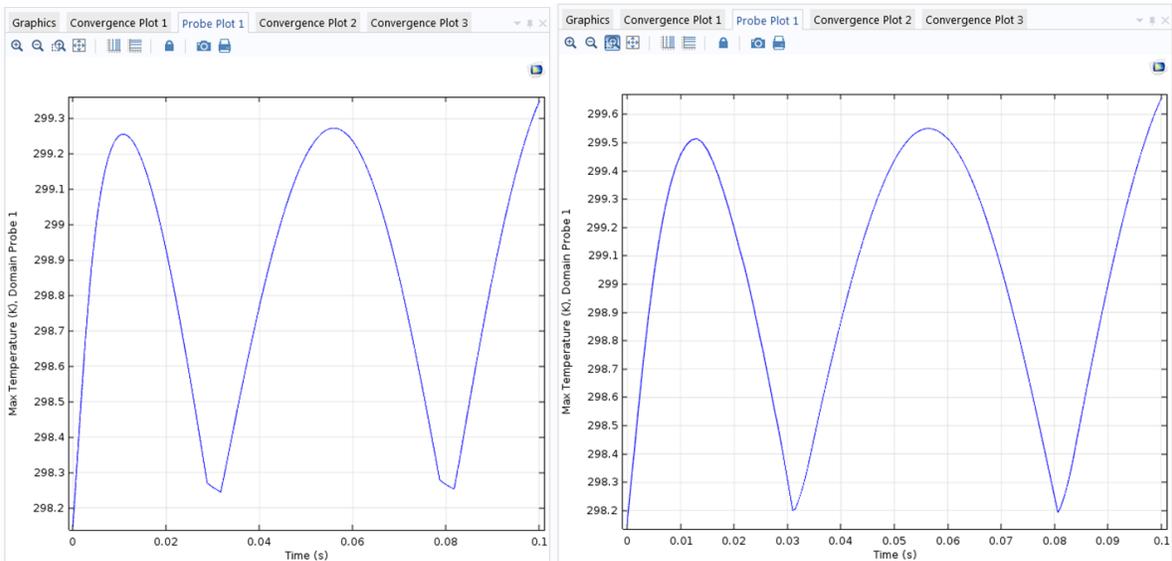**Figure 56: Comparison of the maximum temperature over time. Former vs. new geometry. The temperature peak is reached at the same time instant t=0.056 s.**
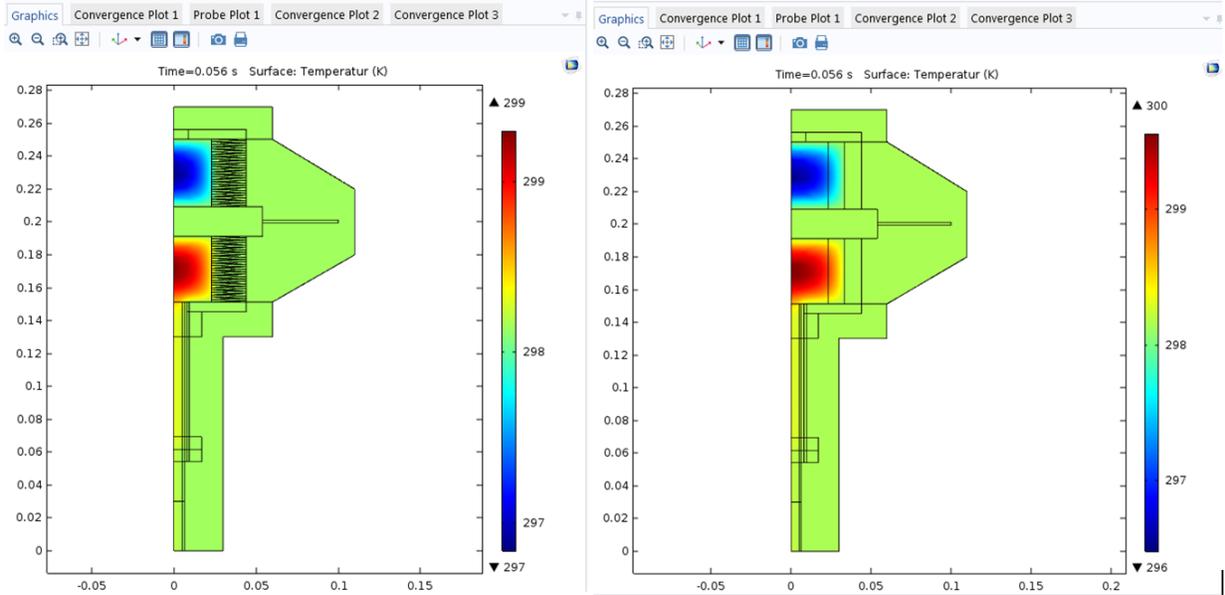

