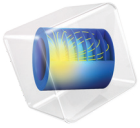

INTRODUCTION TO

Chemical Reaction Engineering Module

5.5

COMSOL

Introduction to the Chemical Reaction Engineering Module

Version: COMSOL 5.5

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Contents

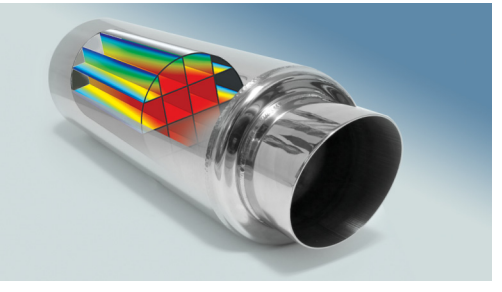
Introducing the Chemical Reaction Engineering Module

The Chemical Reaction Engineering Module is tailor-made for the modeling of chemical systems primarily affected by chemical composition, reaction kinetics, fluid flow, and temperature as functions of space and time. It has several interfaces to model chemical reaction kinetics; mass transport in dilute, concentrated and electric potential-affected solutions; laminar and porous media flows, and energy transport.

Included in these interfaces are the kinetic expressions for reacting systems, in bulk solutions and on catalytic surfaces, and models for the definition of mass transport. You also have access to a variety of ready-made expressions in order to calculate a system's thermodynamic and transport properties.

While a major focus of the module is on chemical reactors and reacting systems, it is also extensively used for systems where mass transport is the major component. This includes unit operations equipment, separation and mixing processes, chromatography, and electrophoresis. The module is also widely used in educational and training courses to explain chemical engineering, chemical reaction engineering, electrochemical engineering, biotechnology, and transport phenomena.

In addition to its application in traditional chemical industries, it is a popular tool for investigating clean technology processes (for example, catalytic monoliths and reactive filters) for applications such as microlaboratories in biotechnology and in the development of sensors and equipment in analytical chemistry.



An overview of the interfaces and their functionality can be found in Chemical Reaction Engineering Module Interfaces.

Chemical Reaction Engineering Simulations

Simulations in chemical reaction engineering are often used during the investigation and development of a reaction process or system.

In the initial stages, they are used to dissect and understand the process or system. By setting up a model and studying the results from the simulations, engineers and scientists achieve the understanding and intuition required for further innovation.

Once a process is well understood, modeling and simulations are used to optimize and control the process' variables and parameters. These "virtual" experiments are run to adapt the process to different operating conditions.

Another use for modeling is to simulate scenarios that may be difficult to investigate experimentally. One example of this is to improve safety, such as when an uncontrolled release of chemicals occurs during an accident. Simulations are used to develop protocols and procedures to prevent or contain the impact from these hypothetical accidents.

In all these cases, modeling and simulations provide value for money by reducing the need for a large number of experiments or to build prototypes, while, potentially, granting alternative and better insights into a process or design.

Modeling Strategy

The flowchart in Figure 1 describes a strategy for modeling and simulating chemical reaction processes and systems.

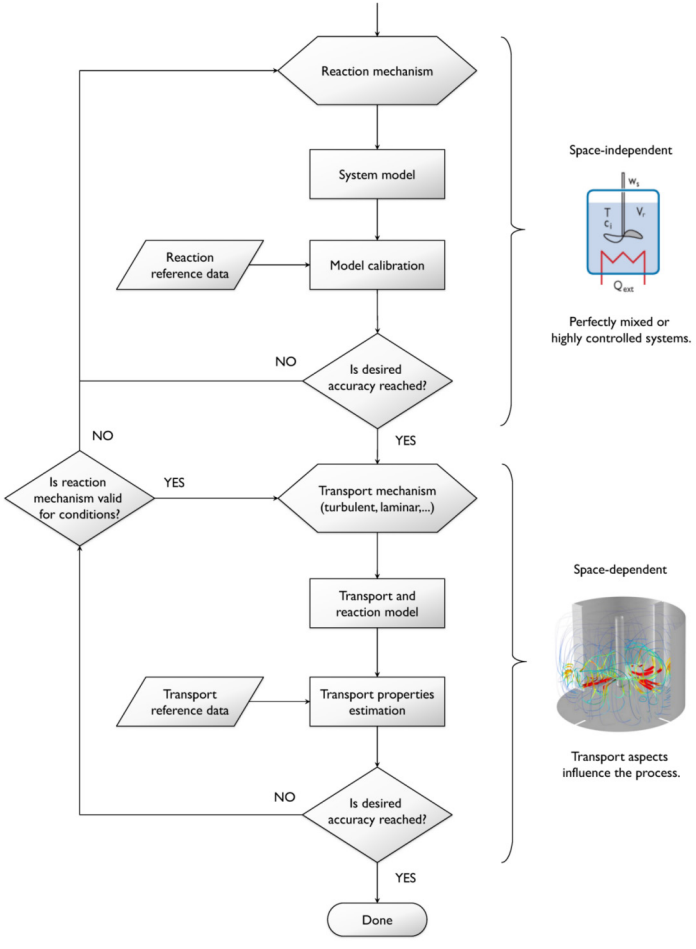


Figure 1: Flowchart summarizing the strategy for modeling reacting systems or designing chemical reactors.

The strategy suggests first investigating a reacting system that is either space-independent, or where the space dependency is very well-defined.

A system where space dependency is irrelevant is usually so well mixed that chemical species concentrations and temperature are uniform throughout and are

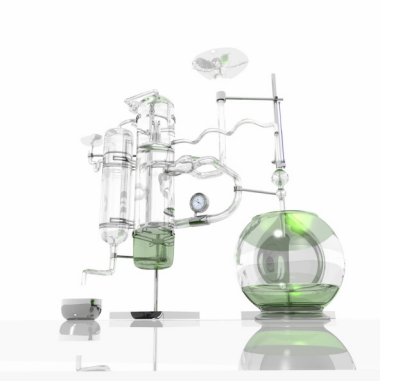
only a function of time — this is often denoted as a perfectly mixed reactor. A plug-flow reactor is a system where the space dependency is well defined.

Once the effects of space dependency are removed or well accounted for, both experimental and modeling investigations can concentrate on the reactions themselves, and the rate laws that control them.

The next step is to apply this information to the chemical reactors or systems that are of interest. These, of course, vary in length, width and height, and are also subject to a range of external parameters including inflows, outflows, cooling, and heating. These are space (and time) dependent systems.

Investigating Chemical Reaction Kinetics — Modeling in Perfectly Mixed, or Plug Flow, Reactors

An important component in chemical reaction engineering is the definition of the respective reaction rate laws, which result from informed assumptions or hypotheses about the chemical reaction mechanisms. Ideally, a reaction mechanism and its corresponding rate laws are found through conducting rigidly controlled experiments, where the influence of spatial and time variations are well known. Sometimes such experiments are difficult to run, and a search of the literature or using the rate laws from similar reactions provides the first hypothesis.



Bench-scale perfectly mixed reactor.

Perfectly mixed or ideal plug-flow reactors models are the most effective reactor types for duplicating and modeling the exact conditions of a rigidly-controlled experimental study. These virtual experiments are used to study the influence of various kinetic parameters and other conditions on the behavior of the reacting system. Then, using parameter estimation, the reaction rate constants for the proposed reaction mechanisms can be found by comparing experimental and simulated results. The comparison of these results to other experimental studies enables the verification or further calibration of the proposed mechanism and its kinetic parameters.

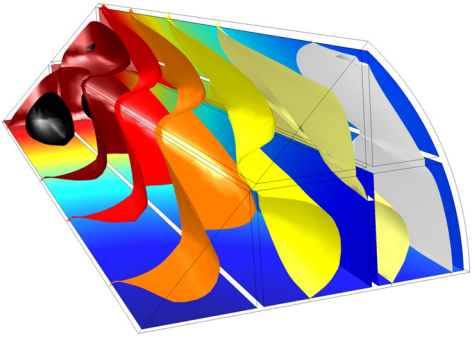
Modeling a reaction system in a well-defined reactor environment also provides an understanding of the influence of various, yet specific, operating conditions on the process, such as temperature or pressure variations. The more knowledge that is gained about a reacting system or process, the easier it is to model and simulate more advanced descriptions of these systems and processes.

Investigating Reactors and Systems — Modeling Space Dependency

Once a reacting process or system's mechanism and kinetic parameters are decided and fine-tuned, they can then be used in more advanced studies of the system or process in real-world environments. Such studies invariably require full descriptions of the variations through both time and space to be considered, which, apart from the reaction kinetics, includes material transport, heat transfer, and fluid flow.

Real world environment.

Depending on assumptions that can (or sometimes must) be made, these descriptions are done in either 1D, 2D, or 3D, where time dependency can also be considered if it is of importance.



The temperature isosurfaces throughout a monolith reactor used in a catalytic converter. The surface plot shows the concentration profile of one of the reactants.

Once again, comparisons between simulation and results, from either the reactor or system itself, or a prototype of them, should always be done if possible. Models that involve material transport, heat transfer, and fluid flow often involve generic material parameters that are taken from the literature or from systems that may be

slightly different, and these may need to be calibrated to improve the accuracy of the model.

When a model's accuracy has been ascertained, then it becomes a model that can be used to simulate the real-world chemical reactor or process under a variety of different operating conditions. The understanding that results from these models, as well as the concrete results they provide, go toward developing or optimizing a chemical reactor with greater precision, or controlling a system with more confidence.

Chemical Reaction Engineering Module Interfaces

Figure 2 shows the chemical reaction engineering interfaces available if you are licensed to the Chemical Reaction Engineering Module. You can use these interfaces to model chemical species transport, fluid flow, and heat transfer. See also The Physics Interface List by Space Dimension and Study Type.

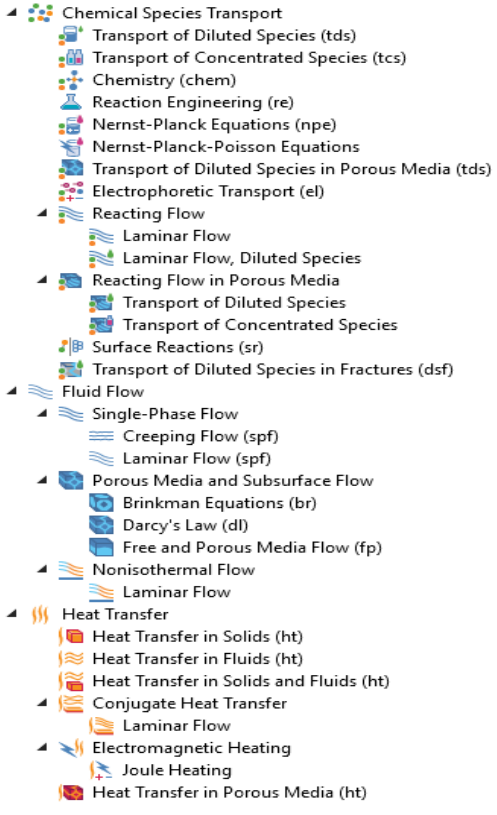


Figure 2: The interface list for the Chemical Reaction Engineering Module as shown in the Model Wizard for a 3D model.

Chemical Reaction and Mass Transport

The Reaction Engineering interface ( ) includes all of the tools required to simulate chemical reaction kinetics in well-defined environments. It sets up simulations of reversible, equilibrium, and irreversible reactions in volumes or on surfaces. You can study the evolution of species concentrations and temperature in controlled environments described by batch, continuous stirred-tank,

semibatch, and plug-flow reactors. Parameter estimation can also be performed, which then requires a license for the Optimization Module.

The Chemistry interface ( ) can do everything the Reaction Engineering interface can do, except modeling a space-independent system. This interface is also always created when a Reaction Engineering model is exported to a space dependent model. As such, it serves as a reaction kinetics and material property provider to the space dependent transport interfaces, such as Transport of Diluted Species.

The Transport of Diluted Species interface ( ) simulates chemical species transport through diffusion, convection (when coupled to fluid flow), and migration in electric fields for mixtures where one component, a solvent, is present in excess. It also handles transport in porous media. It supports cases where either the solid phase substrate is exclusively immobile, or when a gas-filling medium is also assumed to be immobile.

The Transport of Concentrated Species interface ( ) models chemical species transport by diffusion, convection, and migration in mixtures where transport properties, such as diffusion, depend on the composition of the mixture. This interface supports multicomponent transport models given by Fickian diffusion, a mixture-average model, as well as the Maxwell-Stefan equations.

The Nernst-Planck Equations interface ( ) includes a migration term, along with convection and diffusion mass transport, together with an equation that guarantees electroneutrality. A part for species concentrations, the interface also solves for the electric potential.

The Nernst-Planck-Poisson Equations interface ( ) is a multiphysics interface for modeling transport of electrolyte species without the otherwise common assumption of local electroneutrality. This allows you to simulate charge separation typically arising close to an electrode surface, where electrolyte ions are attracted and repelled by unscreened excess charge on the electrode. The charge separation region, also called the diffuse double layer, normally extends a few nanometers away from the electrode surface into the electrolyte.

The Electrophoretic Transport interface ( ) is used to solve for the electrophoretic transport of species in water-based system subject to potential gradients. The species transported can be any combination of weak and strong acids and bases, ampholytes and uncharged species. The interface supports dissociation equilibria for weak acids, bases, and ampholytes, as well as the water auto-ionization reaction.

The Laminar Flow, Concentrated Species interface ( ) under Reacting Flow combines the functionality of the Single-Phase Flow and Transport of Concentrated Species interface.

The Laminar Flow, Diluted Species interface ( ) under Reacting Flow combines the functionality of the Single-Phase Flow and Transport of Diluted Species interface.

The Reacting Flow in Porous Media, Transport of Diluted Species interface ( ) treats diluted reacting mixtures transported by a free and/or porous media flow. This multiphysics interface combines the functionality of the Brinkman Equations and Transport of Diluted Species in Porous Media interface.

