INTRODUCTION TO

Chemical Reaction Engineering Module

6.0

COMSOL

Introduction to the Chemical Reaction Engineering Module

Contact Information

Visit the Contact COMSOL page at www.comsol.com/contact to submit general inquiries or search for an address and phone number. You can also visit the Worldwide Sales Offices page at www.comsol.com/contact/offices for address and contact information.

If you need to contact Support, an online request form is located at the COMSOL Access page at www.comsol.com/support/case. Other useful links include:

- Support Center: www.comsol.com/support
- Product Download: www.comsol.com/product-download
- Product Updates: www.comsol.com/support/updates
- COMSOL Blog: www.comsol.com/blogs
- Discussion Forum: www.comsol.com/forum
- Events: www.comsol.com/events
- COMSOL Video Gallery: www.comsol.com/videos
- Support Knowledge Base: www.comsol.com/support/knowledgebase

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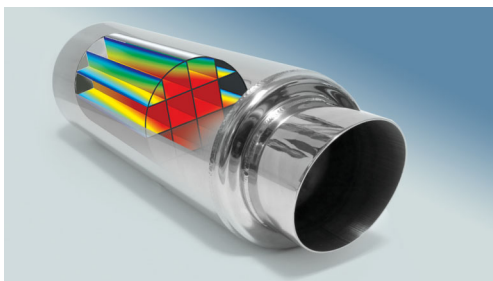
An overview of the interfaces and their functionality can be found in Chemical Reaction Engineering Module Interfaces.

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.
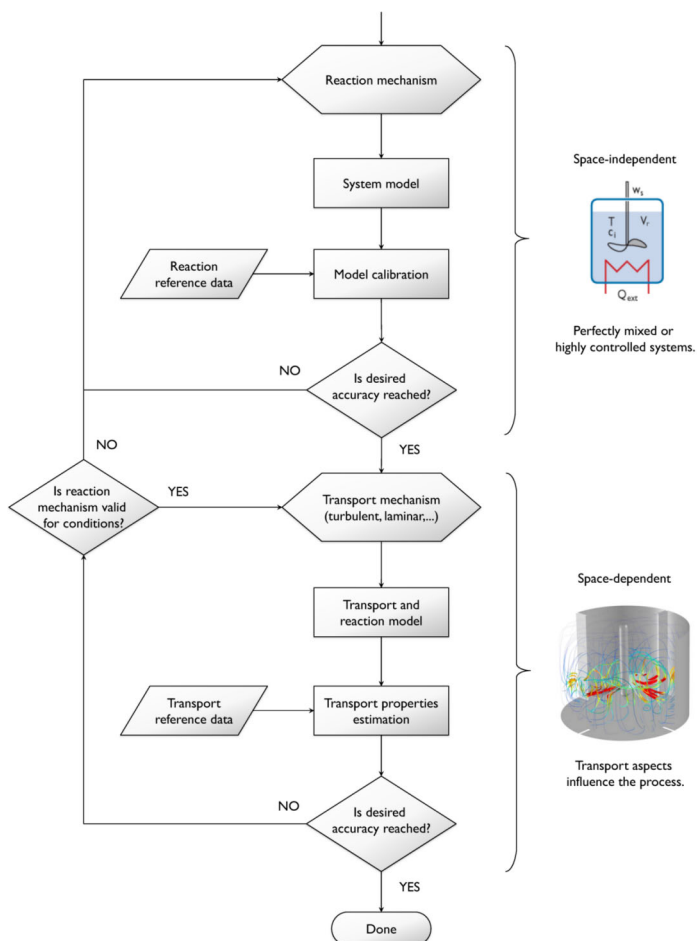

Figure 1: Flowchart summarizing the strategy for modeling reacting systems or designing chemical reactors.

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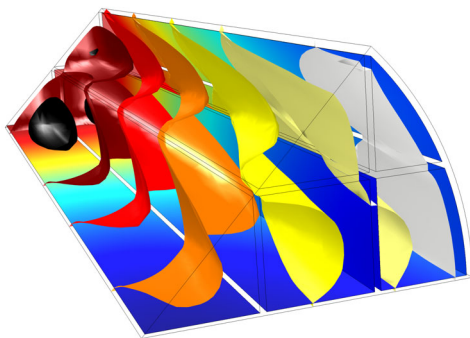
The temperature isosurfaces throughout a monolith reactor used in a catalytic converter. The surface plot shows the concentration profile of one of the reactants.

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.

By combining the Chemical Reaction Engineering Module with the CFD, and Heat Transfer Module, you are also able to incorporate turbulent flow, multiphase flow, and nonisothermal flow, as well as radiation heat transfer.

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 (⚬) provides libraries of chemical reactions for use by other physics interfaces. It also provides kinetic expressions for reaction rates, reaction heat sources, and species transport properties to other interfaces. This interface is 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 (that is, 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 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. Similar to the Transport of Diluted Species interface, 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 assumed to be immobile.

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 from 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 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 Nonisothermal Reacting Flow, Laminar Flow interface ( ) combines Transport of Concentrated Species, Chemistry, Laminar Flow and Heat Transfer in Fluids interfaces to treat the transport of mass, heat and momentum. The Heat Transfer in Fluids can take reaction heat and species enthalpy from Chemistry.

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

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

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

The Reacting Flow in Porous Media, Packed Bed, Transport of Concentrated Species interface ( ) treats concentrated reacting mixtures transported by a free

and/or porous media flow in a reactive pallet bed reactor. This multiphysics interface combines the functionality of the Brinkman Equations and Transport of Concentrated Species in Packed Beds.

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 Reacting Flow interfaces, and the Electrochemistry interfaces. The Electrochemistry interfaces require the addition of one of the Battery Design Module, the Corrosion Module, the Electrochemistry Module, the Electrodeposition Module, or the Fuel Cell & Electrolyzer 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 the 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 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 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 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 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 ( ), Heat Transfer in Porous Media ( ), Heat Transfer in Packed Beds ( ), and account for conductive and convective heat transfer. These features interact seamlessly and can be used in combination in a single model.

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 Multiphysics 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
Transport of Concentrated Species in Porous Media		tcs	all dimensions	stationary; time dependent
Nernst-Planck Equations		npe	all dimensions	stationary; time dependent
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

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE
≋ Reacting Flow				
Laminar Flow	≋	—	3D, 2D, 2D axisymmetric	stationary; time dependent
Laminar Flow, Diluted Species[1]	≋	—	3D, 2D, 2D axisymmetric	stationary; time dependent
≋ Nonisothermal Reacting Flow				
Laminar Flow	≋	—	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
Transport of Diluted Species, Porous Catalyst	▦	tds	3D, 2D, 2D axisymmetric	stationary; time dependent
Transport of Concentrated Species, Porous Catalyst	▦	tcs	3D, 2D, 2D axisymmetric	stationary; time dependent
Transport of Diluted Species, Packed Bed	▦	tds	3D, 2D, 2D axisymmetric	stationary; time dependent
Transport of Concentrated Species, Packed Bed	▦	tcs	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

PHYSICS INTERFACE	ICON	TAG	SPACE DIMENSION	AVAILABLE STUDY TYPE
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
Nonisothermal Flow				
Brinkman Equations		—	3D, 2D, 2D axissymmetric	stationary; time dependent; stationary, one-way NITF; time dependent, one-way NITF
Fluid-Structure Interaction				
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 Model: NO Reduction in a Monolithic Reactor

Introduction

This tutorial model presents a detailed description of how to set up a model of a catalytic converter for exhaust gas treatment. 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 the catalytic 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.

The system to be modeled is the selective reduction of nitrogen oxide (NO) in a monolithic reactor placed in the exhaust system of a diesel car. Exhaust gases from the engine pass through the channels of a monolithic catalytic reactor where, by adding ammonia (NH_3) to this stream, NO is 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.

Tutorial Modeling Strategy

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

In short, two models, hereafter referred to as Single Channel Model, and 3D Reactor Model, are set up.

The Single Channel Model is set up in two steps. The first step investigates the selectivity aspects of the kinetics. This is accomplished by modeling reaction rates as a function of temperature and relative reactant amounts. A plug flow reactor with a fixed temperature ramp is used. Reactant molar flow rates are kept constant as to isolate the effect of temperature and relative reactant amounts. Information from this model point to the general conditions required to attain the desired selectivity.

Having a better understanding of the reaction kinetics aids in the development of a more complex model. So, in the next step, the Single Channel Model is improved by including variations in flow rates as well as temperature, both as a result of catalytic activity. This more advanced model 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, the 3D Reactor Model of the catalytic converter is set up and solved. Suitable NH_3 dosing level resulting from the Single Channel Model is used. The 3D Reactor Model, using the Single Channel Model as a base, adds model geometry that enables modeling of mass transport, heat transfer, and fluid flow. The 3D Reactor Model thus provides insight and information for optimizing the dosing levels and other operational parameters.