Figure 57: Comparison of the graphihc results of temperature for the instant t=0.056 s. Fromer vs. new geometry. The maximum temperature is reached in both cases at the centre of the lower part of the volume-modulation unit

12.2 Concentration of the Inner Fluid in the Porous Material

Once the geometry is simplified, the main objective is the study of the implementation of the porous material and the diffusion and adsorption-desorption processes. The 'Transport of Diluted Species in Porous Media' interface permits the study of the species concentration variation due to mass transport. This study is combined with the study of the pressure in the reactor, which is the output of the Frequency Response (FR) apparatus in the real experiment.

The next results correspond to the model using carbon dioxide as the inner fluid. The reason for this is the availability of experimental data needed for the implementation of the 'Transport of Diluted Species in Porous Media' interface. The zeolite 5A is defined and implemented as the porous material in the reactor, and the 'Transport of Diluted Species in Porous Media' interface is set.

To study the pressure in the reactor, another 'Domain Probe' is incorporated in 'Definitions'. The expression selected to study is the pressure of the inner fluid, and the 'Average' type is chosen. This 'Domain Probe' plots the evolution of the average gauge pressure in the reactor over time.

Additionally, COMSOL Multiphysics permits to export the pressure evolution data as a table containing every pressure value over time. This table can be later used to compare several pressure responses.

In the next figure, the average pressure evolution in the reactor over time is shown:
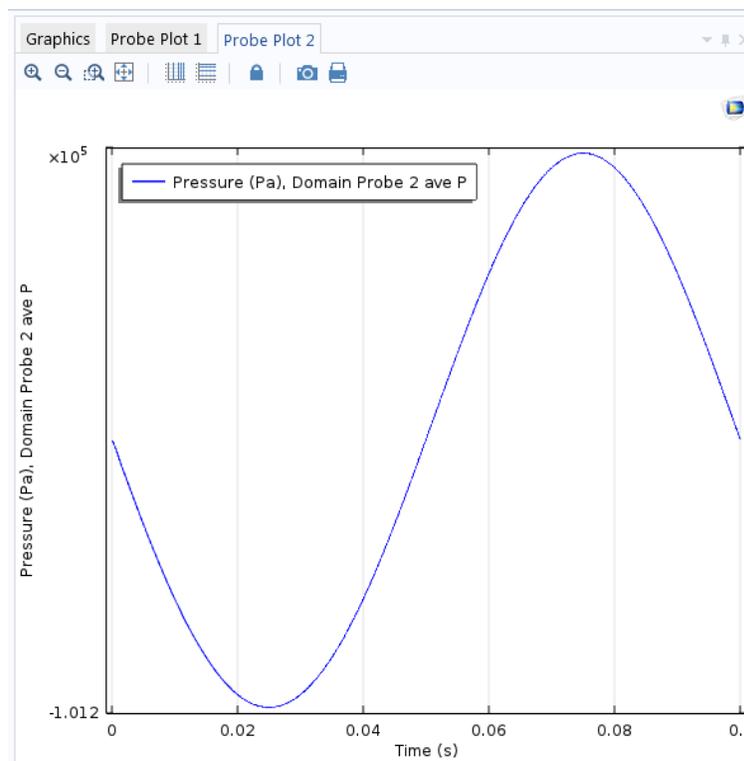

Figure 58: Pressure evolution in the reactor

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It can be seen in the graph that the pressure in the reactor – initially 133 Pa (absolute pressure) –decreases when the experiment starts, reaching its minimum value at t = 0.025 s – this corresponds to the travel plate ascending, allowing the inner fluid to expand, and reaching its highest position at t = 0.025 s.

Then the pressure increases, recovering its initial value of 133 Pa at t = 0.05 s, and continuing to increase until its maximum value at t = 0.075 s – which corresponds to the lowest position of the travel plate, which has descended, compressing the inner fluid.

Finally, the pressure decreases again until it reaches its initial value, corresponding to the end of the cycle, and thus, the end of the experiment – the travel plate has ascended and is now located at its initial position.