The Reacting Flow in Porous Media, Transport of Concentrated Species interface ( ) treats concentrated reacting mixtures transported by a free and/or porous media flow. This multiphysics interface combines the functionality of the Brinkman Equations and Transport of Concentrated Species interface.

The Surface Reactions interface ( ) models reactions involving surface adsorbed species and species in the bulk of a reacting surface. This interface is used on a model boundary, and is coupled to a mass transport interface active on a model domain. The interface can be used together with the following species transport interfaces, Reacting Flow interfaces, and the Electrochemistry interfaces. The Electrochemistry interfaces require the addition of one of the Batteries & Fuel Cells Module, the Corrosion Module, the Electrochemistry Module, or the Electrodeposition Module. Predefined expressions for the growth velocity of the reacting surface makes it easy to set up models with moving boundaries.

The Transport of Diluted Species in Fractures interface ( ) is used to model solute species transported along fracture surfaces where the thickness is very small compared to their other dimensions. Geometries like these are often hard to mesh. In this interface the fractures are defined by boundaries in the model geometry, circumventing the need for a mesh in the thin dimension. The interface allows you to define the average fracture thickness and also the porosity, for cases when the fracture is considered to be a porous structure. Different effective diffusivity models are available for such cases. The interface includes support for transport due to convection, diffusion, and dispersion, as well as chemical reactions.

Single-Phase Flow

The Creeping Flow interface ( ) is used to model flow at very low Reynolds numbers, in which case the inertial term in the Navier-Stokes equations can be neglected. Creeping flow, also referred to as Stokes flow, occurs in systems with high viscosity or small geometrical length scales, for example in microfluidics and MEMS devices.

The Laminar Flow interface ( ) is used to model flow at low to intermediate Reynolds' numbers, and often in combination with mass transport and heat transfer. The interface solves the Navier-Stokes equations and assumes by default that a flow is incompressible. This simplifies the numerical scheme and provides

fast and efficient flow simulations. You can also choose to model compressible flow in which case the density may depend on pressure, composition, and temperature. The interface supports compressible flow at speeds of less than Mach 0.3.

Another useful tool is the ability to describe other material properties such as density and viscosity by entering equations that describe these terms as a function of other parameters such as material concentration, pressure, or temperature. Many materials in the material libraries use temperature- and pressure-dependent property functions.

Porous Media and Subsurface Flow

The Darcy's Law interface ( ) is used to model fluid movement through interstices in a porous medium where a homogenization of the porous and fluid media into a single medium is done. Together with the continuity equation and equation of state for the pore fluid (or gas) this interface can be used to model flows for which the pressure gradient is the major driving force. The penetration of reacting gases through a catalytic washcoat or membrane is a classic example for the use of Darcy's Law.

Darcy's law can be used in porous media where the fluid flow pattern is mostly influenced by the frictional resistance within the pores. Its use is within very slow flows, or media where the porosity is relatively small. Fluid penetration through filters and packed beds are applications that are suitable to model with this interface.

The Brinkman Equations interface ( ) is used to model porous flow when the size of the interstices is larger; the Brinkman interface extends Darcy's law to describe the dissipation of the kinetic energy by viscous shear, similar to the Navier-Stokes equations. The interface includes the possibility to add a Forchheimer drag term, which simulates viscous drag in very open beds where turbulent drag becomes important. Forchheimer drag is sometimes called Ergun's equations. For very low speed flows or small geometrical length scales, you can also choose to neglect the inertial term (Stokes flow).

The Free and Porous Media Flow interface ( ) is useful for equipment that contain domains where free flow is connected to porous media, such as packed-bed reactors and catalytic converters. It should be noted that if the porous region is large in comparison to the free fluid region, and you are not primarily interested in results in the region of the interface, then you can always couple a fluid flow interface to the Darcy's Law interface, to make your overall model computationally cheaper.

As always, the interface gives you direct access to defining, with either constants or expressions, the material properties that describe the porous media flow. This

includes the density, dynamic viscosity, permeability, porosity, and matrix properties.

Heat Transfer

The various Heat Transfer interfaces include Heat Transfer in Fluids (), Heat Transfer in Solids (), and Heat Transfer in Porous Media (), and account for conductive and convective heat transfer. These features interact seamlessly and can be used in combination in a single model. Surface-to-surface radiation can also be included in the energy equation, although this requires a license for the Heat Transfer Module.

The Physics Interface List by Space Dimension and Study Type

The table lists the physics interfaces available with this module in addition to those included with the COMSOL basic license.

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE
Chemical Species Transport				
Surface Reactions		sr	all dimensions	stationary (3D, 2D, and 2D axisymmetric models only); time dependent
Transport of Diluted Species[1]		tds	all dimensions	stationary; time dependent
Transport of Diluted Species in Porous Media		tds	all dimensions	stationary; time dependent
Transport of Diluted Species in Fractures		dsf	3D, 2D, 2D axisymmetric	stationary; time dependent
Electrophoretic Transport		el	all dimensions	stationary; stationary with initialization; time dependent; time dependent with initialization
Chemistry		chem	all dimensions	stationary; time dependent
Transport of Concentrated Species		tcs	all dimensions	stationary; time dependent
Nernst-Planck Equations		npe	all dimensions	stationary; time dependent

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE
Nernst-Planck-Poisson Equations		tds+es	all dimensions	stationary; time dependent; stationary source sweep; small-signal analysis, frequency domain
Reaction Engineering		re	0D	time dependent; stationary plug flow
Reacting Flow				
Laminar Flow		—	3D, 2D, 2D axisymmetric	stationary; time dependent
Laminar Flow, Diluted Species[1]		—	3D, 2D, 2D axisymmetric	stationary; time dependent
Reacting Flow in Porous Media				
Transport of Diluted Species		rfds	3D, 2D, 2D axisymmetric	stationary; time dependent
Transport of Concentrated Species		rfcs	3D, 2D, 2D axisymmetric	stationary; time dependent
Fluid Flow				
Single-Phase Flow				
Creeping Flow		spf	3D, 2D, 2D axisymmetric	stationary; time dependent
Laminar Flow[1]		spf	3D, 2D, 2D axisymmetric	stationary; time dependent
Porous Media and Subsurface Flow				
Brinkman Equations		br	3D, 2D, 2D axisymmetric	stationary; time dependent
Darcy's Law		dl	all dimensions	stationary; time dependent
Free and Porous Media Flow		fp	3D, 2D, 2D axisymmetric	stationary; time dependent

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE
Heat Transfer				
Heat Transfer in Fluids[1]		ht	all dimensions	stationary; time dependent
Heat Transfer in Solids and Fluids[1]		ht	all dimensions	stationary; time dependent
Heat Transfer in Porous Media		ht	all dimensions	stationary; time dependent
[1] This physics interface is included with the core COMSOL package but has added functionality for this module.				

Tutorial Example: NO Reduction in a Monolithic Reactor

This is a model of a catalytic converter that removes nitrogen oxide from a car exhaust through the addition of ammonia. The example shows an application of the modeling strategy, described in the section Chemical Reaction Engineering Simulations and demonstrates through a series of simulations how an understanding of this reactor and its system can be improved. To do this, it uses a number of the interfaces and features found in the Chemical Reaction Engineering Module. Transport and thermodynamic properties are provided by the Thermodynamics feature under Global Definitions.

Introduction

This example models the selective reduction of nitrogen oxide (NO) by a monolithic reactor in the exhaust system of an automobile. Exhaust gases from the engine pass through the channels of a monolithic reactor filled with a porous catalyst and, by adding ammonia (NH_3) to this stream, the NO can be selectively removed through a reduction reaction.

Yet, NH_3 is also oxidized in a parallel reaction, and the rates of the two reactions are affected by temperature as well as composition. This means that the amount of added NH_3 must exceed the expected amount of NO, while not being so excessive as to release NH_3 to the atmosphere.

The goals of the simulations are to find the optimal dosing of NH_3, and to investigate some of the other operating parameters in order to gauge their effects.

Catalytic converters reduce the NOx levels in the exhaust gases emitted by combustion engines.

You may want to revisit the flowchart in Figure 1 to follow the modeling strategy for this model as described next.

First, the selectivity aspects of the kinetics are studied by modeling inlet reaction rates as function of temperature and relative reactant amounts, and for nonisothermal conditions. This is done with the plug-flow reactor type. Information from these studies point to the general conditions required to attain the desired selectivity. This reveals the necessary NH_3 dosing levels based on the working conditions of the catalytic converter and assumed flow rate of NO in the exhaust stream. Last, a 3D model of the catalytic converter is set up and solved. This includes mass transport, heat transfer, and fluid flow and provides insight and information for optimizing the dosing levels and other operational parameters.

Chemistry

Two parallel reactions occur in the V_2O_5/TiO_2 washcoat of the monolithic reactor. The desired reaction is NO reduction by ammonia:

$$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O \tag{1}$$

However, ammonia can at the same time undergo oxidation:

$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O \tag{2}$$

The heterogeneous catalytic conversion of NO to N_2 is described by an Eley-Rideal mechanism. A key reaction step involves the reaction of gas-phase NO with surface-adsorbed NH_3. The following rate equation (mol/(m^3·s)) has been suggested in Ref. 1 for Equation 1:

$$r_1 = k_1 c_{NO} \frac{a c_{NH3}}{1 + a c_{NH3}} \tag{3}$$

where

$$k_1 = A_1 \exp\left(-\frac{E_1}{R_g T}\right)$$

and

$$a = A_0 \exp\left(-\frac{E_0}{R_g T}\right)$$

For Equation 2, the reaction rate (mol/(m^3·s)) is given by

$$r_2 = k_2 c_{NH3} \tag{4}$$

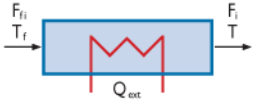
where

$$k_2 = A_2 \exp\left(-\frac{E_2}{R_g T}\right)$$

Nonisothermal Channel Model

To find the minimal level of NH_3 required to reduce the NO present in the exhaust gas requires a reactor model accounting for changing reactant concentrations and system temperature.

From a mass transfer point of view, channels of the reactor monolith can be considered to be independent of each other. Therefore, it is reasonable to perform initial simulations where a single reactive channel, modeled by nonisothermal plug flow equations, represents the monolith reactor.



This model is set up and solved using the Reaction Engineering interface.

Model Equations

Assuming steady-state, the mass balance equation for a plug-flow reactor is given by:

$$\frac{dF_i}{dV} = R_i \tag{5}$$

where F_i is the species molar flow rate (mol/s), V represents the reactor volume (m^3), and R_i is the species net reaction rate (mol/(m^3·s)). The energy balance for the ideal reacting gas is:

$$\sum_i F_i C_{p,i} \frac{dT}{dV} = Q_{\text{ext}} + Q \tag{6}$$

where $C_{p,i}$ is the species molar heat capacity (J/(mol·K)), and Q_{ext} is the heat added to the system per unit volume (J/(m^3·s)). Q denotes the heat due to chemical reaction (J/(m^3·s)).

$$Q = -\sum_j H_j r_j$$

where H_j the heat of reaction (J/mol), and r_j the reaction rate (mol/(m^3·s)).

The reactor equations are solved for a channel 0.36 m in length with a cross sectional area of 12.6 mm^2. It is assumed that exhaust gas containing 41.1 mmol/m^3 of NO at a temperature of 523 K passes through the channel at 0.3 m/s.

Results

Reaction Kinetics

The competing chemical reactions, given by Equation 1 and Equation 2, raise the issue of optimal dosing of NH_3 to handle the reduction process. Stoichiometry suggests a 1:1 ratio of NH_3 to NO as a lower limit. It is likely that a stoichiometric excess of NH_3 is necessary but, at the same time, unnecessarily high levels of NH_3 in the gas stream leaving the catalytic converter need to be avoided.

Analyzing the kinetics can help identify conditions favoring the desirable reduction reaction. A first study looks at the inlet reaction rates of the reduction and oxidation reactions as a function of temperature and relative amounts of reactants. Figure 3 shows inlet rates for the reduction reaction (Equation 1). The curves represent a set of NH_3:NO ratios ranging from 1 to 2. The concentration of NO in the exhaust gas entering the catalytic converter is known to be 41.1 mmol/m^3.

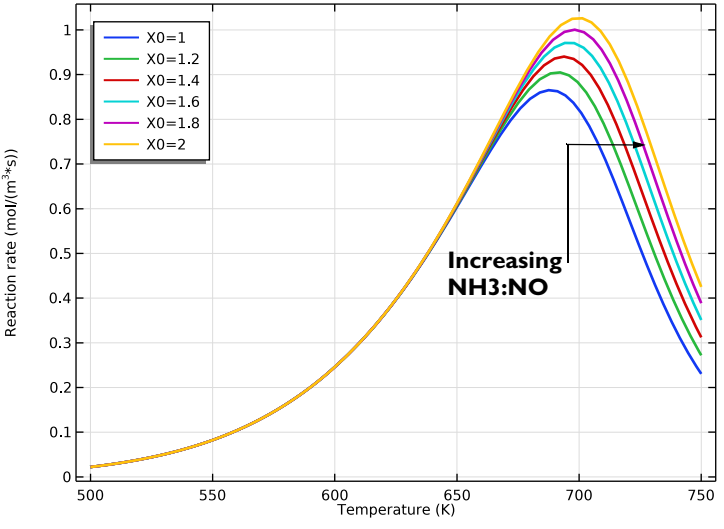


Figure 3: Inlet reaction rates of the NO reduction reaction (r_1) as a function of temperature. The NH_3:NO ratio ranges from 1 to 2.