Chemistry

Two parallel reactions occur in the monolithic reactor. The desired reaction is NO reduction by ammonia:

$$4NO + 4NH_3 + O_2 \longrightarrow 4N_2 + 6H_2O \tag{1}$$
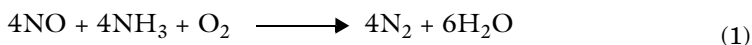
However, ammonia can at the same time undergo oxidation:

$$4NH_3 + 3O_2 \longrightarrow 2N_2 + 6H_2O \tag{2}$$
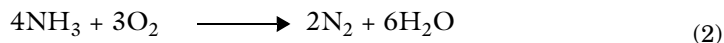
The heterogeneous catalytic conversion of NO to N_2 is described by an Eley-Rideal mechanism. A key reaction step involves the reaction of gas-phase NO with surface-adsorbed NH_3. The following rate equation (SI unit: $mol/(m^3 \cdot s)$) has been suggested in Ref. 1 for the desired reduction reaction (Reaction 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 reaction 2, the reaction rate (SI unit: mol/(m³·s)) is given by

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

where

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

The competing chemical reactions 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, it is important to avoid unnecessarily high levels of NH_3 in the gas stream leaving the catalytic converter.

Single 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.
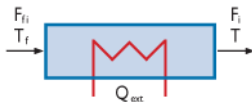
These equations are available withing the Plug flow reactor type in the Reaction Engineering interface.

MODEL EQUATIONS

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

$$\frac{dF_i}{dV} = R_i,$$ (5)

where F_i is the species molar flow rate (SI unit: mol/s), V represents the reactor volume (SI unit: m^3), and R_i is the species net reaction rate (SI unit: mol/(m^3·s)). The molar flow rate is related to the species concentrations, c_i (SI unit: mol/m^3), through the volumetric flow rate, v (SI unit: m^3/s):

$$F_i = vc_i,$$ (6)

where the volumetric flow rate is given by the average flow velocity, u (SI unit: m/s), multiplied by the reactor cross-section A (SI unit: m^2):

$$v = uA.$$ (7)

The energy balance for the ideal reacting gas is:

$$\sum_i F_i C_{p,i} \frac{dT}{dV} = Q_{ext} + Q,$$ (8)

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

$$Q = -\sum_j H_j r_j,$$

where H_j the heat of reaction (SI unit: J/mol), and r_j the reaction rate (SI unit: 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.

The model is first solved with Equation 5, Equation 6, and Equation 7 for several different ratios of reactant concentrations (NH$_3$:NO) and with a temperature ramp along the reactor. The molar flow rates of NH$_3$ and NO are kept constant throughout the reactor to investigate the temperature impact alone. Thereafter, Equation 8 is included; that is, nonisothermal conditions due to heat of reaction are studied.

Results

REACTION KINETICS STUDY

The competing chemical reactions, given by Reaction 1and Reaction 2 above, 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. The Reaction Kinetics Model looks at the reaction rates of the reduction and oxidation reactions as a function of temperature and relative amounts of reactants, keeping molar flow rates constant. Figure 3 shows reaction rates for the reduction reaction (Reaction 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.

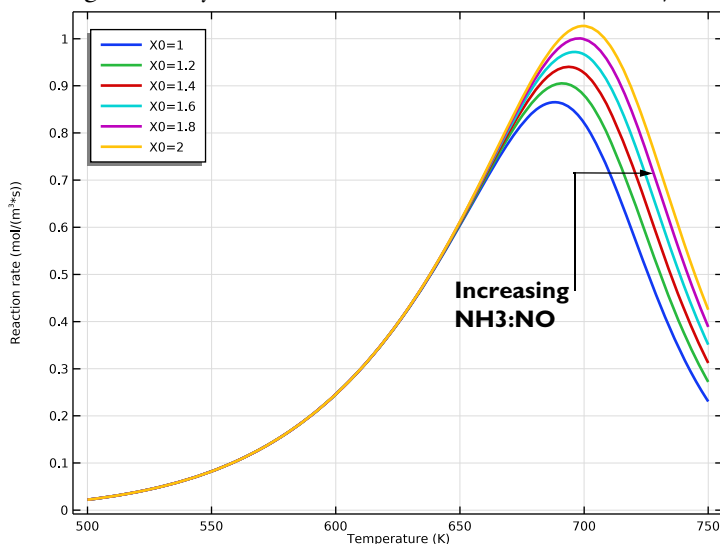Figure 3: Reaction rates of the NO reduction reaction (r_1) as a function of temperature. The NH_3:NO ratio ranges from 1 to 2 and the molar flow rates of NH_3 and NO are kept constant throughout the reactor.

The rate of NO reduction goes through a maximum and falls off at higher temperatures. Higher NH_3 concentration in the gas phase leads 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 toward 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.
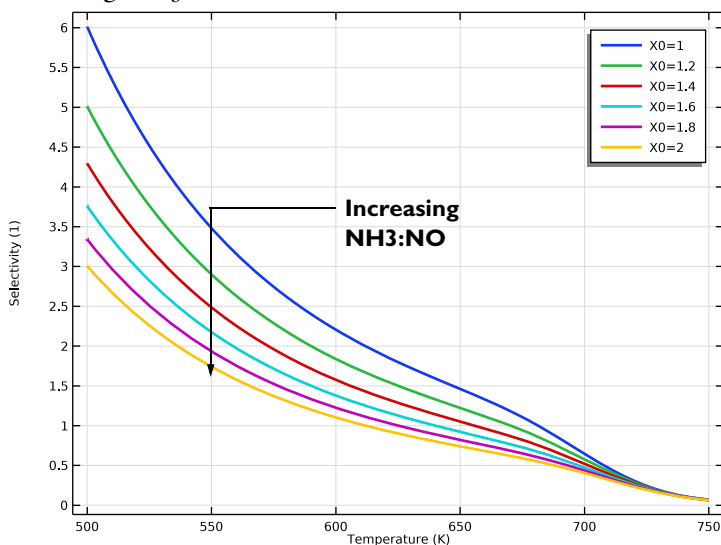

Figure 4: Selectivity parameter (r_1/r_2) as a function of temperature. The NH$_3$:NO ratio ranges from 1 to 2.

The Reaction Kinetics study results suggest that preferred working conditions involve moderate temperatures and relatively low ratios of NH$_3$:NO.

SINGLE CHANNEL MODEL

To further optimize the dosage of reducing agent, 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.
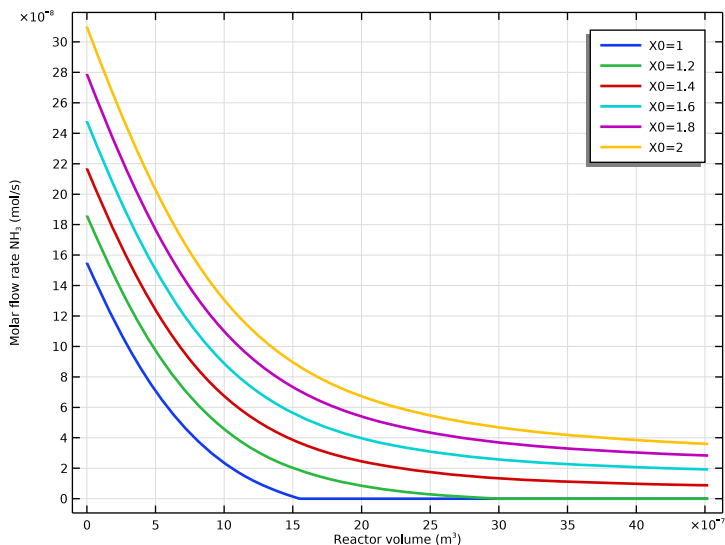

Figure 5: Molar flow rate (mol/s) of NH_3 as function of channel volume.

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.
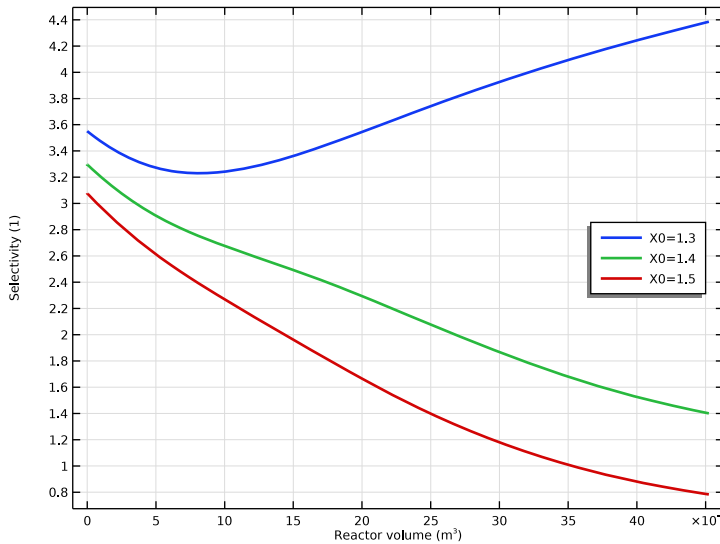
Figure 6: Selectivity parameter (r_1/r_2) as a function of channel volume. The NH_3:NO ratio ranges from 1.3 to 1.5.