The time instants in which adsorption and desorption occur can be observed in the pressure evolution graph. When the pressure decreases, the porous material releases gas, so the desorption process will occur from t = 0 s to t = 0.05 s. Then, when the pressure increases, the porous material will adsorb gas, as the higher pressure favors the adsorption process.

The next results correspond to the first attempts to simulate the mass transport of the inner fluid in the porous material, placed at the bottom of the reactor. This mass transport is caused by diffusion and the adsorption-desorption processes mentioned above.

The first steps consist of establishing the influence of the pressure on the concentration variation, as depending on the pressure, a bigger or smaller flux of mass will enter the reactor, and the mass transport processes will be more or less favored. In order to achieve this, the 'Transport of Diluted Species in Porous Media' and the necessary settings are used to simulate the concentration variation of inner fluid in the porous material. By using a 'Domain Probe', the concentration variation over time can also be stored in a graph:
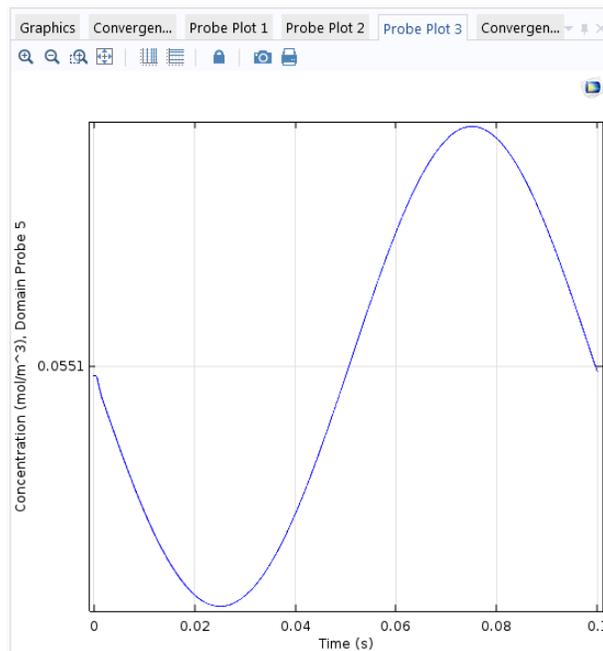
Figure 59: Inner fluid concentration in the porous material. Evolution over time

The graphic results for the concentration variation over time for the instants $t = 0$ s, $t = 0.025$ s, $t = 0.05$ s, $t = 0.075$ s and $t = 0.1$ s are shown in the following images:
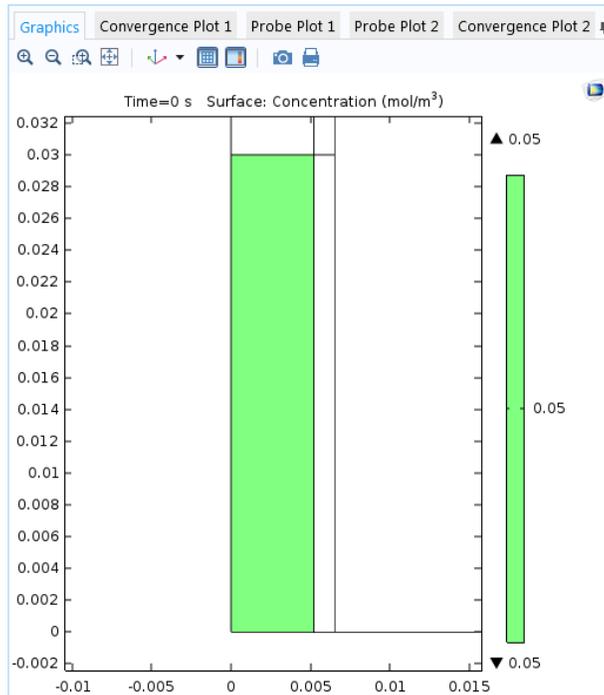
Figure 60: Concentration of the inner fluid in the porous material at t=0
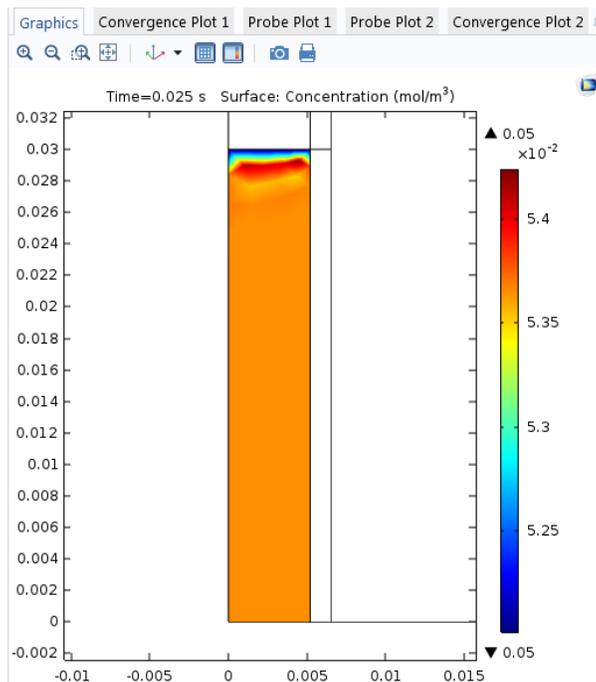
Figure 61: Concentration of the inner fluid in the porous material at t=0.025 s