The rate of NO reduction goes through a maximum and falls off at higher temperatures. Higher NH_3 concentrations in the gas phase lead to increased levels of surface-adsorbed NH_3, in turn favoring the conversion of gas-phase NO to N_2. This explains the shifts of the rate maximum towards higher temperatures as the NH_3:NO ratio increases. The decrease in the NO reduction rate at the highest temperatures is explained by the desorption rate of NH_3 from the catalyst surface becoming faster than the reaction of adsorbed NH_3 with gas-phase NO.

According to Equation 4, the ammonia oxidation rate increases with temperature and NH_3 concentration. Figure 4 shows the selectivity parameter, defined as:

$$S = \frac{r_1}{r_2}$$

A value greater than one means that NO reduction is favored, while a value of less than one means NH_3 oxidation is the preferred reaction pathway. Clearly the selectivity for NO reduction drops both with increasing temperature and increasing NH_3:NO ratio.

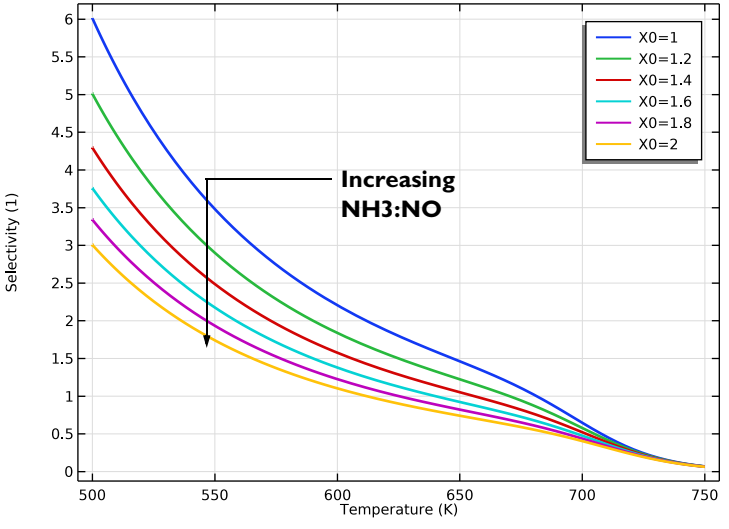


Figure 4: Selectivity parameter (r_1/r_2) as a function of temperature. The NH_3:NO ratio ranges from 1 to 2.

The kinetic analysis suggests that preferred working conditions involve moderate temperatures and relatively low ratios of NH_3:NO.

Nonisothermal Channel Model

To further optimize the dosage the reactor model needs to account for changing reactant concentrations and system temperature. For this purpose, a nonisothermal plug-flow reactor serves to simulate the behavior of a reactive channel.

The plot in Figure 5 shows the molar flow rate of NH_3 as function of position in the reactor. The set of lines represent NH_3:NO ratios ranging from 1 to 2. Under these conditions results show that a NH_3:NO ratio of at least 1.3 is needed to guarantee that NH_3 is available as a reductive agent throughout the entire reactive channel.

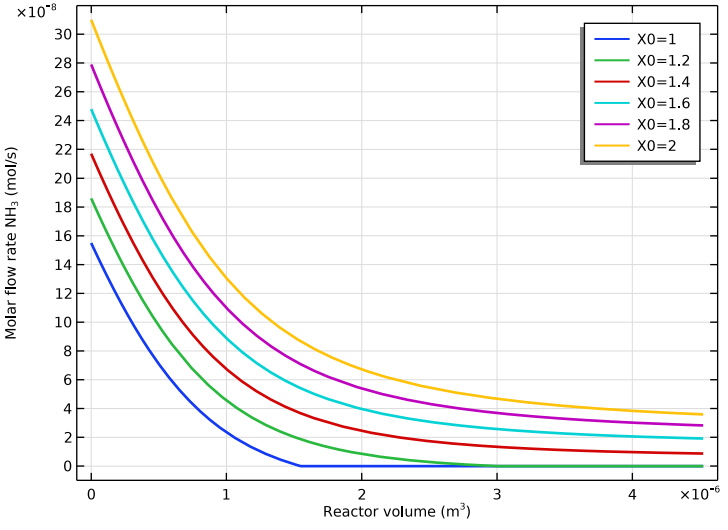


Figure 5: Molar flow rate (mol/s) of NH_3 as function of channel volume.

A plot of the selectivity parameter in Figure 6 confirms that NO reduction is favored in the entire channel for a dosage level between 1.3 and 1.4.

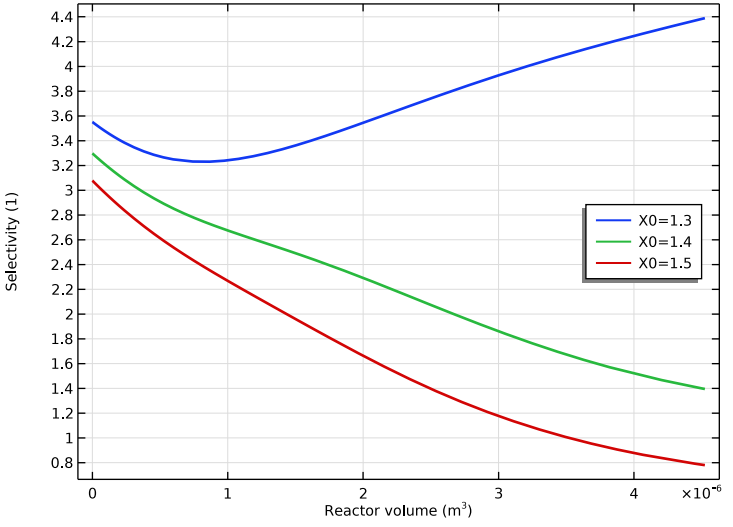


Figure 6: Selectivity parameter (r_1/r_2) as a function of channel volume.

Investigating a 3D Reactor

It is clear from the kinetic analysis as well as from the single channel model that temperature plays a central role in affecting the optimal dosing of NH_3. As the temperature distribution is likely to vary from channel to channel in a catalytic converter, a full 3D reactor model is required.

Model Geometry

The monolithic reactor has a modular structure made up of monolith channel blocks and supporting solid walls. The reactor is 0.36 m long with a 0.1 m radius.

Each reactive channel has a cross sectional area of 12.6 mm^2, and in a channel block the void fraction is 0.75.

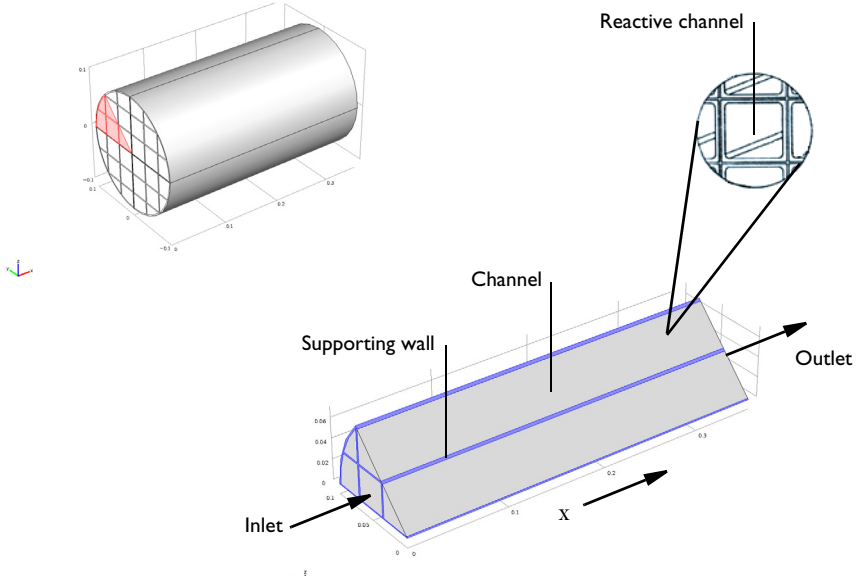


Figure 7: NO reduction chemistry takes place in the channel blocks. Supporting walls hold together the full reactor structure. Symmetry reduces the modeling domain to one eighth of the reactor geometry.

Model Equations and Assumptions

In this example a pseudo homogeneous approach is used to model the hundreds of channels present in the monolith reactor. As no mass is exchanged between channels, each channel is described by 1D mass transport equations. Furthermore, fully developed laminar flow in the channels is assumed, such that the average flow field is proportional to the pressure difference across the reactor. The fluid flow transports mass and energy only in the channel direction. The energy equation describes the temperature of the reacting gas in the channels, as well as the conductive heat transfer in the monolith structure and the supporting walls. As the temperature affects not only the reaction kinetics but also the density and viscosity of the reacting gas, the energy equation is what really connects the channels in the reactor structure turning this into a 3D model.

Mass Transport

The mass balances describing transport and reaction in the reacting channels are given by diffusion-convection equations at steady state:

$$\nabla \cdot (-D_i \nabla c_i) + \mathbf{u} \cdot \nabla c_i = R_i \tag{7}$$

In Equation 7, D_i denotes the diffusion coefficient (m^2/s), c_i is the species concentration (mol/m^3), and $\mathbf{u}$ equals the velocity vector (m/s). The term R_i ($mol/(m^3 \cdot s)$) corresponds to the species' rate expression.

Mass transport is only allowed in the direction of the channels, corresponding to direction of the x-axis in the 3D geometry used in this example. For the diffusive transport, this is accomplished by setting the y and z-components of the diffusivity matrix to zero. The pressure-driven flow in the monolith is also defined in the direction of the x-axis, hereby restricting the convective mass transport to the channel direction as well. Each monolith channel thus behaves as a 1D plug flow model with included diffusion. These separate channel models are connected through the heat transfer equations for the reactor monolith.

Fluid Flow

Assuming there is fully developed laminar flow in the channels, the average flow field is proportional to the pressure difference across the reactor. The flow of reacting gas through the monolith can then be modeled using a Darcy's Law interface with the following governing equations:

$$\nabla \cdot (\rho \mathbf{u}) = 0 \tag{8}$$

$$\mathbf{u} = -\frac{\kappa}{\mu}\nabla p \tag{9}$$

The monolith is treated as a porous matrix with the effective permeability κ (m^2). Similarly to the diffusivity, the y- and z-components of the permeability matrix are set to zero. The density, ρ (kg/m^3), and viscosity, μ (Pa·s), represent properties of the reacting gas.

Heat Transfer

A single temperature equation describing the heat transfer in the porous monolith reactor can be written as:

$$(\rho C_p)_{\text{eff}}\frac{\partial T}{\partial t} + \rho_{\text{f}} C_{p\text{f}}\mathbf{u} \cdot \nabla T = \nabla \cdot (k_{\text{eff}}\nabla T) + Q \tag{10}$$

For the stationary case this reduces to:

$$\rho_{\text{f}} C_{p\text{f}}\mathbf{u} \cdot \nabla T = \nabla \cdot (k_{\text{eff}}\nabla T) + Q \tag{11}$$

where ρ_{f} (kg/m^3) is the fluid density, $C_{p\text{f}}$ ($J/(kg \cdot K)$) is the fluid heat capacity, and k_{eff} ($W/(m \cdot K)$) is the equivalent thermal conductivity. Furthermore, $\mathbf{u}$ (m/s) is the fluid velocity field, which in this model is calculated in the Darcy's Law interface, and Q (W/m^3) is the heat source, which is due to exothermic chemical reactions:

$$Q = Q_1 + Q_2 = -r_1 H_1 - r_2 H_2 \tag{12}$$

The effective conductivity of the solid-fluid system, k_{eff}, is related to the conductivity of the solid, k_{p}, and to the conductivity of the fluid, k_{f}, by:

$$k_{\text{eff}} = \Theta_{\text{p}} k_{\text{p}} + \Theta_{\text{f}} k_{\text{f}} \tag{13}$$

In Equation 13, Θ_{p} denotes the solid material's volume fraction, here 0.25, which is related to the volume fraction of the fluid Θ_{f} by:

$$\Theta_f + \Theta_{\text{p}} = 1 \tag{14}$$

Equation 11 is the equation set up by the Heat Transfer interface for a fluid domain. For the supporting walls in the reactor, only heat transfer by conduction applies:

$$-\nabla \cdot (k_s \nabla T) = 0 \tag{15}$$

where k_{s} (W/(m·K)) is the thermal conductivity for the solid walls.

As mentioned, the temperature affects not only reaction kinetics but also the density and viscosity of the reacting gas. In this way the heat transfer equation connects the channels in the reactor structure.

Thermodynamic and Transport Properties

Accurate thermodynamic data is required as input to energy balance equations, both in the plug flow model (Equation 6) and the 3D monolith model (Equation 11). In addition to thermodynamic properties, the model equations also require transport properties to describe the space dependent reactor model.

The Thermodynamics feature provides all necessary properties for the simulation. Different models are available for thermal and transport property calculations (see Thermodynamic Models and Theory). In this system, thermodynamic properties are calculated based on the ideal gas law while transport properties such as diffusivity, viscosity, and thermal conductivity are calculated from Fuller Schettler Giddings, Brokaw, and Kinetic Theory, respectively.

Results

The plot in Figure 8 shows the conversion of NO in the monolith channel blocks for the optimal NH_3:NO ratio of 1.35. The average conversion at the outlet is

96%. The isosurfaces in the plot show how a channel's performance depends on its position in the reactor, clearly pointing to the 3D nature of the problem.