Figure 7 shows the temperature, as well as the conversion of NO, throughout the single channel reactor. The maximum values for these properties are included. The highest temperature in the reactor is 532 K for $X0$ = 1.3, and 533 K for $X0$ = 1.5. The conversion of NO is practically 1 (99%) for both $X0$ values.
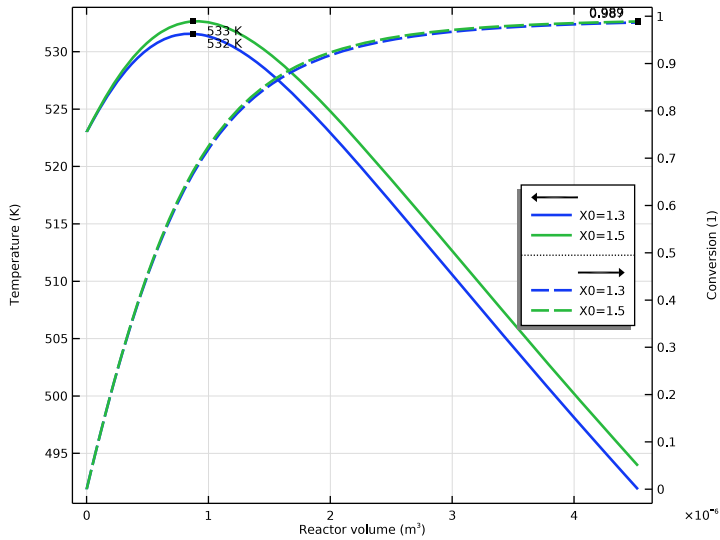
Figure 7: Temperature and conversion as a function of channel volume.

Investigating a 3D Reactor

It is clear 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.
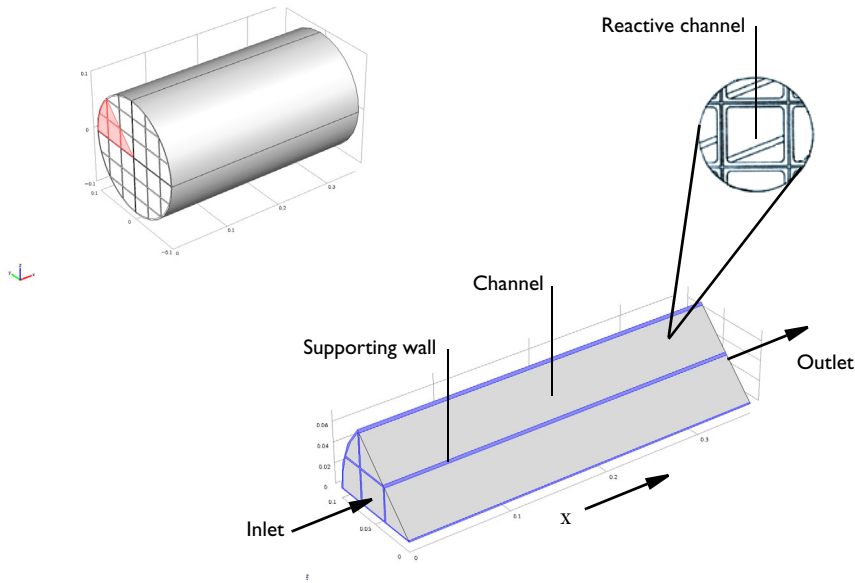
Figure 8: NO reduction chemistry takes place in the channel blocks. Supporting walls hold together the full reactor structure. Symmetry reduces the modeling domain to one eighth of the reactor geometry.

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 solid parts of the monolith structure. 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:

$$\nabla \cdot (-D_i \nabla c_i) + \mathbf{u} \cdot \nabla c_i = R_i \tag{9}$$

In Equation 9, D_i denotes the diffusion coefficient (SI unit: m^2/s), c_i is the species concentration (SI unit: mol/m^3), and $\mathbf{u}$ equals the velocity vector (SI unit: m/s). The term R_i (SI unit: mol/(m^3·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.

Species concentrations are defined at the reactor inlet boundaries:

$$c = c_{in}.$$

At the outlet, use the Outflow condition:

$$\mathbf{n} \cdot (-D\nabla c) = 0.$$

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:

$$\nabla \cdot (\rho \mathbf{u}) = 0 \tag{10}$$

$$\mathbf{u} = -\frac{\kappa}{\mu}\nabla p \tag{11}$$

The monolith is treated as a porous matrix with the effective permeability κ (SI unit: m^2). Similarly to the diffusivity, the y- and z-components of the permeability matrix are set to zero. The density, ρ (SI unit: kg/m^3), and viscosity, μ (SI unit: Pa·s), of the gas are assumed to be well represented by the temperature-dependent properties of nitrogen, as only relatively small concentrations of NO and NH$_3$ are present.

Pressure conditions are set at the reactor inlet and outlet boundaries.

Heat Transfer

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

$$(\rho C_p)_{eff}\frac{\partial T}{\partial t} + \rho_f C_{pf}\mathbf{u} \cdot \nabla T = \nabla \cdot (k_{eff}\nabla T) + Q \tag{12}$$

For the stationary case this reduces to:

$$\rho_f C_{pf} \mathbf{u} \cdot \nabla T = \nabla \cdot (k_{eff} \nabla T) + Q \qquad (13)$$

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

$$Q = Q_1 + Q_2 = -r_1 H_1 - r_2 H_2. \qquad (14)$$

Above, H_1 and H_2 (SI unit: $J/(mol \cdot K)$) are the heats of reaction.

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

$$k_{eff} = \Theta_s k_s + \Theta_f k_f. \qquad (15)$$

In Equation 15, Θ_s denotes the solid material's volume fraction, which is related to the volume fraction of the fluid Θ_f by:

$$\Theta_f + \Theta_s = 1. \qquad (16)$$

Equation 13 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:

$$-\nabla \cdot (k_s \nabla T) = 0, \qquad (17)$$

where k_s (SI unit: $W/(m \cdot K)$) is the thermal conductivity for the solid walls.

The temperature is specified at the reactor inlet walls boundary:

$$T = T_0,$$

and the Inflow condition; that is,

$$-\mathbf{n} \cdot \mathbf{q} = \rho \Delta H \mathbf{u} \cdot \mathbf{n}$$

is used at the inlet of the geometry. ΔH (SI unit: $J/(kg)$) is the sensible enthalpy. At the outlet, use the Outflow condition:

$$\mathbf{n} \cdot (k \nabla T) = 0.$$

For the reactor walls, the heat flux through the boundaries is given by

$$\mathbf{q}_m \cdot \mathbf{n} = h(T - T_{amb}),$$

where h (SI unit: W/(m²·K)) denotes the heat transfer coefficient, and T_{amb} (K) equals the ambient temperature.

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 Single Channel Model (plug flow model, (Equation 8)) and the 3D Reactor Model (Equation 13). 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 9 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 97% not seen in the plot, see Average Conversion and Maximum Temperature section on how to derive these values). This is somewhat lower than the 99% conversion predicted by the single channel model. 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.
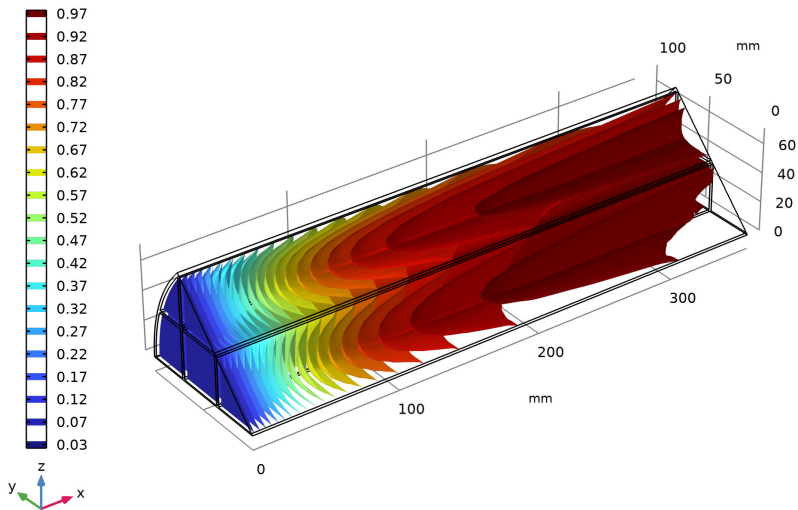
Figure 9: Isosurfaces showing the conversion of NO in the reactor. Fluid flow from left to right.