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Figure 62: Concentration of the inner fluid in the porous material at t=0.05 s

Figure 63: Concentration of the inner fluid in the porous material at t=0.075 s

Figure 64: Concentration of the inner fluid in the porous material at t=0.1 s

The variation over time of the concentration of the inner fluid – carbon dioxide – in the porous material – zeolite 5A – can be seen in the images above. The initial concentration of inner fluid in the porous material is 0.054 mol/m^3, and it is uniform when the experiment starts.

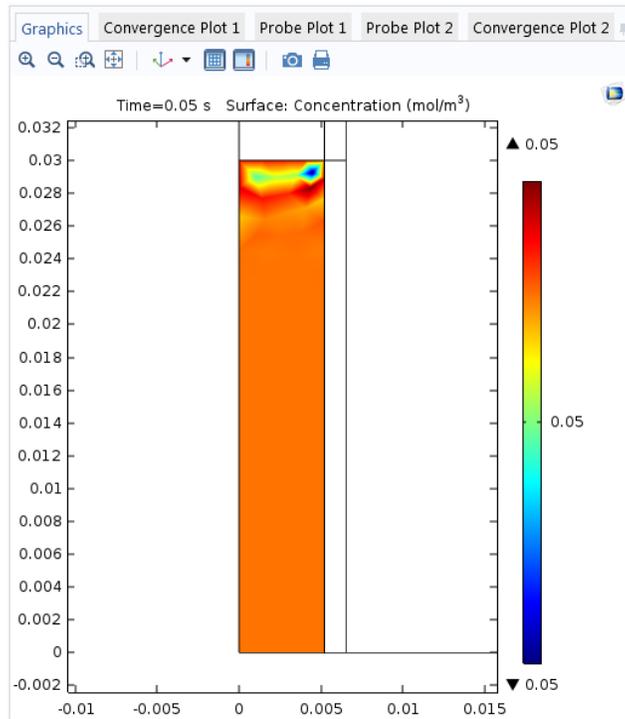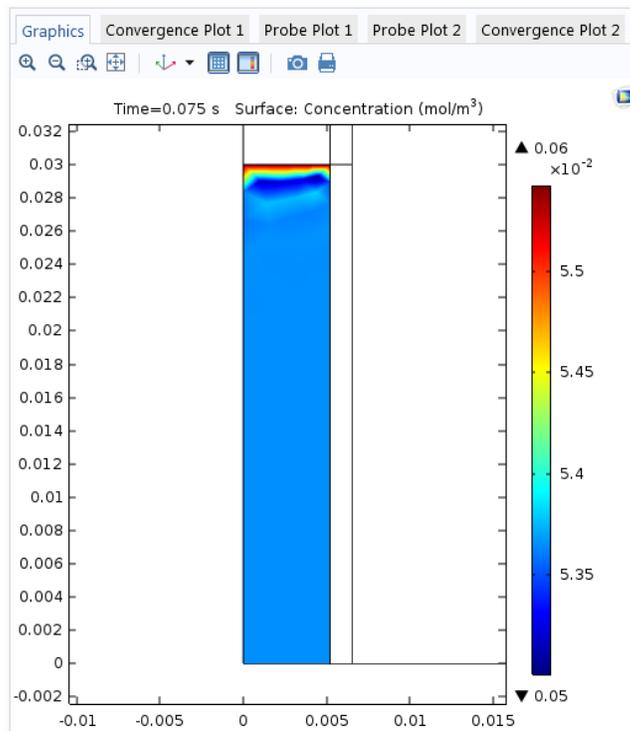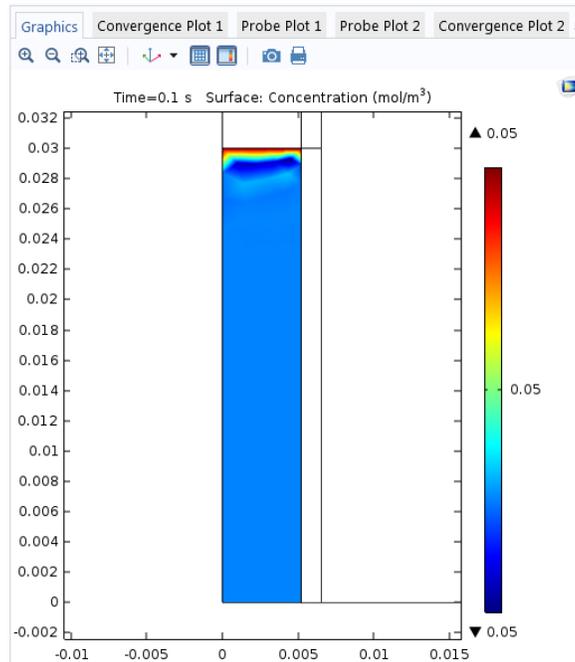The desorption process has its maximum effect at $t = 0.025$ s, when the pressure in the reactor reaches its minimum value. It can be observed how desorption occurs in different layers of the porous material, having the biggest effect on the surface in contact with the fluid. It is in this top surface where the concentration decreases the most, to approximately 0.052 mol/m^3. As one layer loses molecules, the next one adsorbs them, and this process occurs several times in the top part of the porous material. This qualitative result is accepted as satisfactory, as it has been seen experimentally that adsorption and desorption take place in this way in the top layers of the porous material.