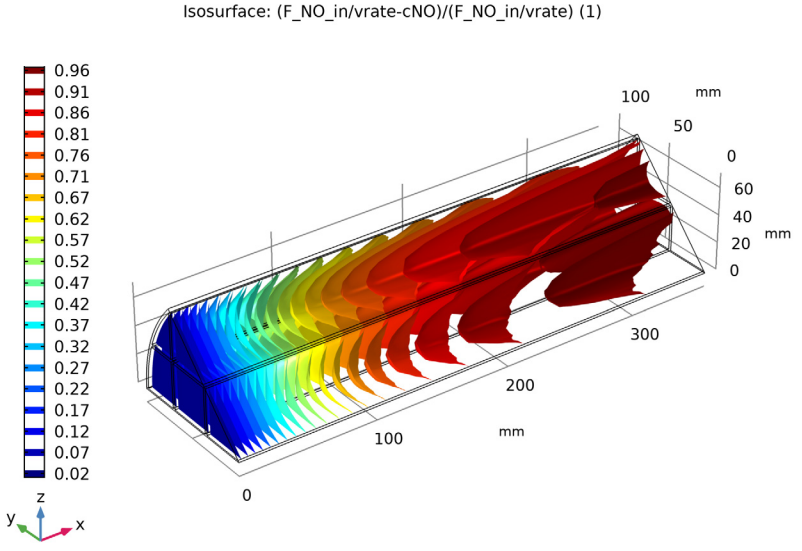


Figure 8: Isosurfaces showing the conversion of NO in the reactor.

The individual channels, although they do not exchange mass, are connected through the temperature distribution in the reactor. The temperature affects both

the flow velocity of the reacting gas as well as the reaction rates. Cross sections of the reactor temperature are shown in Figure 9.

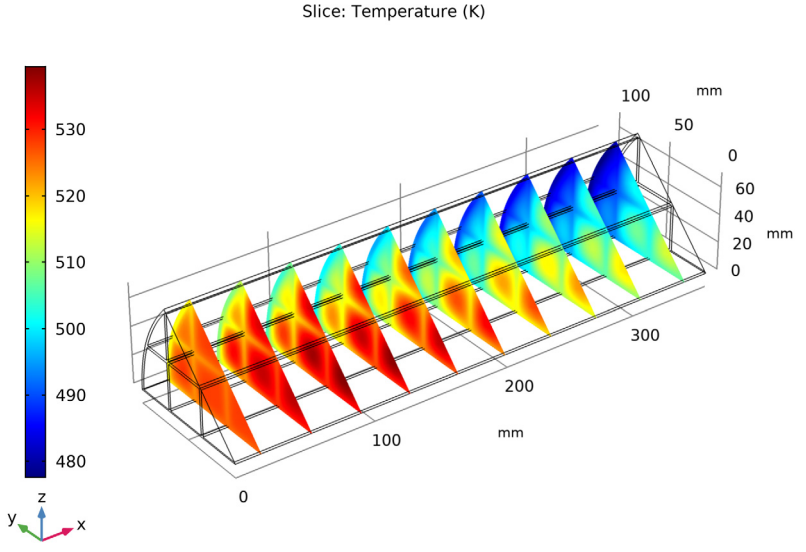


Figure 9: Temperature distribution in cross sections of the reactor.

The exothermic reactions increase the temperature in the central parts of the reactor, while the temperature is decreased through heat loss to the surroundings. The maximum temperature calculated for the 3D reactor is about 540 K. The effect of the relatively high thermal conductivity of the supporting walls is clearly visible.

A seen from the inlet kinetic analysis, elevated temperatures have a detrimental effect on the selectivity, leading to ammonia getting oxidized (Equation 2) rather than be consumed in the NO reducing reaction (Equation 1). A plot of r_1/r_2 on the symmetry surface of the monolith is shown in Figure 10. The fact that r1/r2 is

greater than 1 signals that the selectivity favors the desired reducing reaction in all regions of the reactor.

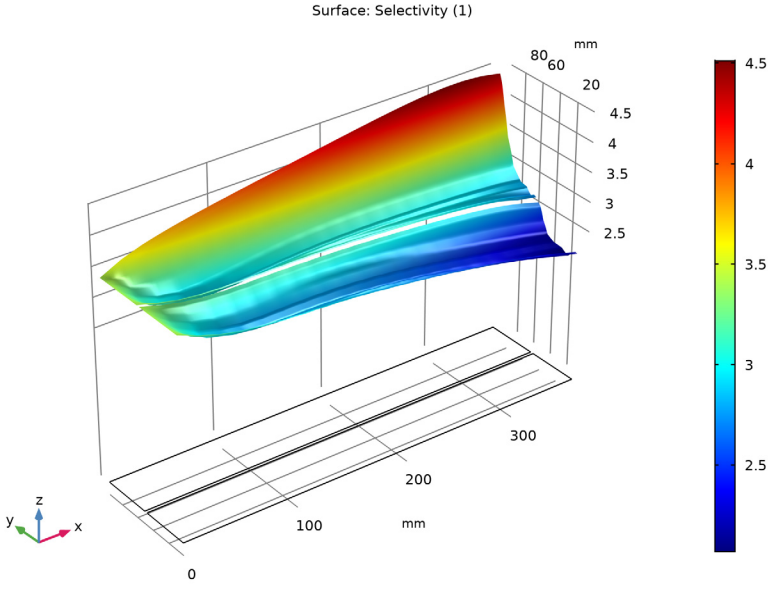


Figure 10: The fact that r_1/r_2 is greater than 1 signals that the selectivity favors the desired NO reducing reaction.

The selectivity plot once again reveals the space-dependent nature of the problem. Channels in the relatively cold region near the reactor outer surface display high selectivity throughout, whereas channels in the region close to the center see selectivity falling off comparatively fast. Compared to the single channel model, the 3D reactor shows notably lower values of the selectivity parameter near the center of the outlet. Nevertheless, NO reduction is still favored throughout.

The information from this 3D model can also be used to investigate other aspects of this reacting system. These results can be compared to other results from prototypes or even real monolith reactors, and material properties, such as the permeability constant, can be fine-tuned. Different operating conditions, such as when the automobile accelerates and decelerates, can be simulated. Alternative catalysts and designs can also be proven.

Summary

The Chemical Reaction Engineering Module is used to perform two different levels of analysis concerning the reduction of NO in a monolithic reactor:

- Channel model — With a simple Plug-Flow reactor model explore the reaction kinetics and narrow down the conditions that promote selectivity towards NO reduction. The tuning of the dosage is further improved with a nonisothermal model setup.
- 3D reactor model — testing the reactor operating conditions in a full 3D reactor representation, noting the space-dependent effect due to coupling between monolith channels.

A reactant ratio NH_3:NO of approximately 1.35 is found to be close to optimal under the investigated conditions. This ratio leads to minimal waste of ammonia without limiting the NO reduction chemistry. It also favors the selectivity for NO reduction while at the same time restricting the possible heat evolved through the chemical reactions. This in turn helps control the temperature in the reactor, again favoring the NO reduction.

The modeling strategy used in this example has several advantages. Starting with fast simulations using easy to set up models makes it easier to identify and narrow down the process condition envelope before moving to more advanced and computationally demanding models. The sequential modeling approach also helps to identify when and how effects such as temperature dependency and space dependency come into play. This deepened system understanding leads to efficient model set-up and solution strategies. Going from perfectly mixed conditions to full space dependency in 3D also puts you in the position to decide on what level of detail that is needed for the particular system.

References

1. G. Shaub, D. Unruh, J. Wang, and T. Turek, "Kinetic analysis of selective catalytic NOx reduction (SCR) in acatalytic filter", *Chemical Engineering and Processing*, vol. 42, p. 365–71, 2003.

Note on the Reactor Models

The following step-by-step instructions guide you through the process to set up and solve two models that simulate the catalytic reduction of NO in a monolith reactor. The first model makes use of a simple plug-flow reactor model. The second model accounts for the full 3D monolith reactor, coupling mass transport to heat transfer and fluid flow.

As an option, you can open the completed model file of the plug-flow reactor model and proceed directly with the setup of the 3D reactor model. See Generate Space-Dependent Model 1 for further details.

Instructions on how to set up and solve the model used for the kinetic analysis are provided in the documentation for the model `monolith_kinetics.mph`. See Tutorial Example: NO Reduction in a Monolithic Reactor for information about how to open this file.

Model Wizard

Note: These instructions are for the user interface on Windows but apply, with minor differences, also to Linux and Mac.

1. To start the software, double-click the COMSOL icon on the desktop. When the software opens, you can choose to use the Model Wizard to create a new COMSOL model or Blank Model to create one manually. For this tutorial, click the Model Wizard button.

   If COMSOL is already open, you can start the Model Wizard by selecting New from the File menu and then click Model Wizard.

   The Model Wizard guides you through the first steps of setting up a model. The next window lets you select the dimension of the modeling space.
2. In the Space Dimension window click the 0D button.
3. In the Select Physics tree under Chemical Species Transport, double-click Reaction Engineering (re) to add it to the Added physics list. You can also right-click and choose Add Selected.
4. Click Study. In the Select Study tree, under Preset Studies for Selected Physics Interfaces, click Stationary Plug Flow.
5. Click Done.

Definitions - Parameters and Variables

Start by importing a set of global parameters defining the process conditions for the monolith reactor, including the dimensions of the reactive channels, the flow rate of the reacting gas, and the temperature conditions. Then import the variables for model specific expressions defining rate constants and the selectivity parameter S.

Note: The location of a file is based on the installation. For example, if the installation is on your hard drive, the file path might be similar to `C:\Program Files\COMSOL55\applications\`.

Parameters

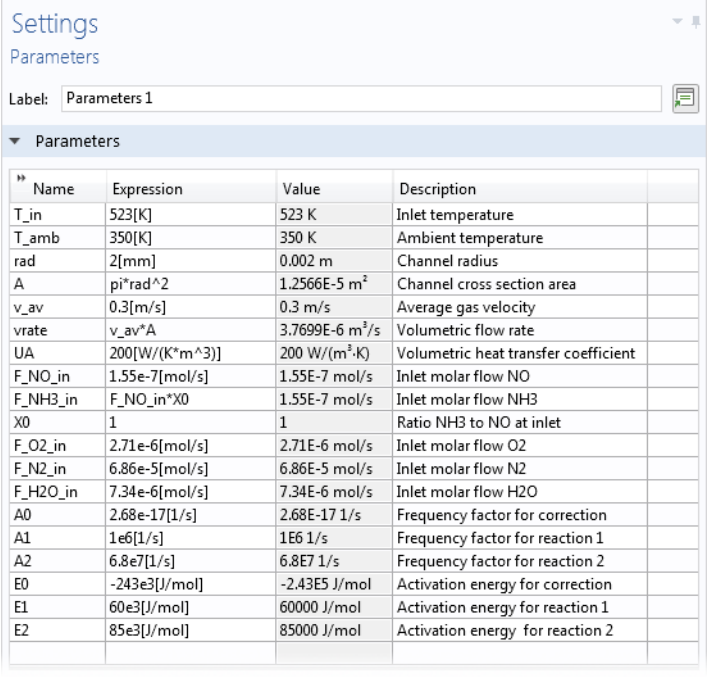
1 On the Home toolbar click Parameters Pi and select Parameter 1 Pi .

Note: On Linux and Mac, the Home toolbar refers to the specific set of controls near the top of the Desktop.

2 In the Settings window under Parameters, click the Load from File button .

3 Browse to the file `monolith_kinetics_parameters.txt` in the application library folder on your computer, `Chemical_Reaction_Engineering_Module\Tutorials`. Double-click to add or click Open.

The parameters are added to the table.



Name	Expression	Value	Description
T_in	523[K]	523 K	Inlet temperature
T_amb	350[K]	350 K	Ambient temperature
rad	2[mm]	0.002 m	Channel radius
A	pi*rad^2	1.2566E-5 m^2	Channel cross section area
v_av	0.3[m/s]	0.3 m/s	Average gas velocity
vrate	v_av*A	3.7699E-6 m^3/s	Volumetric flow rate
UA	200[W/(K*m^3)]	200 $W/(m^3 \cdot K)$	Volumetric heat transfer coefficient
F_NO_in	1.55e-7[mol/s]	1.55E-7 mol/s	Inlet molar flow NO
F_NH3_in	F_NO_in*X0	1.55E-7 mol/s	Inlet molar flow NH3
X0	1	1	Ratio NH3 to NO at inlet
F_O2_in	2.71e-6[mol/s]	2.71E-6 mol/s	Inlet molar flow O2
F_N2_in	6.86e-5[mol/s]	6.86E-5 mol/s	Inlet molar flow N2
F_H2O_in	7.34e-6[mol/s]	7.34E-6 mol/s	Inlet molar flow H2O
A0	2.68e-17[1/s]	2.68E-17 1/s	Frequency factor for correction
A1	1e6[1/s]	1E6 1/s	Frequency factor for reaction 1
A2	6.8e7[1/s]	6.8E7 1/s	Frequency factor for reaction 2
E0	-243e3[J/mol]	-2.43E5 J/mol	Activation energy for correction
E1	60e3[J/mol]	60000 J/mol	Activation energy for reaction 1
E2	85e3[J/mol]	85000 J/mol	Activation energy for reaction 2

Variables 1

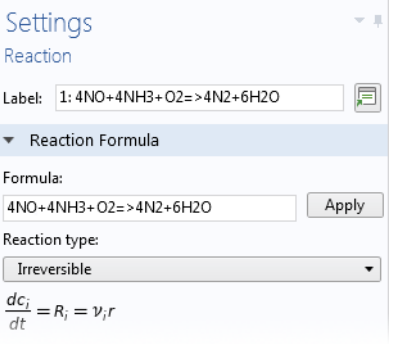
1. In the Home toolbar, click Variables a= and select Local variables (or in the Model Builder under Component 1, right-click Definitions ≡ , and select Variables a=).
2. In the Settings window for Variables window locate the Variables section.
3. In the table, enter these settings:

NAME	EXPRESSION	UNIT	DESCRIPTION
S	re.r_1/re.r_2		Selectivity
a	A0*exp(-E0/(R_const*re.T))	1/s	Arrhenius correction

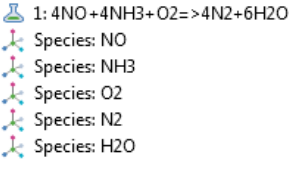
Now define the chemical reactions. First, enter the reaction formula for NO reduction. The Reaction Engineering interface automatically interprets the reaction formula and suggests a reaction rate based on the mass action law (that is, stoichiometry).