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 10.
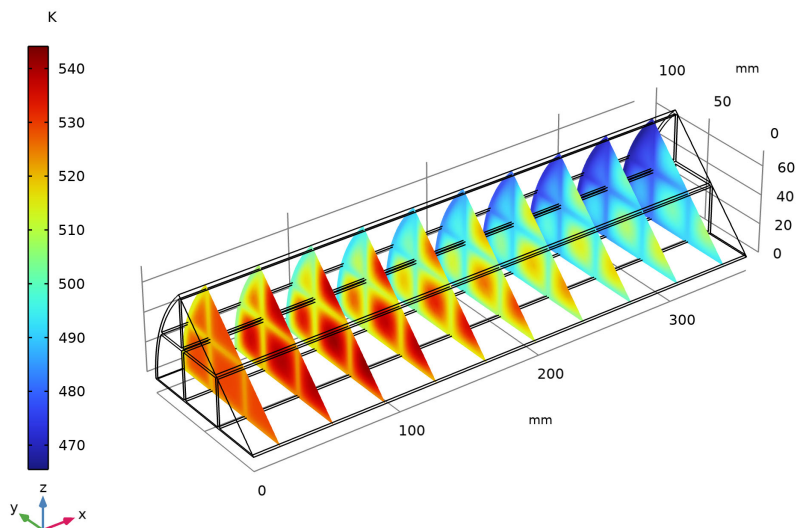
Figure 10: Temperature distribution in cross sections of the reactor. Fluid flow from left to right.

The exothermic reactions increase the temperature in the central parts of the reactor, while the temperature in the outer parts is decreased through heat loss to the surroundings. The maximum temperature calculated for the 3D reactor is 544 K (see Average Conversion and Maximum Temperature section on how to derive this value), which is about 10 K higher than for the single channel model. The effect of the relatively high thermal conductivity of the supporting walls is clearly visible.

A seen from the kinetic analysis in the Single Channel Model, elevated temperatures have a detrimental effect on the selectivity, leading to ammonia getting oxidized (Reaction 2) rather than be consumed in the NO reduction reaction (Reaction 1). The connection between temperature and selectivity is

clearly seen in the final plot in Figure 11, where both S and T are shown. Here, symmetry is used to visualize the full monolithic structure.
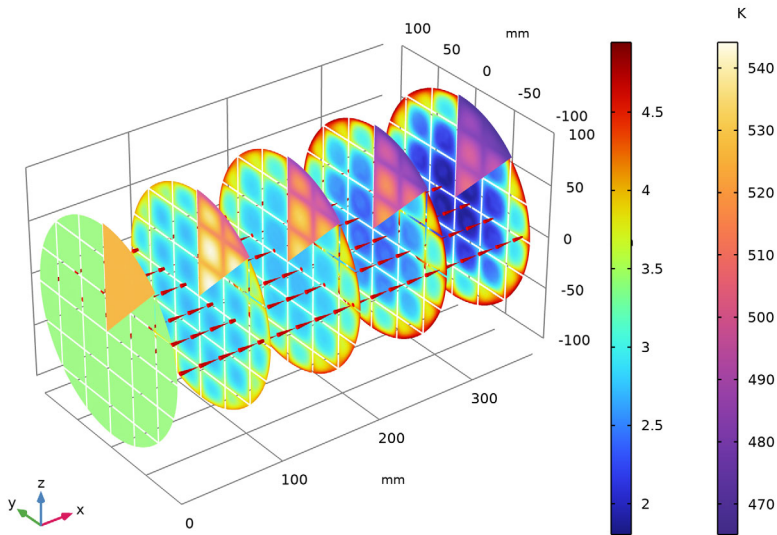
Figure 11: Selectivity and temperature in slices throughout the monolith reactor. Fluid flow from left to right.

Figure 11 shows that 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. The fact that r_1/r_2 is greater than 1 throughout the whole reactor means that the desired reduction reaction is favored. The inclusion of Darcy's velocity field aids in showing the flow direction through the reactor.

The information from this 3D model can also be used to investigate other aspects of this reacting system. For example, the 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 investigated.

Summary

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

- Single Channel Model — With a simple plug flow reactor model explore the reaction kinetics and narrow down the conditions that promote selectivity toward NO reduction. The tuning of the dosage is improved by performing the modeling in two steps; that is, by first isolating the impact of temperature and reactant ratio.

- 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 setup 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 Models

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

As an option to first build the Single Channel Model, you can open the completed model file for the Single Channel Model and proceed directly with the setup of the 3D Reactor Model. See Modeling Instructions: 3D Reactor Model for further details.

Both the Single Channel Model and the 3D Reactor Model are available in the Application Libraries, see `monolith_kinetics.mph` and `monolith_3d.mph`, respectively.

Here follows the step-by-step instructions guide to how to build the Single Channel Model and the 3D Reactor Model.

Modeling Instructions: Single Channel Model

By following these steps you will be able to set up the Single Channel Model.

Model Wizard

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

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

If COMSOL Multiphysics is already open, start the Model Wizard by choosing 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 choose the dimension of the modeling space.

2 In the Select Space Dimension window click the 0D · button.

3 In the Select Physics tree, expand the Chemical Species Transport node. Then double-click Reaction Engineering (re) ⚗ to add it to the Added physics list. Optionally, right-click and choose Add Physics + .

4 Click Study ➡ . In the Select Study tree, under Preset Studies for Selected Physics Interfaces, select 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 for example the dimensions of the reactive channels, the flow rate of the incoming gas and the inlet temperature. 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\COMSOL56\Multiphysics\applications\`.

PARAMETERS

1 In the Home toolbar, click Parameters P_i and choose Parameter 1 P_i .

Note: On Linux and macOS, 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 from the `txt`-file 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
L	0.36[m]	0.36 m	Channel length
A	pi*rad^2	1.2566E-5 m²	Channel cross section area
v_av	0.3[m/s]	0.3 m/s	Average gas velocity
vrate	v_av*A	3.7699E-6 m³/s	Volumetric flow rate
UA	200[W/(K*m^3)]	200 W/(m³·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[m^3/mol]	2.68E-17 m³/mol	Concentration correction factor
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 In the Home toolbar, click Variables $a=$ and choose Local variables (or in the Model Builder under Component 1, right-click Definitions ☰ , and choose 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))	m^3/mol	Concentration correction

Here, *re.r_1* is the variable name for the reaction rate for Reaction 1, see Equation 3. Since the reactions have not yet been added to the model, the expression for S is shown in yellow, indicating unknown variables. One way to find the generated variable names is shown in Equation View below.

Also notice the inbuilt function that automatically recognizes and adds the unit for variable a.

Thermodynamic System

Next, create a Thermodynamic System that includes all thermodynamic properties needed in the simulation of the reacting system. Included with the system comes the ability to set up predefined expressions for transport and thermodynamic properties. The transport expressions, for instance the species diffusivity coefficients, are used in the 3D reactor model described further on.

The thermodynamic properties are automatically coupled to the Reaction Engineering interface. The Thermodynamics feature is available under Global Definitions.

1 In the Reaction Engineering toolbar, click 📐 Thermodynamics and choose Thermodynamic System.

This opens the Thermodynamic System Wizard which is used to define a system, including phase and species, and to set up thermodynamics and transport properties models.

2 In the first step in the wizard, keep Gas as the Selected system. Click Next ➡ in the window toolbar.
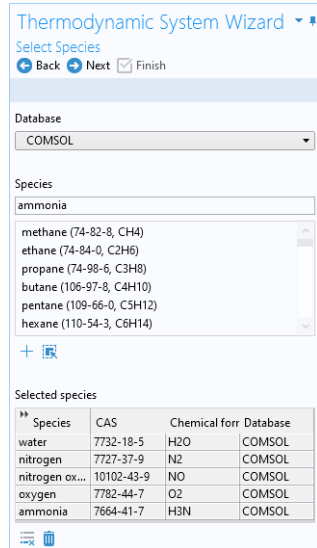
3 In Select Species window, type the name of the gas species that are present in the reactor system and Add ➕ them to the Selected species table. Click Next ➡.

4 In the Select Thermodynamic Model, keep Ideal gas as Gas phase model.

As an option, check the Advanced options check box to select transport properties for later use in the space-dependent model. For now, keep the default selection by leaving the box unchecked.

5 Click Finish ☑.

In the Settings window it is possible to review all the properties of the created Gas System 📈.

Reaction Kinetics

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).
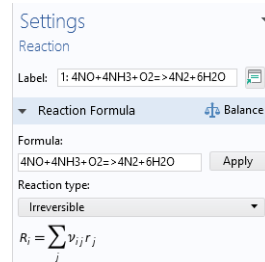
REACTION 1

1 In the Reaction Engineering toolbar, click Reaction 🏺 (or in the Model Builder window, under Component 1, right-click Reaction Engineering (re) 🏺 and choose Reaction 🏺).

2 In the Settings window for Reaction under Reaction Formula, type 4NO+4NH3+O2=>4N2+6H2O in the Formula text field.

3 Click Apply to generate the Reaction node as well as one Species node for each of the species in the Reaction Formula.

1: 4NO+4NH3+O2=>4N2+6H2O
Species: NO
Species: NH3
Species: O2
Species: N2
Species: H2O
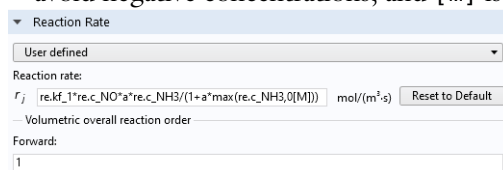
Notice that, there being several ways to balance this formula, the button Balance ⚖ is not applicable in this case.