At the instant $t = 0.05$ s, when the travel plate is back to its original position and the pressure in the reactor is again 133 Pa – the initial pressure value –, the concentration of fluid in the porous material is uniform again and presents the initial value of, 0.054 mol/m^3. The different color parts, in spite of the uniform concentration, are due to the color scale used for the plots. However, what really confirms the uniform value of the concentration are the maximum and minimum values placed at the top and bottom of the color legend. This variation of color due to the color scale also affects the concentration at the middle and bottom part of the reactor, whose color changes at $t = 0.025$ s, and at $t = 0.075$ s. Nonetheless, this concentration remains uniform, and presenting a value close to the initial one, during the whole experiment.

At the instant $t = 0.075$ s, the maximum pressure is reached – the travel plate is its lowest position – and the effect of adsorption is maximum. In the same way that when desorption was maximum for $t = 0.025$ s, the different concentrations in the top layers of the porous material can be noticed, alternating layers in which the gas molecules are adsorbed, with layers that lose molecules. The top layer is the one which presents the highest concentration – approximately 0.057 mol/m^3 –, as it is the layer which adsorbs the most.

Finally, for $t = 0.1$ s, the gas concentration in the porous material returns to its initial value and is presented in a uniform distribution, in spite of the color scale effect explained above.

Once the adsorption and desorption processes present satisfactory results, and managing to relate the variation of the concentration with the pressure in the reactor – consequence of the volume-modulation unit – the next objective is to achieve the mass transport effect on the pressure response.

12.3 Pressure Response affected by Mass Transport

The final steps consist of coupling the pressure in the reactor with the influence of the concentration variation. As it was mentioned above, the variation of the pressure – compression and expansion of the inner gas, due to the volume modulation – favors the adsorption and desorption of the gas in the porous material, situation which has been described in the previous results. However, the changes which the pressure suffers when gas molecules are adsorbed and desorbed had not been implemented to the model yet.

This variation of the pressure has a great importance, as it implies the phase shift and amplitude change which serve to study the diffusion and adsorption-desorption constants when using the Frequency Response (FR) method – the pressure in the reactor is the studied output.

Once the obtained results for the concentration variation are satisfactory, the feedback towards the pressure of the inner gas is finally implemented in the model by using a 'Pointwise Constraint' and the adequate settings. The results of the pressure evolution suffering the influence of the diffusion and adsorption-desorption processes are exported as tables, so that they can be compared with the previous pressure evolution result with no influence due to the mass transport – results which, regarding the pressure, are the same as if no diffusion and no adsorption-desorption occurred.