Reaction 1

1. On the Reaction Engineering toolbar, click Reaction (or in the Model Builder, right-click Reaction Engineering (re) and select Reaction).
2. In the Settings window for Reaction under Reaction Formula, enter `4NO+4NH3+O2=>4N2+6H2O` in the Formula text field.
3. Click Apply, to generate the reaction and Species nodes for each one of the species in the Reaction Formula.



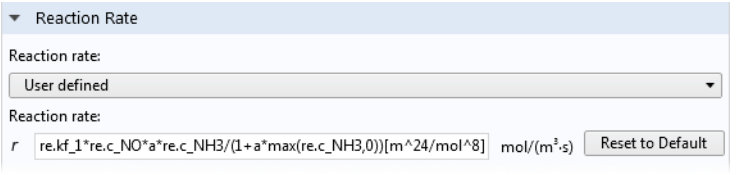
4. In the Model Builder click the 1: 4NO+4NH3+O2=>4N2+6H2O node .



In this example, replace the automatically generated reaction rate expression with the rate expression known in the literature. Adjust the unit to eliminate any unit error caused by the default settings assuming that the reaction rates follow mass action law.

5 Locate the Reaction Rate section. From the Reaction Rate list select User defined.

In the Reaction rate (r) text field enter `re.kf_1*re.c_NO*a*re.c_NH3/(1+a*max(re.c_NH3,0))[m^24/mol^8]`. The max operator in the denominator helps avoid negative concentrations,

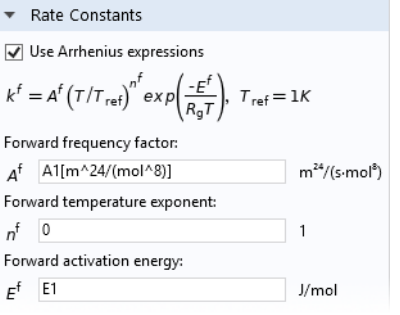


Enter the Arrhenius parameters for the temperature dependent rate constant used for the reaction.

1 Under Rate Constants select the Use Arrhenius expressions check box.

2 Enter the Arrhenius parameters for the reaction. Since a default irreversible reaction is used, you only need to enter Forward reaction parameters.

- In the Forward frequency factor (A^f) text field, enter `A1[m^24/mol^8]`.
- In the Forward activation energy (E^f), enter `E1`.



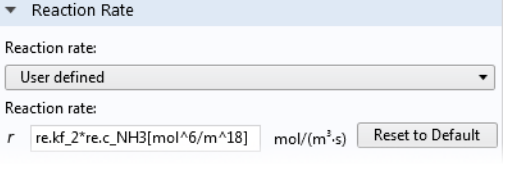
Reaction 2

1 On the Reaction Engineering toolbar, click Reaction to add a second reaction for the oxidation of NH_3.

2 In the Settings window for Reaction locate the Reaction Formula section. Enter (or copy and paste) `4NH3+3O2=>2N2+6H2O` in the Formula text field.

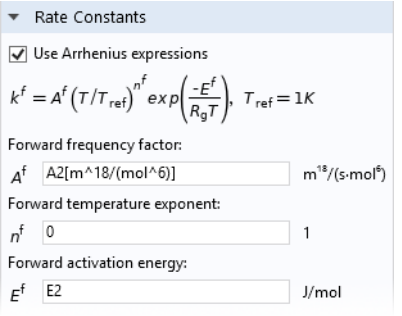
3 Click Apply.

4 Locate the Reaction Rate section. From the Reaction Rate list select User defined. Enter `re.kf_2*re.c_NH3[mol^6/m^18]` in the Reaction rate (r) text field.



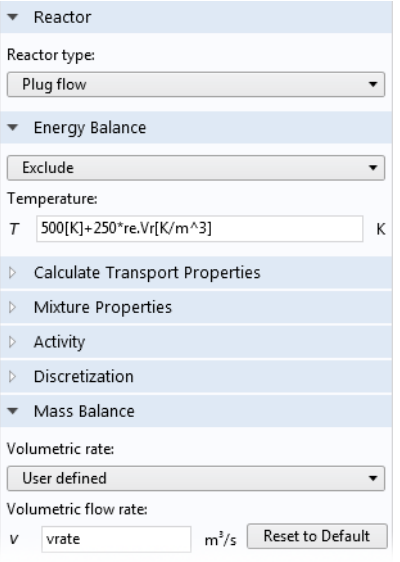
5 Locate the Rate Constants section. Select the Use Arrhenius expressions check box.

- In the A^f text field, type `A2[m^18/mol^6]`.
- In the E^f text field, type `E2`.



After setting up the reaction kinetics, define the suitable reactor model where the reaction takes place. Using the Reaction Engineering node you can select one of the predefined reactor types. Since you are planning to set up a simple channel model, having selected the Stationary Plug Flow study type previously, select the Plug-Flow Reactor.

You want to start the investigation of the reaction kinetics, by studying the inlet reaction rates as functions of temperature and compositions:



1 In the Model Builder, click the Reaction Engineering (re) node.
2 In the Settings window under Reactor Settings, from the Reactor type list select Plug flow.
3 Expand the Mixture Properties section, and from the Reactor pressure list, select Ideal gas law.
4 Under Mass Balance, in the v text field, enter `vrate`.
5 Under Energy Balance in the Temperature (T) text field, enter `500[K]+250*re.Vr[K/m^3]`. This will ramp the reactor temperature between 500 K and 750 K with the independent variable Vr (reactor volume) with the use of the Stationary Plug Flow study type.

Initial Values 1

In the next steps, define inlet values for the reactor.

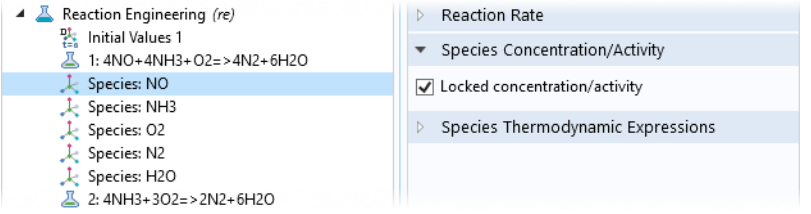
1 In the Model Builder under Reaction Engineering click Initial Values 1 .
2 In the Settings window for Initial Values, locate the Volumetric Species Initial Value section.
3 In the table enter the following settings:

SPECIES	MOLAR FLOW RATE (MOL/S)
H2O	F_H2O_in
N2	F_N2_in
NH3	F_NH3_in
NO	F_NO_in
O2	F_O2_in

Species: NO and Species NH3

Next, lock the concentrations of reactants NO and NH3 to only investigate the impact of the temperature on the inlet reaction rates.

1. One at a time in the Model Builder, click the Species: NO and the Species: NH3 nodes. In each Settings window expand the Species Concentration/Activity section.
2. Select the Locked concentration/activity check box in these sections to set the species concentration constant.

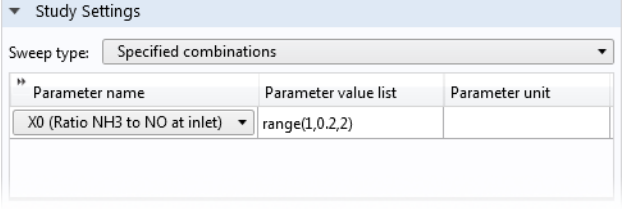


Study 1

Select various inlet ratios to examine the impact of the NH3:NO dosage ratio on the inlet reaction rate.

Parametric Sweep

1. On the Study toolbar click Parametric Sweep.
2. Under Study Settings, click the Add button under the table. In the Parameter name column, select `X0 (Ratio NH3 to NO at inlet)`.
3. Start with a quite wide dosage range and narrow down the optimal dosage later. In the Parameter value list column, enter `range(1,0.2,2)` to solve for a dosage from 1 to 2.



It is good practice to tighten the default solver tolerances and make sure that the solution plots do not change. Both the relative and absolute tolerance should be

tightened so that the solutions does not change between consecutive test runs. In this case the relative tolerance needs to be reduced to 1e-7.

Step 1: Stationary Plug Flow

1 In the Model Builder under Study 1, click Step 1: Stationary Plug Flow .

2 In the Settings window locate the Study Settings section. From the Tolerance list, select User controlled and enter `1e-7` in the text field.

3 On the Study toolbar click Compute .

Results — Inlet Reaction Rates

When a model many times is re-computed with small or large sets of changes in the conditions, it is advisable to save the solution after each computation.

Parametric Solutions 1 - Copy 1

1 In the Model Builder under Study 1>Solver Configurations, right-click Parametric Solutions 1 and from the Solution menu choose Copy .

2 In the Settings window for the copied node, type `Kinetics` in the Label text field (or press F2 to rename the node). The solution named Kinetics is now available for further postprocessing.

Follow these steps to generate the first figures (Figure 3 and Figure 4) displaying the results for the single channel model with the inlet dosage conditions and temperature ramp.

Molar Flow Rate (re)

1 Under Results click the Molar Flow Rate (re) node. Type `Reaction rate` in the Label text field in the Settings window to change the name of the plot group.

2 Under the Data section of the Reaction rate node, from the Data set list, choose the saved solution `Study 1/Kinetics`.

3 The title is removed to reduce the information in the plot. Click to expand the Title section and in the Title type list choose None.

4 Locate the Plot Settings section. Select the x-axis label check box.

5 In the associated text field, type Temperature (K).

6 Locate the Legend section and choose Upper left in the Position list.

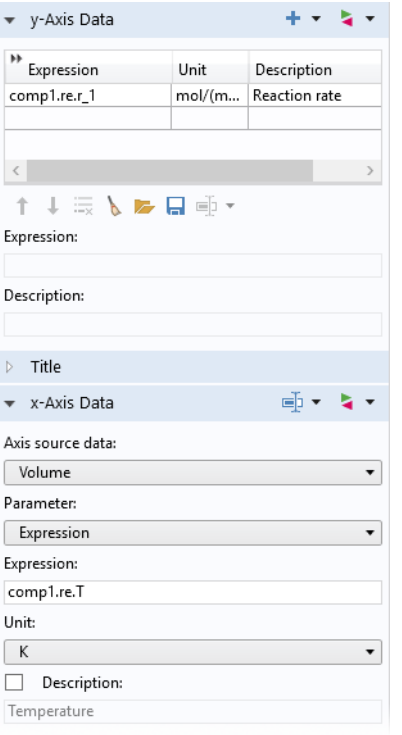
7 Expand the Reaction rate node and click Global 1.

8 In the Settings window locate the y-Axis Data section. Click Replace Expression and either search or select `comp1.re.r_1` under Component 1>Reaction Engineering.

9 In the x-Axis Data section choose Expression from the Parameter list. Enter `comp1.re.T` in the Expression text field.

10 Find the Coloring and Style section and expand it. Type 2 in the Width text field.

11 Expand the Legends section. In the Include subsection click to clear the Expression check box.



12 Click Plot to generate Figure 3. Click the Zoom Extents button on the Graphics toolbar.

Selectivity

The most efficient way to create a similar plot is to duplicate an existing one.

1 Right-click the Reacting rate node and choose Duplicate.

2 This plot is intended to display the selectivity. In the Settings window for the duplicated node, enter `Selectivity` in the Label text field.

3 Locate the Legend section and choose Upper right in the Position list.

4 Expand the Selectivity node and click Global 1.

5 In the Settings window, locate the y-Axis Data section. Click Replace Expression and under Component 1>Definitions>Variables choose `comp1.S - Selectivity`.

6 On the Settings window or Results toolbar click Plot to generate Figure 4.

Reaction Engineering Interface - Nonisothermal Single Channel Model

With the input from the previous section (Results - Inlet Reaction Rates), you now have an idea of how the reaction kinetics behave and you can continue the monolith system investigation by setting up a single channel model running under nonisothermal conditions.

The thermal properties are from Thermodynamics feature. First, create a thermodynamic system and then couple it to Reaction Engineering. The Thermodynamics can set up predefined expressions for transport and thermodynamic properties. The transport expressions, for instance the species diffusivity coefficients, are used in the 3D monolith model described further on. Thermodynamics feature is available under Global Definitions.

THERMODYNAMICS

1 In the Model Builder, right-click on Global Definition and select Thermodynamics ( ) and then Thermodynamic System ( ).

This opens Thermodynamic System Wizard which helps us to create a property package including phase, species and set up thermo and transport model.

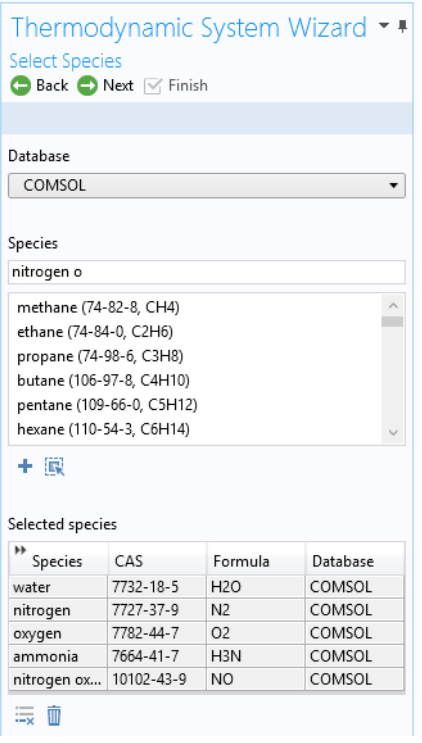
2 At the first step in the wizard, select Gas as thermodynamic system. click Next ( ).

3 In Select Species window, type name of the species that are available in the system (Reaction Engineering) and Add ( ) them to the Selected species table. Click Next ( ).