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 from the literature.

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

6 In the Reaction rate (r_j) text field type re.kf_1*re.c_NO*a*re.c_NH3/ (1+a*max(re.c_NH3,0[M])). The max operator in the denominator helps avoid negative concentrations, and [M] is the unit molar.

▼ Reaction Rate

User defined ▾

Reaction rate:

r_j | re.kf_1*re.c_NO*a*re.c_NH3/(1+a*max(re.c_NH3,0[M])) | mol/(m³·s) | Reset to Default

Volumetric overall reaction order

Forward:

1

In the next step, update the reaction order to avoid unit errors.
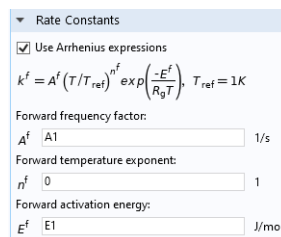
7 Under Volumetric overall reaction order, enter a Forward value of 1. This implies a rate constant with the unit 1 / s.

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, only the Forward reaction parameters are needed.

- In the Forward frequency factor (A^f) text field, type A1.

- In the Forward activation energy (E^f), type E1.

▼ Rate Constants

☑ Use Arrhenius expressions

$$k^f = A^f \left(T/T_{ref} \right)^{n^f} exp\left(\frac{-E^f}{R_g T} \right), \; T_{ref} = 1K$$

Forward frequency factor:

A^f | A1 | 1/s

Forward temperature exponent:

n^f | 0 | 1

Forward activation energy:

E^f | E1 | J/mol

In the same fashion, now define the reaction for ammonia oxidation.

REACTION 2

1 In the Reaction Engineering toolbar, click Reaction ⚗.

2 In the Settings window for Reaction, locate the Reaction Formula section. Type (or copy and paste) NH3+O2=>N2+H2O in the Formula text field.

3 Click Apply.

4 Click Balance ⚖ in the upper-right corner of the Reaction Formula section. This reaction can be balanced since there is only one solution to the balancing problem.

5 Locate the Reaction Rate section. From the Reaction Rate list choose User defined. Type `re.kf_2*re.c_NH3` in the Reaction rate (r_j) text field. Change Forward reaction order to 1.

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

-In the A^f text field, type A2.

-In the E^f text field, type E2.

Now that the reactions and kinetics settings are set, use Equation View to check what variable names that were generated.

Equation View

1 In the Model Builder window, click Show More Options 👁 .

2 Under Physics, check Equation View ∂u∂f check box. Click OK.

3 In the Model Builder window, expand the 1: 4NO+4NH3+O2=>4N2+6H2O node 🧪 . Click Equation View. Scroll through the Variables list to see the generated variable names, their expressions, units and descriptions.

Name	Expression	Unit	Description	Selection
re.Qheat	-re.r_1*re.H_1	W/m³	Heat source of reactions	Global
re.R_NH3	-4*re.r_1	mol/(m³·s)	Reaction rate for species NH3	Global
re.Rsum_N...	-4*re.r_1	mol/(m³·s)	Reaction rate for species NH3	Global
re.R_O2	-re.r_1	mol/(m³·s)	Reaction rate for species O2	Global
re.Rsum_O2	-re.r_1	mol/(m³·s)	Reaction rate for species O2	Global
re.R_N2	4*re.r_1	mol/(m³·s)	Reaction rate for species N2	Global
re.Rsum_N2	4*re.r_1	mol/(m³·s)	Reaction rate for species N2	Global
re.R_H2O	6*re.r_1	mol/(m³·s)	Reaction rate for species H2O	Global

After setting up the reaction kinetics, define the suitable reactor model where the reactions take place. Using the Reaction Engineering node you can choose one of the predefined reactor types. Since you are planning to set up a simple channel model, having chosen the Stationary Plug Flow study type previously, choose the Plug flow reactor.

As mentioned in the Tutorial Modeling Strategy, the first step is to investigate the selectivity aspects of the kinetics. This is accomplished by modeling reaction rates as a function of temperature and relative reactant amounts. A plug flow reactor with a fixed temperature ramp is used. Reactant molar flow rates are kept constant as to isolate the effect of temperature and relative reactant amounts.

1 In the Model Builder, click the Reaction Engineering (re) 🧪 node.

2 In the Settings window under Reactor Settings, from the Reactor type list choose Plug flow.

Now couple all species in Reaction Engineering to the corresponding species in the created Thermodynamic System.

3 Locate the Mixture Properties section. Select the Thermodynamics check box.

4 Locate the Species Matching section. In the table, match the species in Reaction Engineering to the same species in Thermodynamics. The table will look like this after matching:
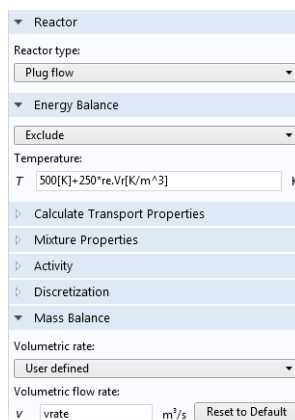
Since the volumetric flow rate should be kept constant in this particular example, choose to compute the pressure from the ideal gas law.

5 In the Mixture Properties section, choose Ideal gas law from the Reactor pressure list.

The following steps allow you to study the reaction rate for fixed reactant concentrations, solely as a function of temperature. First, use the independent variable V (reactor volume, written `re.Vr`) to set up a temperature ramp between 500 K and 750 K. Then, after defining initial values, lock the concentrations of reactant NO and NH_3 and add a Parametric sweep feature.

6 Locate the Energy Balance section. From the list, choose Exclude.

7 In the Temperature (T) text field, type `500[K]+250[K/m^3]*re.Vr`.

| 43

8 Locate the Reactor section. Find the Mass balance subsection. In the Volumetric flow rate (v) text field, type `vrate`, previously defined in the Parameters section.

INITIAL VALUES

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

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

2 In the Settings window for Initial Values, locate the Volumetric Species Initial Values 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 and reactant ratios 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 Constant concentration/activity check box in these sections to set the species concentration constant.
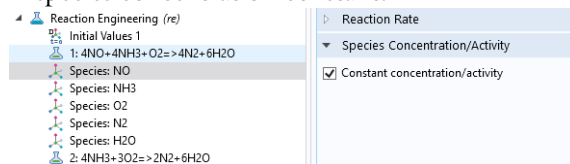
Study — Reaction Kinetics

Add a Parametric Sweep feature to solve the model for a set of NH_3:NO ratios.

PARAMETRIC SWEEP

1 In the Study toolbar click Parametric Sweep [icon].

2 Under Study Settings, click the Add ✛ button below the table. In the Parameter name column, choose `X0 (Ratio NH3 to NO at inlet)`.

3 Start with a quite wide range and narrow down the optimal *X0* values later. In the Parameter value list column, type `range(1,0.2,2)` to solve for ratios ranging from 1 to 2.
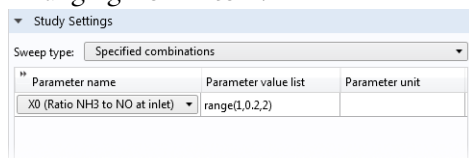
It is good practice to tighten the default solver tolerances and make sure that the solution plots do not change between consecutive runs. Both the relative and absolute tolerance should be tightened. In this case the relative tolerance needs to be reduced to 1e-7.

STEP 1: STATIONARY PLUG FLOW

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

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

3 In the Study toolbar click Compute ═ .

All the solutions generated by pressing Compute in the Study interface are saved and can be copied and modified. This step enables easy postprocessing of the results, since several different case studies, within the same model, can be saved and compared.

Results — Reaction Kinetics

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

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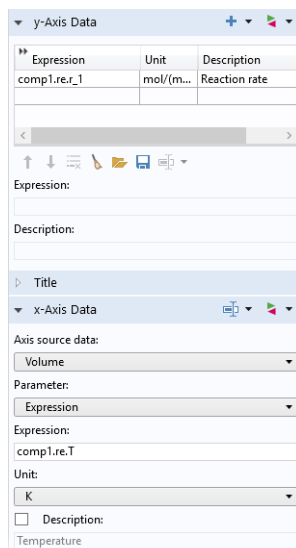
1 In the Model Builder under Study 1>Solver Configurations, right-click Parametric Solutions 1 and from the Solution menu choose Copy [icon].

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 fixed reactant ratios and temperature ramp.

REACTION RATE - FIGURE 3

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 Dataset 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. Ensure the x-axis label check box is ticked.

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

6 Scroll down to the Legend section and choose Upper left in the Position list.

7 In the Model Builder window, 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 choose `re.r_1` under Component 1>Reaction Engineering. Double-click the expression.

9 In the x-Axis Data section choose Expression from the Parameter list. Type `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 in the Graphics toolbar.