The expected results when the mass transport has its influence on the pressure in the reactor imply that, at the instant of maximum volume under the travel plate – $t = 0.025$ s – the pressure in the reactor will suffer a certain decrease due to desorption. And at the instant of minimum volume under the travel plate – $t = 0.075$ s – the pressure in the reactor will experience a certain increase due to the adsorption of the molecules of the inner fluid in the porous material.

These two instants of maximum and minimum volume are shown in the following images, presenting the pressure of the inner fluid up and down the travel plate for each of the instants:
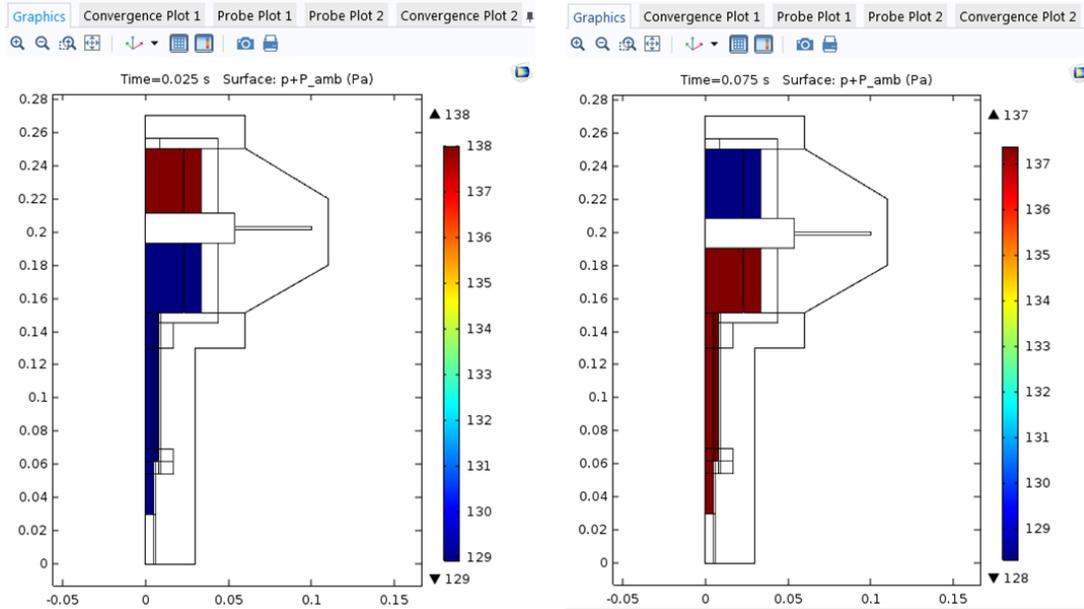

Figure 65: Pressure graphic results for instants of maximum and minimum volume under the travel plate

The next table presents the comparison of the pressure in the reactor in the model where the mass transport processes do not affect the pressure response – no concentration variation effect – , and in the model where diffusion and adsorption-desorption have an effect on the pressure:

Table 3: Pressure in the reactor comparison for instants of maximum and minimum volume under the travel plate

	t=0.025 s – Maximum Volume	t=0.075 s – Minimum Volume
No concentration variaton effect	128.91 Pa	137.37 Pa
Concentration variation effect	128.95 Pa	137.37 Pa

As it is expected to occur, at $t = 0.025$ s – instant of maximum volume under the travel plate – when desorption takes place, the pressure in the reactor does not decrease as much as it does when there is no mass transport effect. However, for $t = 0.075$ s – instant of minimum volume under the travel plate – he pressure reaches the same value with and without the influence of the mass transport properties. This can be interpreted as the existence of an amplitude change of the pressure response at the maximum volume instant, and no change at the minimum volume instant.