4 In the Select Thermodynamic Model, keep Ideal gas as Gas phase model. Click Finish ( ).

You can select Advanced options check box to select transport properties for later use in space dependent model. We keep the default selection.

5 In the Settings window, you can review all properties of created Gas System ( ) for simulation.

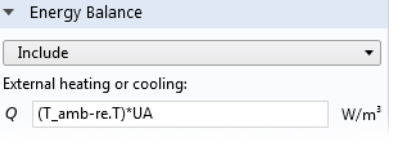


Now we need to couple Thermodynamics feature to Reaction Engineering interface. This happens by matching the species available in Thermodynamics and Reaction Engineering. When all species are matched, thermodynamic properties such as enthalpy are coupled automatically to that in Thermodynamics.

Reaction Engineering

1 In the Model Builder under Component 1 (comp1), click the Reaction Engineering (re) node.

2 In the Settings window, locate the Energy Balance section. Choose Include and replace the expression in the External heating or cooling (Q) text field with `(T_amb-re.T)*UA`.



3 In the Settings window, locate Mixture Properties section and select the Thermodynamics check-box.

Activating Thermodynamics, go to the Species Matching section in the Settings window.

4 In the Settings window, locate Species Matching section. Go through all species in the table and from the drop-box in From Thermodynamics column, select equivalent species in Gas system.

When all species are selected and matched, system is fully coupled and all the setting for properties are updated from Thermodynamics.

Initial Values 1

The inlet temperature needs to be defined as well.

1 In the Model Builder under Reaction Engineering, click Initial Values 1 .

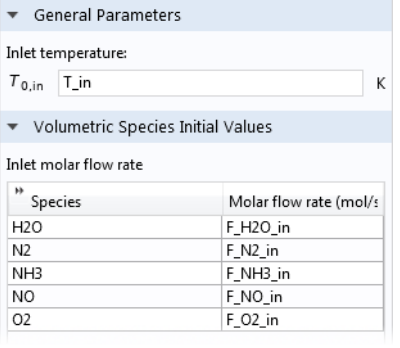
2 In the Settings window for Initial Values, locate the General Parameters section. Type `T_in` in the Inlet temperature ($T_{0,in}$) text field.

Species: NO and Species NH3

The concentration within the reactor should be variable in the single channel model.

1 In the Model Builder, one at a time click the Species: NO and Species: NH3 nodes.

2 Click to clear the Locked concentration/activity check box in the Species Concentration/Activity section.



Study 1

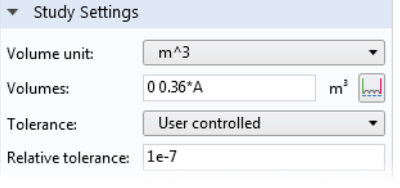
Solve the model.

Step 1:Stationary Plug Flow

1 In the Model Builder under Study 1, click Step 1: Stationary Plug Flow .

2 In the Settings window locate the Study Settings section. In the Volumes text field, type 0 0.36*A to solve the model for a tube reactor with the volume 0.36[m]*A[m^2].

3 Click Compute .



Parametric Solutions 1 - Copy 1

First save the current solution.

1. In the Model Builder under Study 1>Solver Configurations, right-click Parametric Solutions 1. From the Solution menu, select Copy.
2. In the Settings window for the copied node, type `Nonisothermal` in the Label text field.

Follow these steps to generate Figure 5.

Molar Flow Rate (re)

1. Under Results click the Molar Flow Rate (re) node. Enter the plot group name, `Molar flow rate NH3, Nonisothermal` in the Label text field.
2. In the Settings window, under the data section, choose the saved solution `Study 1/Nonisothermal` from Data set list.
3. The title can be removed. Click to expand the Title section and in the Title type list choose None.
4. Expand the plot group node and click the Global 1 node. In the Settings window, click Replace Expression in the y-Axis Data section. Under Component 1>Reaction Engineering choose `comp1.re.F_NH3`.
5. Find the Coloring and style section and expand it. Type `2` in the Width text field.
6. Expand the Legends section. In the Include subsection click to clear the Expression check box.
7. .Click Plot on the 1D Plot Group toolbar to generate Figure 5.

Study 1

Furthermore, the single channel model can be solved to check the selectivity within a narrower inlet dosage ratio, for example between 1.3 and 1.5.

Parametric Sweep

1. Under Study 1 click Parametric Sweep.
2. In the Settings window, locate the Study Settings section. Change the text in the Parameter value list to `range(1.3,0.1,1.5)`.
3. On the Home toolbar, click Compute.

Parametric Solutions 1 - Copy 1

First save the current solution.

1. In the Model Builder under Study 1>Solver Configurations, right-click Parametric Solutions 1 . From the Solution menu, select Copy .
2. In the Settings window for the copied solution, type `Nonisothermal 2` in the Label text field.

Temperature (re)

Follow these steps to generate the results in Figure 6.

1. Under Results click the Temperature (re) node. In the Settings window, enter `Selectivity, Nonisothermal` in the Label text field.
2. Under the Data section from the Data set list, choose the saved solution Study 1/Nonisothermal 2.
3. Click to expand the Title section. From the Title type list choose None.
4. Move the legend box by choosing Middle right in the Position list in Legend section.

Selectivity, Nonisothermal

1. In the Model Builder expand the plot group node and click Global 1 .
2. In the Settings window in the y-Axis Data section click Replace Expression . Either search for or select `comp1.S` from the Component 1>Definitions>Variables menu.
3. Expand the Coloring and style section. Type `2` in the Width text field.
4. Locate the Legends section. In the Include subsection click to clear the Expression check box.
5. Click Plot to generate Figure 6.

It can also be interesting to have a plot group displaying the temperature within the reactor.

1. Right-click the Selectivity Nonisothermal node and choose Duplicate .
2. In the Settings window of the duplicated node, enter `Temperature, Nonisothermal` in the Label text field.

1 Expand the plot group node and click the Global 1 node. In the Settings window, click Replace Expression in the y-Axis Data section. Under Component 1>Reaction Engineering choose `comp1.re.T`.

2 Click Plot on the 1D Plot Group toolbar.

Note: The model so far is available from the Application Libraries under the folder `Tutorials`. As an option, you can open the model file `monolith_kinetics.mph` from this folder and continue with the following step-by-step instructions.

The 3D model aims to make use of several inbuilt thermal and transport properties. This needs first to be accounted for in the Reaction Engineering ( ) interface.

Global Definitions - Parameters

The optimal NH_3:NO ratio in `monolith_kinetics.mph` is utilized in this model.

1 In the Model Builder, expand Global Definitions then click Parameters 1 .

2 In the Parameters table enter `1.35` in the Expression column for the parameter `X0`. Replace the existing value.

At the end of the parameter list, add following new parameters:

3 The 3D model will also make use of a porosity parameter (the gas phase volume fraction) in several locations. Add the parameter `por`, with the value `0.75` and the description `Gas phase volume fraction`.

4 Add `Density of nitrogen at inlet` temperature as a parameter `d_N2_in` with value of `0.65[kg/m3]`. This value is extracted from density function for nitrogen at Thermodynamics (see Species Property).

5 Add parameter `A_in` for `Inlet cross sectional area`. This is evaluated as `3359.9[mm]` by selecting the inlet area from measure feature under Geometry .

6 Add parameter `M0_in`, with value of `v_av*por*A_in*d_N2_in` and the description `Mass flow inlet`.

Reaction Engineering (re)

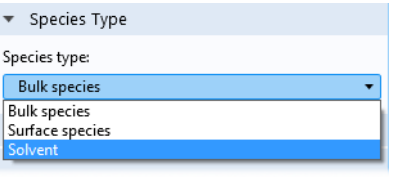
Now, locate settings window in the Reaction Engineering (re) node to activate transport properties that are to be used in the space-dependent 3D model.

Species: N2

In many gaseous systems with nitrogen, this species is often in excess and therefore acts as a solvent. This can be assumed in this model too. This simplifies computation of several transport properties considerably.

1 In the Model Builder click Species: N2 .

2 In the Settings window locate the Species Type section. Choose Solvent from the Species type list.



Thermodynamics node provides all such information for the system by Selecting Calculate Transport Properties check-box under Reaction Engineering settings window. Besides heat of reaction, all other thermo and transport properties are calculated from solvent properties, therefore all the functions are independent of mixture composition. To speed up the calculations, we can generate a Materials node with required properties from a Thermodynamic System.

In the next stage of the example, the actual 3D model of the monolithic reactor is set up, including reaction, mass transport, heat transfer, and fluid flow.

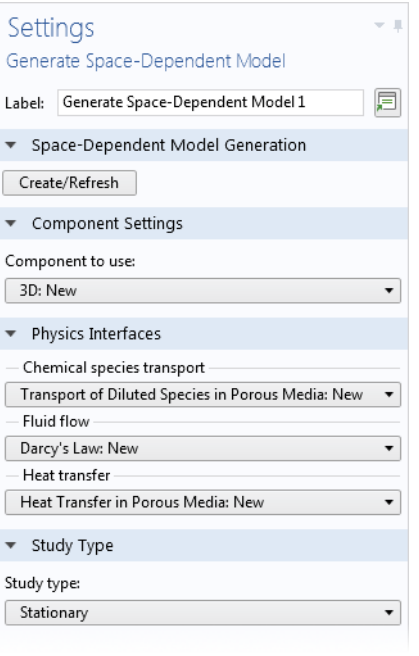
Generate Space-Dependent Model 1

The Generate Space-Dependent Model feature exports the reacting system set up in the plug flow channel model in the Reaction Engineering interface to a full 3D monolith model. Specifically, reaction kinetics, thermodynamics, and transport properties are transferred to the physics interfaces describing the space-dependent system. The reaction kinetics are all collected in a Chemistry interface within the 3D model.

1 On the Reaction Engineering toolbar click Generate Space-Dependent Model (or right-click Reaction Engineering (re) and choose it from the menu).

2 In the Physics Interfaces section:

- From the Chemical Species Transport list, choose Transport of Diluted Species in Porous Media: New.
- From the Fluid flow list, choose Darcy's Law: New.
- From the Heat transfer list, choose Heat Transfer in Porous Media: New.



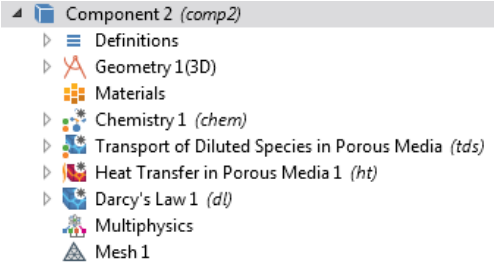
A Mass Balance is always required in this step and is therefore included in the model by default. No change in this setting is required, since the Transport of Diluted Species interface fits the gaseous mixture with a solvent well.

3 Go to the Space-Dependent Model Generation section. Click Create/Refresh. A 3D (the default in Component Settings section) component setup is initiated.

Add Physics Interfaces and Local Variables

In addition to the physics interfaces set up by the Generate Space-Dependent Model feature, you can add additional interfaces by clicking Add Physics on the Home toolbar.

Note: Under Component 2, a Chemistry node is automatically created for the 3D model. It includes the kinetic, thermal, and transport properties setup in the Reaction Engineering interface. If necessary, changes can be made directly to this node.



Component 2

First rename the Component node.

1. In the Model Builder click Component 2 (comp2).
2. Enter `3D Model` in the Label text field.

Variables 2

1. In the Home toolbar, click Variables a= and select Local variables. You can also go to the Model Builder under 3D Model, right-click Definitions , and select Variables a= .
2. In the Settings window for Variables, locate the Variables section.
3. In the table, enter the following settings:

NAME	EXPRESSION	UNIT	DESCRIPTION
S	`chem.r_1/chem.r_2`		`Selectivity`
a	`A0*exp(-E0/(R_const*chem.T))`	`1/s`	`Arrhenius correction`

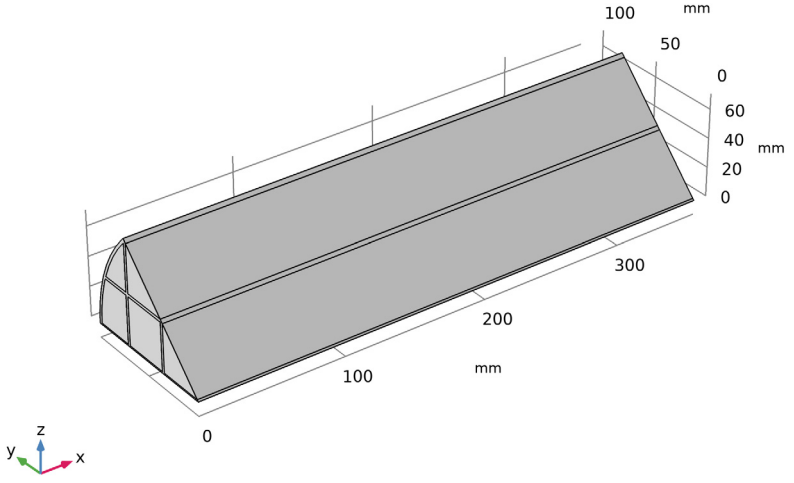
Geometry

Use the Geometry node to import a file with the reactor geometry. Symmetry reduces the modeling domain to one eighth of the full monolith.

1. On the Geometry toolbar click Insert Sequence .
2. Browse to the file `monolith_3d_geom_sequence.mph` in the application library folder on your computer, `Chemical_Reaction_Engineering_Module\Tutorials`. Double-click to add.

Note: The location of a file is based on the installation. For example, if the installation is on your hard drive, the file path might be similar to `C:\Program Files\COMSOL55\applications\`.