SELECTIVITY - FIGURE 4

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

1 In the Model Builder window, right-click the Reaction rate $\smile$ node and choose Duplicate $\boxed{\oplus}$.

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

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

4 Expand the Selectivity $\smile$ node and click Global 1 $\boxed{\circleddash}$.

5 In the Settings window, locate the y-Axis Data section. Click Replace Expression $\blacktriangleright$ $\blacktriangledown$ and under Component 1>Definitions>Variables choose `S - Selectivity` by double clicking.

6 In the Settings window for Global, click Plot $\boxed{\circeq}$ to generate Figure 4. Click the Zoom Extents $\boxed{\oplus}$ button in the Graphics toolbar.

Single Channel Model

With the results from the reaction kinetics study (Figure 3 and Figure 4) you now have an idea of how the reaction kinetics behave. With this information, continue the monolith system investigation by setting up a single channel model where the effects of generated heat, as well as varying reactant concentrations, are studied.

ENERGY BALANCE

1 In the Model Builder under Component 1 (comp1), click the Reaction Engineering (re) $\boxed{\triangle}$ node.

2 In the Settings window, locate the Energy Balance section. Choose Include.

3 Replace the expression in the External heating or cooling (Q) text field with (`T_amb-re.T`)`*UA`. Remember to use Equation View to find the variable names.

▼ Energy Balance		
Include		▼
External heating or cooling:		
Q	(T_amb-re.T)*UA	W/m³
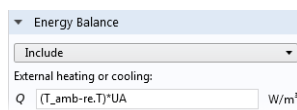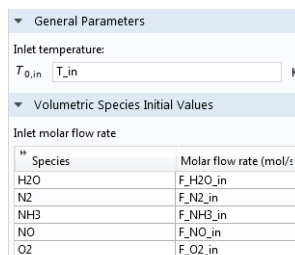
INITIAL VALUES

The inlet temperature needs to be defined as well.

1 In the Model Builder under Reaction Engineering, click Initial Values I $\boxed{\cdot}$.

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

SPECIES: NO AND SPECIES: NH3

The concentration within the reactor should be variable in the Single Channel Model.

General Parameters
Inlet temperature:
$T_{0,\text{in}}$ T_in   K

Volumetric Species Initial Values
Inlet molar flow rate
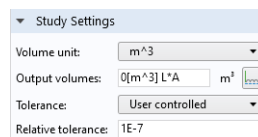
Species	Molar flow rate (mol/s)
H2O	F_H2O_in
N2	F_N2_in
NH3	F_NH3_in
NO	F_NO_in
O2	F_O2_in

1 In the Model Builder, one at a time click the Species: NO and Species: NH3 ⚛ nodes.
2 Click to clear the Constant concentration/activity check box in the Species Concentration/Activity section.

Study — Broad Parametric Sweep

Solve the model with the new reactor settings. The Parametric Sweep settings are active and will be applied.

STEP 1:STATIONARY PLUG FLOW

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

Study Settings		
Volume unit:	m^3	
Output volumes:	0[m^3] L*A	m³
Tolerance:	User controlled	
Relative tolerance:	1E-7	

2 In the Settings window locate the Study Settings section. In the Output volumes text field, type 0[m^3] L*A to solve the model for a tube reactor with the length L [m] and cross section area A [m^2]. These two variables were added in Parameters.
3 Click Compute ⚌.

Results — Figure 5

PARAMETRIC SOLUTIONS

First save the current solution.

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

Follow these steps to generate Figure 5.

1 In the Model Builder window, under Results click the Molar Flow Rate (re) $\sim$ node. Type 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 Dataset list.

3 The title can be removed. Click to expand the Title section and in the Title type list choose None.

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

5 Type `Molar flow rate NH<sub>3</sub> (mol/s)` in the associated text field.

6 In the Model Builder window, expand the Molar flow rate NH3, Nonisothermal node, then click Global 1 . In the Settings window, click Replace Expression in the y-Axis Data section. Under Component 1>Reaction Engineering choose `re.F_NH3`.

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

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

9 Click Plot in the 1D Plot Group toolbar to generate Figure 5.

Study — Narrow Parametric Sweep

Use the results presented in Figure 5 to refine the range of reactant ratios *X0* to solve the model for.

1 In the Model Builder window, 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 In the Home toolbar, click Compute .

Results — Figure 6

First save the current solution.

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

2 In the Settings window for the copied solution, type `Nonisothermal 2` in the Label text field.

SELECTIVITY - FIGURE 6

Follow these steps to generate the results in Figure 6.

1 Under Results click the Temperature (re) ∿ node. In the Settings window, type `Selectivity, Nonisothermal` in the Label text field.

2 Under the Data section from the Dataset 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.

5 In the Model Builder expand the plot group node and click Global 1 ⊝.

6 In the Settings window in the y-Axis Data section click Replace Expression ▶ ▾ . Either search for or choose `S-Selectivity` from the Component 1>Definitions>Variables menu.

7 Expand the Coloring and Style section. Type `2` in the Width text field.

8 Locate the Legends section. In the Include subsection click to clear the Expression check box.

9 Click Plot ▣ to generate Figure 6.

In the last steps of the Single Channel Model tutorial, create Figure 7, displaying temperature and conversion as a function of reactor volume. Graph markers are added to display the maximum temperature and conversion reached in the reactor.

TEMPERATURE - FIGURE 7

1 In the Model Builder window, under Results, right-click the Selectivity Nonisothermal ∿ node and choose Duplicate ⎘.

2 In the Settings window of the duplicated node, type `Temperature, Nonisothermal` in the Label text field.

3 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 `re.T-Temperature-K`.

Now add the Graph Markers for the temperature data.

1 Click Plot ▣ in the 1D Plot Group toolbar.

2 Right-click Global 1 and choose Graph Marker.

3 In the Settings window for Graph Marker, locate the Display section.

4 From the Display list, choose Max.

5 Locate the Text Format section. In the Display precision text field, type **3**.

6 Select the Include unit check box.

CONVERSION - FIGURE 7

1 Right-click Global 1 and choose Duplicate ▣.

2 In the Settings window for Global, locate the y-Axis Data section.

3 Click Clear Table ▲ .

4 In the table, enter the expression for conversion, and add a description in the Description field. The table will look like this:

Expression	Unit	Description
(F_NO_in/vrate-re.c_NO)/(F_NO_in/vrate)	1	Conversion

Now add the Graph Marker for conversion.

1 In the Model Builder window, expand the Global 2 node, then click Graph Marker 1.

2 In the Settings window for Graph Marker, locate the Text Format section and clear the Include unit check box.

3 Click to expand the Coloring and Style section. From the Anchor point list, choose Lower right.

We have now added temperature and conversion data, as well as Graph Markers to the plot group called Temperature, Nonisothermal. In the last few steps, exclude some of the data curves from the plot group, add a secondary y-axis and change line styles.

1 In the Model Builder window, click Temperature, Nonisothermal.

2 Locate the Data section in the Settings window and choose From list in the Parameter selection X0 list

3 In the Parameter values (X0) list, choose 1.3 and 1.5.

Data	
Dataset:	Study 1/Nonisothermal 2 (sol32)
Parameter selection (X0):	From list
Parameter values (X0):	
1.3	
1.4	
1.5	

4 Locate the Plot Settings section. Select the Two y-axes check box.

5 In the table, select the Plot on secondary y-axis check box for Global 2.

6 In the Temperature, Nonisothermal toolbar, click Plot ▣ .

7 Click Global 2 and locate the Coloring and Style section in the Settings window.

8 From the Color list, choose Cycle (reset).

9 Find the Line style subsection. From the Line list, choose Dashed.

Modeling Instructions: 3D Reactor Model

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 Reactor 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 found in the Single Channel Model, that is, `monolith_kinetics.mph`, is utilized in this model. Start by changing this value in the Parameters section.

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

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

At the end of the parameter list, add the 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 T_in` as a parameter `d_N2_in` with a value of `0.65[kg/m^3]`. This value is extracted from the density function for nitrogen at Thermodynamics (see Species Property).

5 Add parameter `A_in` for `Inlet cross sectional area` with the value `3359.9[mm]`. (For information: The value for this parameter can be calculated by selecting the inlet area from the Measure feature under Geometry . This can be done when the Geometry is defined.)

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

The 3D Reactor Model uses the 0D Single Channel Model as a base. Before connecting the 0D model to the other physics interfaces, as well as a reactor geometry, implement the assumption that nitrogen, being in excess, works as a solvent. This simplifies computation of several transport properties considerably. After that, generate a space-dependent model.

N2 AS SOLVENT

1 In the Model Builder window, expand the Reaction Engineering node under Component 1.

2 Click Species: N2.

3 In the Settings window locate the Species Type section. Choose Solvent from the Species type list.
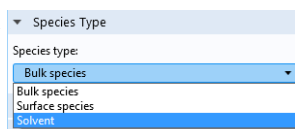
GENERATE SPACE-DEPENDENT MODEL

The Generate Space-Dependent Model feature creates a link between the plug flow single channel model and the full 3D reactor model. This enables transfer of reaction kinetics, thermodynamics, and transport properties, set up in the Reaction Engineering interface, to the physics interfaces describing space and time-dependent systems. The reaction kinetics are all collected in a Chemistry interface within the 3D model.