In order to compare in detail the different pressure values reached for both models – with the pressure experiencing the concentration variation effect or not – the tables obtained by applying the pressure 'Domain Probes' are exported and combined as graphs in a spreadsheet. The two graphs of pressure evolution – expressed as gauge pressure – are shown in the following image:
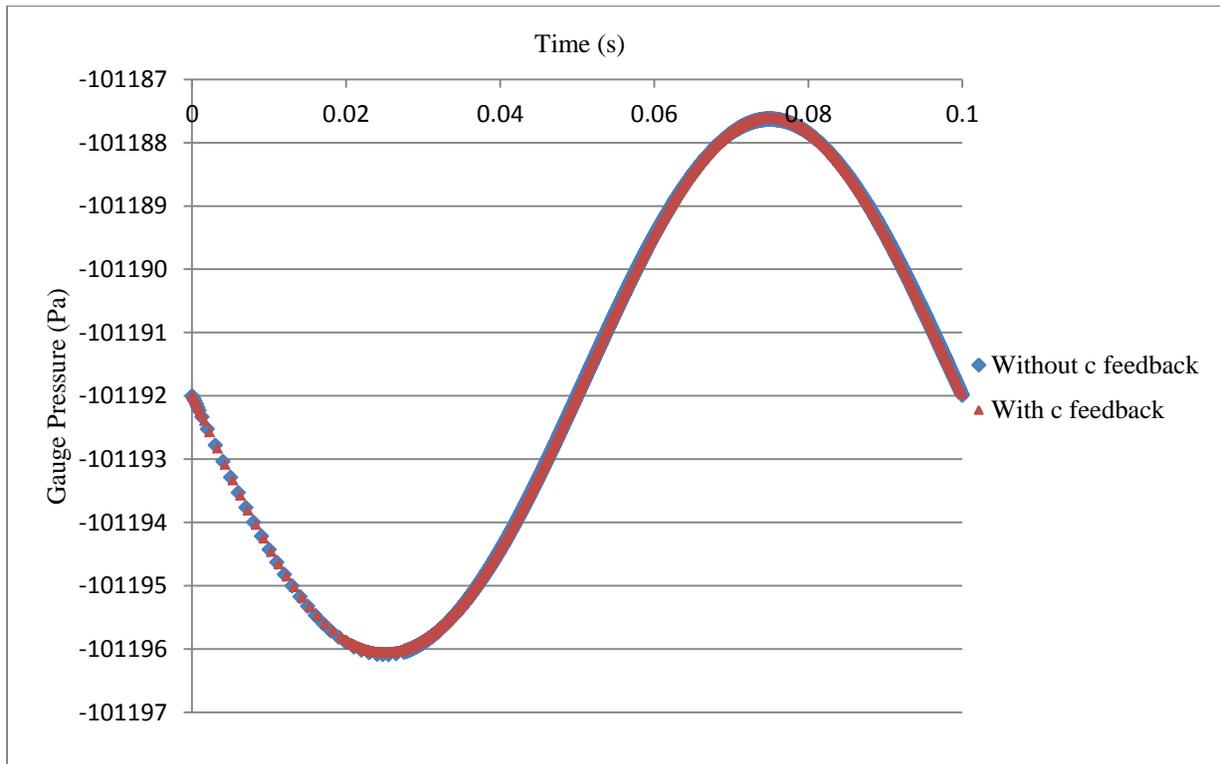
Figure 66: Pressure evolution in the reactor. Case with no concentration variation effect vs. case with concentration variation influence on the pressure

It can be observed that for the current simulation settings, both pressure evolutions have very similar values over time. Nonetheless, it can be seen that the pressure response of the model which incorporates the diffusion and adsorption-desorption effect – referred as concentration feedback – presents a slight phase shift with respect to the pressure evolution of the model without the effect of these processes. This phase shift seems to be present until the instant $t = 0.075$ s. Finally, if it is wanted to see if this amplitude change and phase shift increase with a higher effect of the adsorption-desorption process, the magnitude of these processes can be increased in the model settings.

13 Summary and Conclusions

In this project, the simulation software COMSOL Multiphysics has been used to create a model with which to study the processes of diffusion and adsorption-desorption of a gas in a porous material, by recreating the conditions of a real Frequency Response (FR) apparatus. This way, the experiment can be studied using both simulations and the real setup. The gas used in the simulation until now is either nitrogen or carbon dioxide, and the used porous material is zeolite 5A.

This project had an already existing model as its starting point. It has been the main objective to make the current model a more complete and optimized simulation of the real experiment, which in the future may help to continue the simulation studies focused on this or other compatible topics, as the simulation settings can be easily changed.

The working process has focused on simplifying the previous geometry of the model – without losing important input factors, such as the volume modulation and its direct relation with the pressure response –, the definition and implementation of the porous material, the selection of an adequate interface – in this case, 'Transport of Diluted Species in Porous Media' –, and the updating and modification of the corresponding settings in the rest of the interfaces and modules, in order to make the pressure response suffer the effect of the mass transport in the porous material.