3 On the Geometry toolbar, Click Build All .



Definitions - Selections

A central part of the model setup consists of assigning features to domains and boundaries of the model geometry. The use of Explicit Selections features added to the geometry makes this process more efficient. The imported geometry sequence contains eight predefined Explicit Selection nodes. The names and the selected entities of these selections are seen in the table below.

NODE NAME	DOMAINS OR BOUNDARIES SELECTED
Supporting walls	domain 1 only
Channel blocks	domains 2, 3, 4, 5, and 6
Inlet	boundaries 4, 9, 13, 19, and 23
Outlet	boundaries 30, 31, 32, 33, and 34
Symmetry	boundaries 2, 3, 6, 8, 15, and 18
Inlet walls	boundary 1 only

NODE NAME	DOMAINS OR BOUNDARIES SELECTED
Outlet walls	boundary **29** only
Reactor surface	boundary **27** only

Domains or boundaries can be assigned to the Explicit nodes by clicking in the geometry. This adds the identification number of the domain or boundary to the Input Entities list. To remove a selection, click again to toggle.

Apart from the above Explicit Selections nodes, the sequence also contains a Union Selection, Inlet end, that contains all boundaries on the inlet. This selection is defined as a the union of the Inlet and the Inlet wall selections.

More Selection nodes are available from the Selections menu on the Geometry toolbar.

Materials

The next step is to specify material properties for the model. Ready-to-use materials can be selected from the available libraries or generated from Thermodynamics. Here we generate a material node for nitrogen (solvent) from our Gas System under Thermodynamics.

Thermodynamics

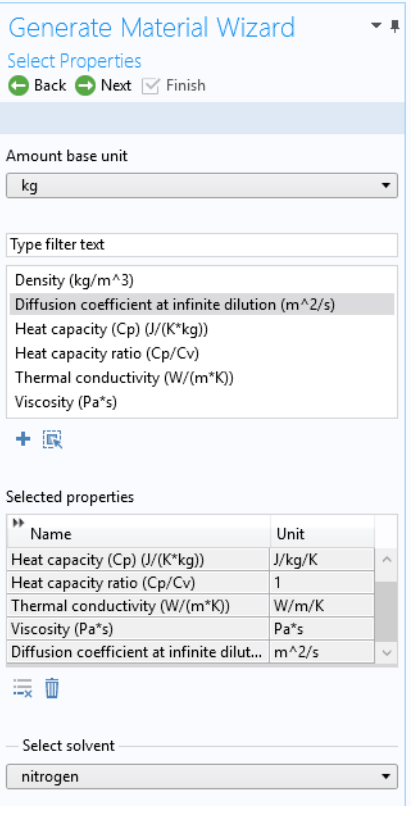
1. In the Model Builder, Under Global Definitions, locate Thermodynamics ( )> Gas System ( ).
2. right-click on Gas System and select Generate Material .

   This opens Generate Material Wizard which consists of several steps to create a Material node from our property package.
3. In Select Phase window, select Gas (default) and click Next ( ).
4. In Select Species window, add all species ( ) to the Select species table.
5. In Material composition section, set the mole fraction of nitrogen as 1 and 0 for others. Click Next ( ).

6 In the Select Properties window, add (✚) Diffusion coefficient at infinite dilution from property list table to the Selected properties table.

7 In the Select solvent section, select nitrogen from the drop-box. Click Next ( ).

8 In Define Material window, select Interpolation from the Function type drop-box. Set the Temperature upper bound (High) to 673. Click Finish ☑.



Assigning a material to selections in the geometry makes the physical properties of the material available in the physics interfaces.

MATERIAL

Material 1

1 In the Model Builder under 3D Model>Materials, click `Gas: ammonia(0)-nitrogen(1)-nitrogen oxide(0)-oxygen(0)- water(0)` .

2 In the Settings window, change the Label to `Gas: Nitrogen`.

3 In the Settings window for Material under Geometric Entity Selection, select Channel Blocks from the Selection list.

Next, create a user-defined material and associate it with the supporting walls.

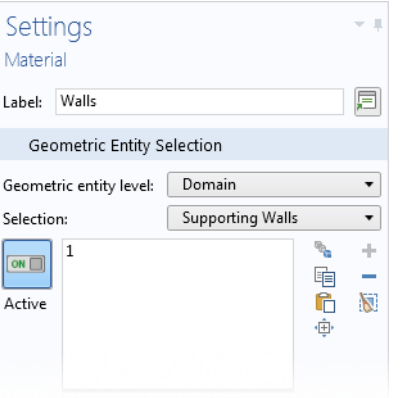
Material 2

1 On the Materials toolbar, click Blank Material .

2 Click Material 2 and press F2.

3 Enter `Walls` in the New label text field. Click OK.

4 In the Material settings window under Geometric Entity Selection, select Supporting walls from the Selection list.



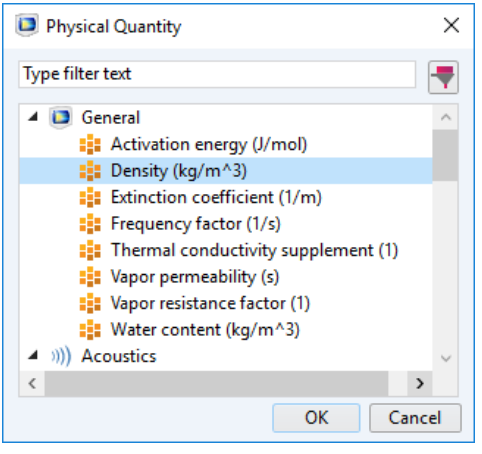
Walls

1 In the Model Builder under Materials, expand the Walls node and click Basic.

2 In the settings window, Locate the Output Properties section

3 Click the Add button under the table. This opens the Physical Quantity dialog.

4 Scroll the list and select Density in the General branch. Alternatively, type in density in the input field and click the Filter button to search for the quantity.



5 Click OK to add density as an output property of the Wall material.

6 In the Output Properties table, enter the following settings:

PROPERTY	VARIABLE	EXPRESSION
Density	rho	`2970[kg/m^3]`

7 Use the Add button + under the Output Property table to repeat the procedure for the heat capacity and thermal conductivity.

8 Add Heat capacity at constant pressure in the Transport branch.

9 In the Output properties table, enter the following settings:

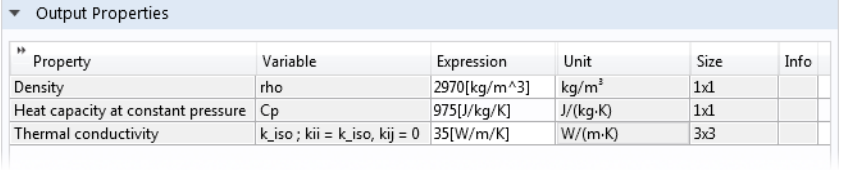
PROPERTY	VARIABLE	EXPRESSION
Heat capacity at constant pressure	Cp	`975[J/kg/K]`

10 Add Thermal conductivity in the Transport branch.

11 In the Output properties table, enter the following settings:

PROPERTY	VARIABLE	EXPRESSION
Thermal conductivity	{k_iso, kii = k, kij = 0}	`35[W/m/K]`

The Output Properties table should now match this figure.



In the next stage of the model, the physics interfaces are set up to describe the mass transport, heat transfer, and fluid flow in the monolithic reactor.

Chemistry 1 (chem)

In the Model Builder toolbar, click Collapse All to get a better overview of the tree for the remainder of the model setup.

Set the pressure to default in order to calculate transport properties (diffusivity) for the mass transport interface.

1 Click to expand 3D Model and click the Chemistry 1 (chem) node.

2 In the Settings window for Chemistry, locate the Model Inputs section.

3 From the p list, choose User defined. In the associated text field, type `1[atm]`.

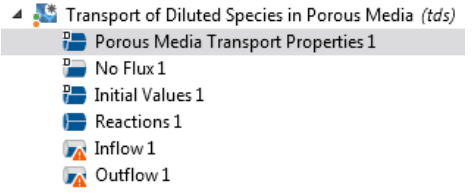
1 Under 3D Model, click Transport of Diluted Species in Porous Media (tds) .

2 In the Settings window under Domain Selection, select Channel blocks from the Selection list.

Porous Media Transport Properties 1

The mass transport model for the monolith channels assumes that there is only diffusive mass transport in the axial direction of the reactor, here, along the x-axis. This can be accomplished by specifying the diffusivity only in the first element of the diagonal diffusion matrix.

1 Expand the Transport of Diluted Species in Porous Media (tds) node and click the Porous Media Transport Properties 1 node . The 'D' in the upper left corner of a node means it is a default node.



2 In the Settings window, locate the Model Input section. The Temperature is automatically set to the Common model input value. Click the Go to Source button to go to the Default Model Inputs node and check that the common model input value is the variable `T` computed by the Heat Transfer in Porous Media interface.

3 Under Matrix Properties, select User defined from the Porosity list. Type `por` in the associated text field.

4 Under Convection, from the **u** list, choose Darcy's velocity field (dl).

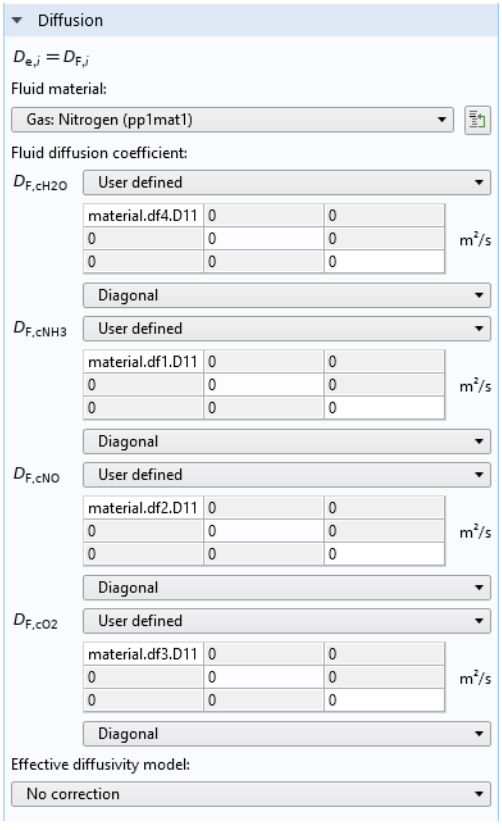
Fill in the tables under Diffusion as indicated in the next steps. Note that the variables predefined in the Diffusion coefficient fields correspond to diffusivity expressions set up by the Generate Space-Dependent Model feature.

5 From the D_{cH2O} Diffusion coefficient list, select Diagonal. In the table, enter the following settings:

`material.df4.D11`	0	0
0	0	0
0	0	0

6 Repeat the procedure for the rest of the species. Set all but the *xx*-component of the diffusion coefficients to zero.

The Diffusion section should now look like this figure:



The features defining reaction rates and inlet concentrations were automatically set up during the Generate-Space Dependent Model procedure. Definitions correspond to the reactor conditions specified for the plug flow channel model. Make sure that the features are assigned to the proper domains and boundaries of the 3D reactor.

This model is highly nonlinear due to the reaction kinetics. In this case, to solve all the physics simultaneously, starting from a non-reacting system leads to a more robust simulation. To achieve this set the initial concentrations to zero.

Initial Values 1

1 In the Model Builder under Transport of Diluted Species in Porous Media, click Initial Values 1 .

2 In the Settings window under Initial Values section, change the default concentrations to zero.

Inflow 1

1 In the Model Builder under Transport of Diluted Species in Porous Media, click Inflow 1 .

2 In the Settings window under Boundary Selection, select Inlet from the Selection list.

Outflow 1

1 In the Model Builder, click Outflow 1 .

2 In the Settings window under Boundary Selection, select Outlet from the Selection list.

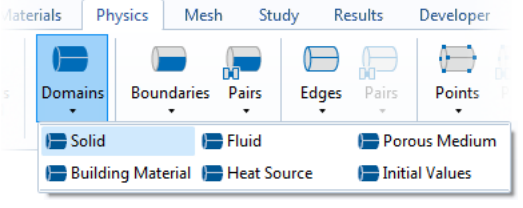
Heat Transfer in Porous Media1

At this point the Heat Transfer in Porous Media interface can be set up. Start by defining the conductive heat transfer in the supporting solid walls. Note that physical properties of the walls are taken from the material called Walls, associated with that domain.

Solids 1

1 In the Model Builder click the Heat Transfer in Porous Media interface node.

2 On the Physics toolbar, click Domains and choose Solid .

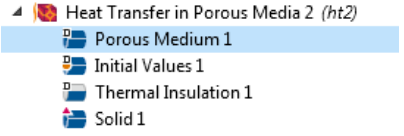


3 In the Settings window under Domain Selection, select Supporting walls from the Selection list.

Next specify the Fluid in Porous Medium feature, accounting for convective and conductive heat transfer in the channel blocks.

Porous Medium I

1 Click the default Porous Medium node .



2 Under Heat Convection section, from the **u** list, choose Darcy's velocity field (dl).

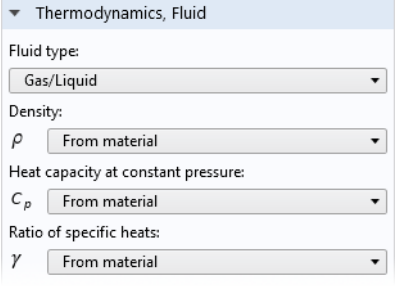
3 Under the Heat Conduction, Fluid section, select User defined from the Thermal conductivity (k) list and select Diagonal from the list.

Specifying the diagonal thermal conductivity elements allows you to represent anisotropic conductive heat transfer in the channel blocks.

4 In the k table, enter these settings:

`0.13[W/(m*K)]`	0	0
0	`0.25[W/(m*K)]`	0
0	0	`0.25[W/(m*K)]`

5 Under the Thermodynamics, Fluid section, select From material from each of these lists—Density (ρ), Heat capacity at constant pressure (C_p), and Ratio of specific heats (γ).