1 In 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.

3 Locate the Space-Dependent Model Generation section. Click Create/Refresh. A 3D (the default in Component Settings section) component setup is initiated.
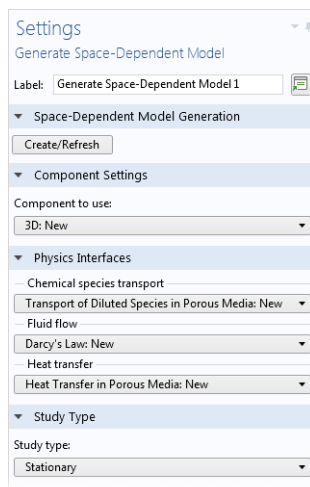
The new 3D component, called Component 2, appears in the Model Builder window. A Chemistry ⚛ node is automatically created. It includes the kinetic, thermal, and transport properties setup in the Reaction Engineering interface. If necessary, changes can be made directly to this node.
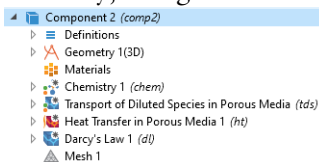
Note: In addition to the three physics interfaces that were added with the Generate Space-Dependent Model feature, additional interfaces can be added by clicking Add Physics ⚛ in the Home toolbar.

Setting up the 3D Model

First rename the Component node.

COMPONENT 2

1 In the Model Builder click Component 2 (comp2).

2 Type 3D Model in the Label text field.

Now define some variables that will be needed.

VARIABLES

1 In the Home toolbar, click Variables a= and choose Local variables. Optionally, go to the Model Builder window, expand the 3D Model node, right-click Definitions ≡ , and choose 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))	$m^3/$ mol	Concentration 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 In 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\COMSOL60\Multiphysics\applications\`.

3 In the Geometry toolbar, click Build All .
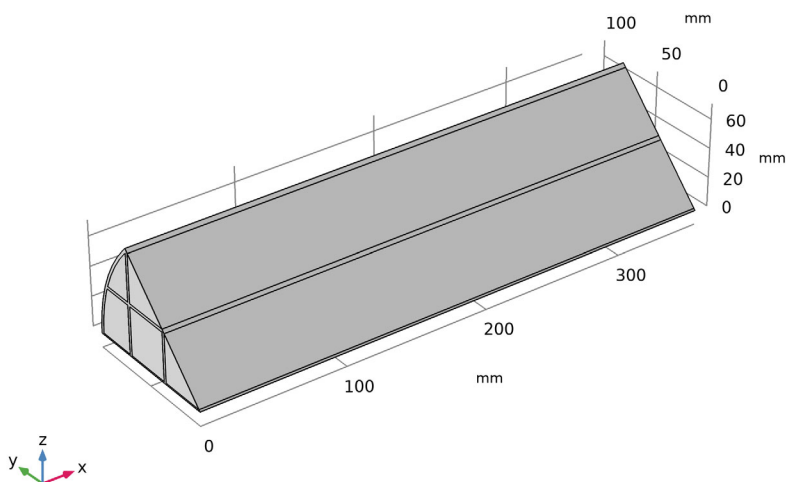
Note: In this step-by-step, focusing on the Chemical Reaction Engineering Module, all geometry settings are already done. For information, a central part of the model setup consists of assigning features to domains and boundaries of the model geometry. The use of Explicit Selections features added to 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**

NODE NAME	DOMAINS OR BOUNDARIES SELECTED
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
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 the union of the Inlet and the Inlet wall selections.

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

Materials
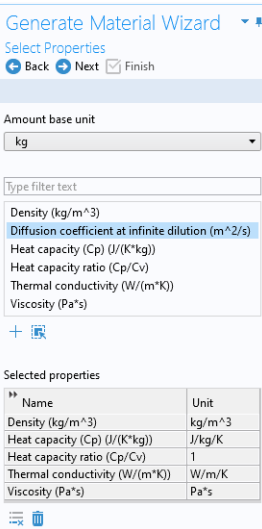
The next step is to specify material properties for the model. Ready-to-use materials can be selected from the available libraries or generated from Thermodynamics. In this model, first generate a material node for nitrogen (solvent) from our Gas System, under Thermodynamics. After that, generate the solid monolith material. Both these materials are then used to create a Porous Material.

The created materials are assigned to the relevant selections in the geometry. This allows the physics interfaces in these selections to access the material properties.

THERMODYNAMICS

1 In the Model Builder, under Global Definitions 🌐, locate Thermodynamics 🔺 > Gas System 🔺.

2 Right-click on Gas System and choose Generate Material 🔧.

This opens the Generate Material wizard which consists of several steps to create a Material node from our property package.

3 In Select Phase window, choose Gas (default) and click Next ➡.

4 In Select Species window, Add all 🔳 to the Select species table (default).

5 In Material composition section, set the mole fraction of nitrogen as 1 and 0 for others.

6 Click the mass fraction button.

7 Click Next ➡ in the wizard.

8 In the Select Properties window, choose Diffusion coefficient at infinite dilution, and click Add Selected ➕ .

9 In the Select solvent subsection, choose nitrogen from the Select solvent list. Click Next ➡ .

10 In Define Material window, choose Global from the Component list. This adds the material to the global Material node and thus makes it accessible for the Porous Material feature.

11 From the Function type list, choose Interpolation. This creates interpolation functions for the material properties, which provides faster property evaluations.

12 Set the Temperature upper bound (High) to 673. Click Finish ☑ .

Generate Material Wizard
Select Properties
Back ● Next ➡ ☑ Finish

Amount base unit
kg

Type filter text
Density (kg/m^3)
Diffusion coefficient at infinite dilution (m^2/s)
Heat capacity (Cp) (J/(K*kg))
Heat capacity ratio (Cp/Cv)
Thermal conductivity (W/(m*K))
Viscosity (Pa*s)

➕ ▣

Selected properties

Name	Unit
Density (kg/m^3)	kg/m^3
Heat capacity (Cp) (J/(K*kg))	J/kg/K
Heat capacity ratio (Cp/Cv)	1
Thermal conductivity (W/(m*K))	W/m/K
Viscosity (Pa*s)	Pa*s

MATERIALS

Gas

1 In the Model Builder, expand the Global Definitions>Materials node, then click
`Gas: ammonia(0)-nitrogen(1)-nitrogen oxide(0)-oxygen(0)-water(0)` ⊞ .

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

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

Solid

1 In the Materials toolbar, click Blank Material ⊞ .

2 In the Model Builder window, expand the Material 1 node, then click Basic (def).

3 In the Settings window for Property group, locate the Output Properties section. Click Select Quantity ➕ below the table.
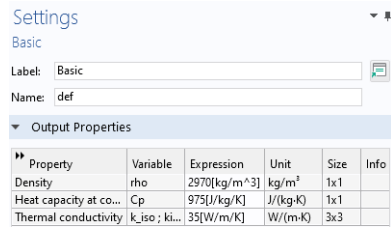
4 In the Physical Quantity dialog box, type `density` in the text field and click Filter 🔽. Select Density (kg/m^3). Click OK.

5 Perform the same action for the properties `heatcapacity` (choose Heat capacity at constant pressure (J/(kg*K)) and `thermalconductivity` (choose Thermal conductivity (W/(m*K)).

6 Add the expressions to the Output Properties section. Type `2970[kg/m^3]` for the density, `975[J/kg/K]` for the heat capacity, and `35[W/m/K]` for the thermal conductivity.

7 In the Model Builder window, right-click Material 1 and choose Rename.

8 In the Rename Material dialog box, type `Solid: Monolith Material` in the New Label text field.

9 Click OK.

In the next stage of the modeling process, add a Porous Material that consists of the two materials that were just defined.

Porous Material

1 In the Materials toolbar, click More Materials and choose Local>Porous Material 🟦.

2 In the Settings window for Porous Material, locate the Geometric Entity Selection section. From the Selection list, choose Channel blocks.

Note: A description of how to set up these selections can be found in Geometry.

Fluid

3 Right-click Porous Material and choose Fluid 🟦. Notice that the generated global material Gas: Nitrogen is predefined for this node.

4 Right-click Porous Material and choose Solid 🟦. From the Solid Properties section, Material list, choose Solid: Monolith Material.

5 In the θ_s text field, type `1-por`.

Add a material for the monolith walls by linking to the global monolith material.

Walls

1 In the Materials toolbar, click More Materials and choose Local>Material Link 🔗.

2 In the Settings window for Material Link, locate the Geometric Entity Selection section and choose Supporting walls from the Selection list.

3 Locate the Link Settings section and choose Solid: Monolith Material (mat 1) from the Material list.

4 In the Label text field, type Walls.

Now it is time to set up the physics interfaces that describe the mass transport, heat transfer, and fluid flow in the monolithic reactor. Before continuing though, in the Model Builder toolbar, click Collapse All 📑 to get a better overview of the tree for the remainder of the model setup.