During the time of the working process, several interfaces and settings have been tried. The results obtained with the currently selected interfaces and adjustments are the most satisfactory ones out of the different approximations realized. In these results, it can be seen how the adsorption and desorption occur in the porous material placed at the bottom of the reactor, with the subsequent changes of fluid concentration in the porous solid. The response of the pressure, when affected by the mass transport, can be compared to the pressure with no influence from the concentration variation to study the existence of amplitude changes and phase shifts: The main aspects which permit to determine rate constants in the Frequency Response (FR) method.

As possible improvements for the future, several ideas have arisen. The current model provides results of the pressure response stored in a table by using the 'Probe Domain' node. By modifying the constants and rates of the mass transport processes, the influence of the concentration variation on the pressure response can be observed – in the form of phase shift and amplitude change.

For efficiency in the use of time, the sinusoidal wave function has been used for the simulations, permitting a close enough representation of reality. However, to compare the pressure response results directly with the experimental results, the square wave form, as defined in chapter 6, can be used, as long as it is able to avoid the convergence problems.

Finally, there are several interfaces in COMSOL Multiphysics, such as 'Free and Porous Media Flow' or 'Heat Transfer in Porous Media', which could be implemented in the model. Some of the settings require very specific data, and the more variables which the software has to evaluate and study, the higher the risk of the simulation not converging is. However, their use may be interesting in order to complement the existing model, if they are considered to improve significantly enough the results.

14 Bibliography

[1] E. Farnetti, R. Di Monte, and J. Kaspar, "Homogeneous and Heterogeneous Catalysis" in *Inorganic and Bio-Inorganic Chemistry - Volume II*, EOLSS Publications, 2009.

[2] A. Ertan, "CO2, N2 and Ar adsorption on modified zeolites" Feb. 2004.

[3] J. Weitkamp, "Zeolites and catalysis", *Solid State Ion.*, vol. 131, no. 1–2, pp. 175–188, Jun. 2000.

[4] M. Hossain, "Volume Swing Frequency Response Method For Determining Mass Transfer Mechanisms in Microporous Adsorbents" Jan. 2014.

[5] I. Tomillo Álvarez, *Simulation of temperature effect in a Frequency Response apparatus*. 2016.

[6] G. G. Stokes, *On the Theories of the Internal Friction of Fluids in Motion and of the Equilibrium and Motion of Elastic Solids*. Trans. Cambridge Philos. Soc., 8, 267-305, 1845.

[7] R. B. Bird, W. E. Stewart, and E. N. Lightfoot, *Transport Phenomena*. 2nd ed., John Wiley & Sons, 2007.

[8] J. U. Keller and R. Staudt, *Gas Adsorption Equilibria: Experimental Methods and Adsorptive Isotherms*. Boston: Kluwer Academic Publishers, 2005.

[9] S. C. Reyes, J. H. Sinfelt, G. J. DeMartin, R. H. Ernst, and E. Iglesia, "Frequency Modulation Methods for Diffusion and Adsorption Measurements in Porous Solids", *J. Phys. Chem. B*, vol. 101, no. 4, pp. 614–622, Jan. 1997.

[10] L. M. Naphtali and L. M. Polinski, "A Novel Technique for Characterization of Adsorption Rates on Heterogeneous Surfaces", *J. Phys. Chem.*, vol. 67, no. 2, pp. 369–375, Feb. 1963.

[11] Y.-E. Li, D. Willcox, and R. D. Gonzalez, "Determination of rate constants by the frequency response method: CO on Pt/SiO2", *AIChE J.*, vol. 35, no. 3, pp. 423–428, Mar. 1989.

[12] E. J. Shokroo, D. J. Farsani, H. K. Meymandi, and N. Yadollahi, "Comparative study of zeolite 5A and zeolite 13X in air separation by pressure swing adsorption", *Korean J. Chem. Eng.*, vol. 33, no. 4, pp. 1391–1401, Apr. 2016.

[13] COMSOL Multiphysics 5.2a, *CFD Module User's Guide*. 2016.

[14]COMSOL Multiphysics 5.2a, *COMSOL Multiphysics Reference Manual*. 2016.

[15]COMSOL Multiphysics 5.2a, *Heat Transfer Module User's Guide*. 2016.

[16]AK Steel, "Austenitic Stainless Steel Data Bulletin 316/316L."

[17]COMSOL Multiphysics 5.2a, *Chemical Reaction Engineering Module User's Guide*. 2016.