6 Under the Immobile Solids, add the volume fraction of the solid by entering `1-por` in the Volume fraction field.

7 Under the Heat Conduction, Porous Matrix and Thermodynamics, Porous Matrix, keep the properties defined from material.

Initial Values 1

1. In the Model Builder under Heat Transfer in Porous Media, click Initial Values 1 .
2. In the Settings window under Initial Values section, set the default Temperature to `T_in`.

Heat Source 1

Associate the heat source to the exothermic chemistry with the channel blocks. Note that the feature and the expressions describing the heat source are generated by the Generate-Space Dependent Model feature.

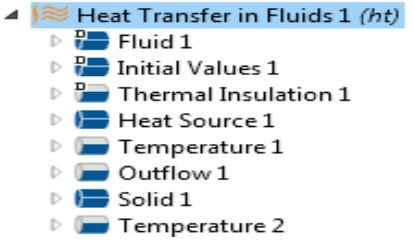
1. Under Heat Transfer in Porous Media 1 (ht) , click the Heat Source 1 node .
2. In the Settings window under Domain Selection, select Channel Blocks from the Selection list.

Setting the Boundary Conditions

Complete the set up of the Heat Transfer interface by assigning the temperature, outflow, heat flux, and symmetry boundary conditions.

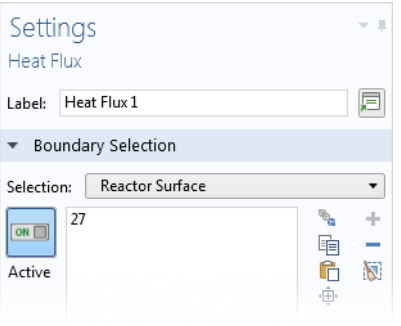
1. Click the Temperature 1 node . In the Settings window under Boundary Selection, select Inlet from the Selection list.
2. Click the Outflow 1 node . In the Settings window under Boundary Selection, select Outlet from the Selection list.
3. On the Physics toolbar, click Boundaries and choose Temperature .
4. In the Settings window under Boundary Selection, select Inlet walls from the Selection list. Under Temperature enter `T_in` in the Temperature (T_0) text field.

   The nodes in the Model Builder should match the figure so far.



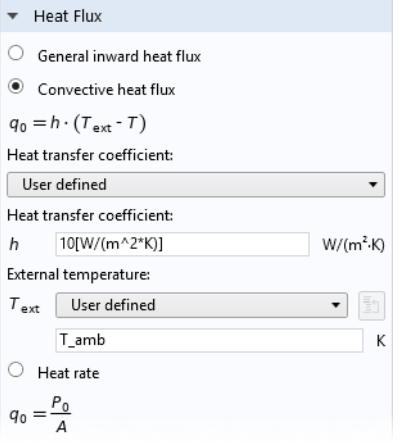
5 On the Physics toolbar, click Boundaries and choose Heat Flux .

6 In the Settings window under Boundary Selection, select Reactor surface from the Selection list.



7 Under Heat Flux click the Convective heat flux button.

- In the Heat transfer coefficient (h) text field enter `10[W/(m^2*K)]`.
- In the External temperature (T_{ext}) text field enter `T_amb`.



8 On the Physics toolbar, click Boundaries and click to add a second Heat Flux node .

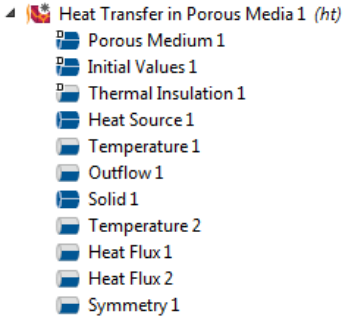
9 In the Settings window:

- Under Boundary Selection, select Outlet walls from the Selection list.
- Under Heat Flux click the Convective heat flux button. In the Heat transfer coefficient (h) text field enter `1`. In the External temperature (T_{ext}) text field enter `T_amb`.

10 On the Physics toolbar, click Boundaries and choose Symmetry .

11 In the Settings window for Symmetry under Boundary Selection, select Symmetry from the Selection list.

The node sequence in the Model Builder under the Heat Transfer in Porous Media interface should match this figure.



Darcy's Law Interface

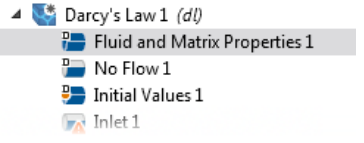
Follow these steps to set up the Darcy's Law interface and describe the fluid flow.

1 In the Model Builder under 3D Model, click the Darcy's Law 1 (dl) node .

2 In the Settings window under Domain Selection, select Channel blocks from the Selection list.

Fluid and Matrix Properties 1

1 Expand the Darcy's Law (dl) node and click Fluid and Matrix Properties 1 .



2 Locate the Model Input section. The Temperature is automatically set to the Common model input value.

3 Under Fluid Properties, from both the Density ρ and Dynamic_viscosity μ lists select From material.

4 Under Matrix Properties:

- From the Porosity ε_p list, select User defined. In the associated text field, enter `por`.

5 From the Permeability κ list, select User defined and `Diagonal`. In the table, enter the following settings:

`3.3e-7`	0	0
0	0	0
0	0	0

Boundary conditions are specified at the inlet and outlet of the monolith reactor.

Inlet 1

1 Under the Darcy's law 1 node click Inlet .

2 In the Settings window under Boundary Selection, select Mass flow from the selection list.

3 Under the Mass Flow section, locate Mass flow type and set it to Mass flow rate.

4 In Mass flow rate M0, enter `M0_in`.

Pressure 1

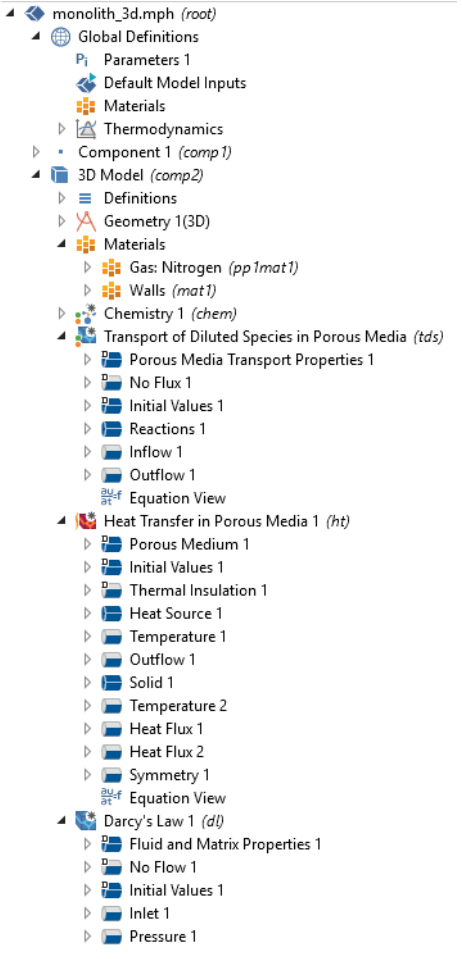
1 In the Physics toolbar, click Boundaries and choose Pressure .

2 In Boundary Selection list, select Outlet.

Outlet 1

1 Remove the unused Outlet 1 node , by right-clicking it and selecting Delete .

This completes the setup of the model equations describing the reacting flow and heat transfer in the monolith. The sequence of nodes for the 3D Model in the Model Builder should match the figure.



Before solving the problem numerically, the geometry needs to be discretized with a mesh.

Mesh

First create an unstructured mesh at the reactor inlet face and then complete the mesh by sweeping in the axial direction of the reactor.

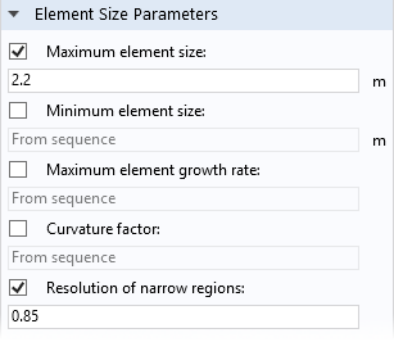
1 On the Mesh toolbar from the Boundary menu, select Free Triangular.

2 In the Settings window under Boundary Selection, select Inlet end from the Selection list.

3 Right-click Free Triangular 1 and select Size.

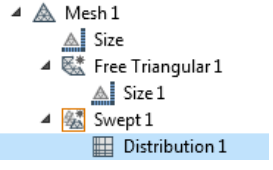
4 In the Settings window for Size:

- Choose Inlet walls from the Selection list.
- Click the Custom button in the Element Size section.
- Under Element size Parameters select the Maximum element size check box, then enter `2.2` in the associated text field. Note that the length unit is mm. This is controlled from the Geometry node.
- Select the Resolution of narrow regions check box and type `0.85` in the text field.



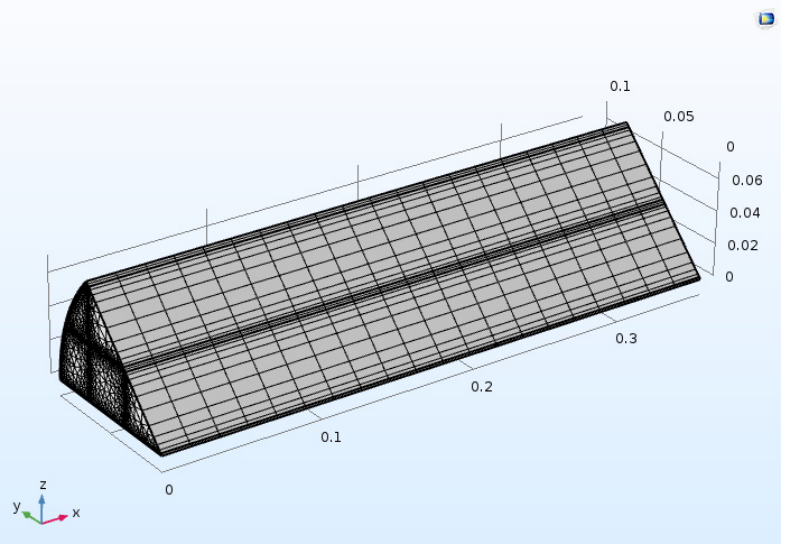
5 On the Mesh toolbar click Swept.

6 Right-click Swept 1 and select Distribution.



7 In the Settings window under Distribution, enter `20` in the Number of elements text field.

8 Click the Build All button then click the Zoom Extents button on the Graphics toolbar to view the entire geometry.



Study 2

It is time to solve the monolith model. Note that the Reaction Engineering interface should not be computed for the space-dependent model, it can only be solved for the 0D case. Therefore, keep the default study settings.

1 Right-click on Study 2 and press Compute .

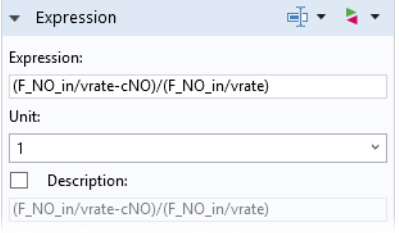
Results — 3D Model

Follow these steps to create Figure 8, Figure 9, and Figure 10 for the 3D monolith model.

3D Plot Group 7 - Conversion

1 In the Model Builder under Results, click to expand the 3D Plot Group 6 .
2 In the Settings window, enter `Conversion 3D Model` in the Label text field.
3 Right-click the Slice 1 node and select Disable .
4 Right-click the Conversion 3D Model node and select Isosurface .

5 In settings window locate the Expression text field, and type `(F_NO_in/vrate-cNO)/(F_NO_in/vrate)`. This plots the conversion of NO in the reactor.



6 Under Levels, in the Total levels text field type `20`.

7 On the Graphics toolbar, click the Zoom Extents button.

8 Click the Plot button .

The plot in Figure 8 is displayed in the Graphics window.

Temperature (ht1)

1 Click to expand the Temperature (ht1) node .

2 In the Settings window, enter `Temperature 3D Model` in the Label text field.

3 Right-click the Surface node and select Disable .

4 On the Temperature 3D Model toolbar, click Slice .

5 Click to select the Slice 1 node.

6 In the Expression section, click the Replace Expression button . Select 3D Model>Heat Transfer in Porous Media 1>Temperature (T) from the list, or enter `T` in the Expression text field.

7 Under Plane Data enter `10` in the Planes text field.

8 In the Graphics window, click the Zoom Extents button.

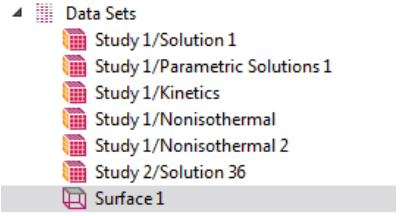
9 Click the Plot button .

The plot in Figure 9 is displayed in the Graphics window.

Data Sets

To generate a plot of the selectivity parameter S, first define a data set on the mirror plane cutting the channel blocks in half.

1 On the Results toolbar, click More Data Sets and choose Surface.



2 Select boundaries 6 and 15 only (the top symmetry boundaries on the channel blocks).

2D Plot Group 14 - Selectivity 3D model

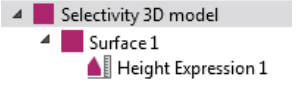
1 On the Home toolbar click Add Plot Group and choose 2D Plot Group.

2 In the Settings window for the created 2D Plot Group 13, type `Selectivity 3D model` in the Label text field.

3 On the Selectivity 3D Home toolbar click Surface.

4 In the Settings window click the Replace Expression button. Select 3D Model>Definitions>Variables>S-Selectivity (or enter `S` in the Expression text field).

5 Right-click Surface 1 and select Height Expression.



6 On the Graphics toolbar, click the Zoom Extents button.

7 Click the Plot button.

The plot in Figure 10 is displayed in the Graphics window.

Plot groups not used can be deleted by right-clicking and selecting Delete.