Transport of Diluted Species in Porous Media Interface

During the Generate Space-Dependent Model procedure several feature nodes were added along with the new physics interfaces. Now go through these features one by one and enter settings, and make sure that they are assigned to the proper domains and boundaries in the 3D reactor.

1 In the Model Builder window, under 3D Model, click Transport of Diluted Species in Porous Media (tds) 🔶.

2 In the Settings window, under Domain Selection, choose Channel blocks from the Selection list. This is the only domain where there is diffusion of diluted species in porous media.

3 In the Model Builder window, expand the Transport of Diluted Species in Porous Media (tds) node.

Porous Medium

1 In the Model Builder window, expand the Porous Medium 1 🔷 node, then click Fluid 1. The 'D' in the upper left corner of a node denotes that it is a default node.

2 In the Settings window, locate the Model Input section. The Temperature is automatically set to Temperature (ht). Click the Go to Source 📑 button to see the Contributing Entities.

3 In the Settings window for Fluid 1, locate the Convection section.
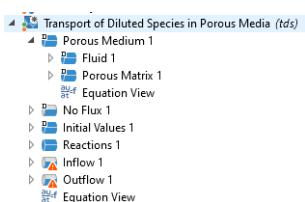
4 From the **u** list, choose Darcy's velocity field (dl/porous1).

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 is modeled by specifying the diffusivity only in the first element of the diagonal diffusion matrix. This is done in the following way:

5 Locate the Diffusion section. From the Source list, choose Material.

6 For each species, change from Isotropic to Diagonal for the Fluid diffusion coefficient.

7 For each species, set all but the *xx*-component of the diffusion coefficients to zero. Then enter the following expressions, one for each species, for the *xx*-component (upper left corner of the matrix):

- For $D_{F,cH2O}$ type `pp1mat1.df4.D11`

- For $D_{F,cNH3}$ type `pp1mat1.df1.D11`

- For $D_{F,cNO}$ type `pp1mat1.df2.D11`

- For $D_{F,cO2}$ type `pp1mat1.df3.D11`

The entered expressions can be found under Global Definitions>Materials>Gas: Nitrogen (pp1mat1) node. `D11` represents the *xx*-component in the diffusivity matrix.

8 From the Effective diffusivity model list, choose No correction.

- Global Definitions
  - P₁ Parameters 1
  - Default Model Inputs
- Materials
  - Gas: Nitrogen *(pp1mat1)*
    - ▷ Basic *(def)*
    - ▷ Diffusion coefficient, ammonia in nitrogen (solvent) 1 *(df1)*
    - ▷ Diffusion coefficient, nitrogen oxide in nitrogen (solvent) 2 *(df2)*
    - ▷ Diffusion coefficient, oxygen in nitrogen (solvent) 3 *(df3)*
    - ▷ Diffusion coefficient, water in nitrogen (solvent) 4 *(df4)*
  - ▷ Solid: Monolith Material *(mat1)*
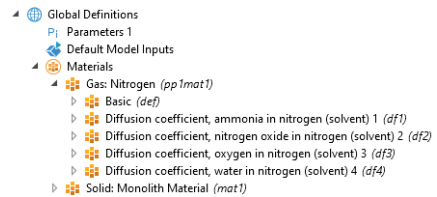
The Diffusion section should now look like this:

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 window, under Transport of Diluted Species in Porous Media, click Initial Values 1 [icon].

2 In the Settings window for Initial Values, locate the Initial Values section and change the default concentrations to zero.

In addition to the default feature nodes, the nodes Reactions 1, Inflow 1 and Outflow 1 were also added during the Generate Space-Dependent Model procedure. The Reaction feature gets input from the Chemistry interface in the 3D model. The inflow and outflow features' icons are marked with the warning sign [icon] in the Model Builder window. The warning message, seen when placing the mouse pointer on top of the icons, reveals that they are empty and need to be assigned to the proper domains and boundaries in the 3D reactor model.

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

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

1 In the Model Builder, click Outflow 1 ▭ .

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

Heat Transfer in Porous Media

Next, set up the Heat Transfer in Porous Media interface. Similarly to the procedure used for the mass transfer interface, go through the generated feature nodes, modify and add as needed.

POROUS MEDIUM

Begin by specifying the Fluid in the Porous Medium feature, accounting for convective and conductive heat transfer in the channel blocks.
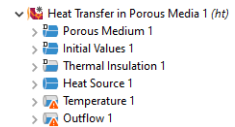
Fluid

1 In the Model Builder window, under the Heat Transfer in Porous Media 1 [icon] interface, expand the default Porous Medium 1 node ▭, then click Fluid 1 ▭.

2 In the Settings window, locate the Heat Convection section and choose Darcy's velocity field (dl/porous1) from the **u** list.

3 Locate the Heat Conduction Fluid section. From the k_f list, choose From material.

4 Locate the Thermodynamics, Fluid section. Choose From material in the corresponding list for each of these properties: ρ_f, $C_{p,f}$, and γ.
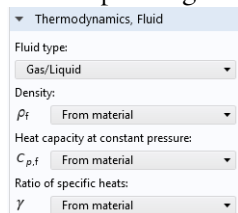
Note that the fluid properties are now defined by the corresponding node of the Porous Material.

Porous Matrix

1 In the Model Builder window, click Porous Matrix 1.

2 In the Settings window for Porous Matrix 1, locate the Matrix Properties section and choose Solid phase properties from the Define list.

3 In the Settings window, locate the Heat Conduction, Porous Matrix section and choose User defined from the k_s list. Additionally, choose Diagonal.

Specifying the diagonal thermal conductivity elements is needed to model anisotropic conductive heat transfer in the channel blocks.

4 In the k_s table, enter the following settings:

0.13[W/m/K]	0	0
0	0.25[W/m/K]	0
0	0	0.25[W/m/K]

Note that apart from the conductivity, the matrix properties are now defined by the Solid node added to the Porous Material.

INITIAL VALUES

1 In the Model Builder window, click Initial Values 1, and locate the Initial Values section in the Settings window. Type T_in in the *T* text field. This parameter was previously defined in Parameters.

HEAT SOURCE

Associate the Heat Source to the exothermic chemistry within the channel blocks. The Heat Source feature and the expressions describing the heat source are generated by the Generate Space-Dependent Model feature, linking the 3D model to the plug flow model.

1 Under Heat Transfer in Porous Media 1 (ht) 🔴, click the Heat Source 1 node 🔲.

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

TEMPERATURE

1 In the Model Builder window, click Temperature 1 and locate the Boundary Selection section in the Settings window.

2 From the Selection list, choose Inlet walls.

Outflow

1 In the Model Builder window, click Outflow 1 and locate the Boundary Selection section in the Settings window.

2 From the Selection list, choose Outlet.

Solids

Now define the conductive heat transfer in the supporting solid walls. Note that the physical properties of the walls are taken from the material Solid: Monolith Material, associated with that domain. The association was performed in the section Walls.

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

2 In the Physics toolbar, click Domains and choose Solid ▣ .
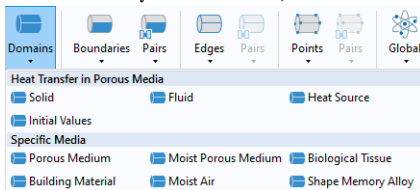
3 In the Settings window, locate the Domain Selection section and choose Supporting walls from the Selection list.

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

Heat Flux 1

1 In the Physics toolbar, click Boundaries and choose Heat Flux ▣ .

2 In the Settings window, locate the Boundary Selection section and choose Reactor surface from the Selection list.

3 Locate the Heat Flux section and click the Convective heat flux button.

- In the Heat transfer coefficient (h) text field type 10[W/(m^2*K)].

- In the External temperature (T_{ext}) text field type T_amb.
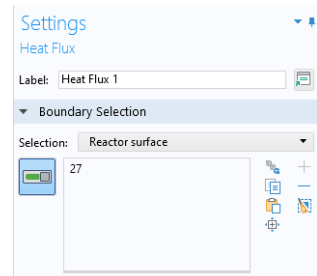
HEAT FLUX 2

1 In the Physics toolbar, click Boundaries and click to add a second Heat Flux node 📘 .

2 In the Settings window:

- In the Boundary Selection section, choose Outlet walls from the Selection list.

- In the Heat Flux section choose the Convective heat flux button. In the Heat transfer coefficient (h) text field type 1. In the External temperature (T_{ext}) text field type T_amb.
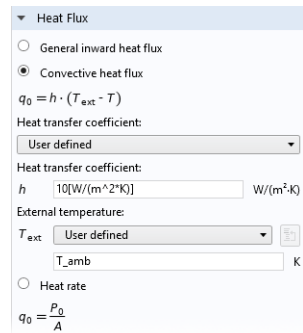
SYMMETRY

1 In the Physics toolbar, click Boundaries and choose Symmetry 📘 .

2 In the Settings window, locate the Boundary Selection and choose Symmetry from the Selection list.

INFLOW

1 In the Physics toolbar, click Boundaries and choose Inflow 📘 .

2 Locate the Boundary Selection section and choose Inlet from the Selection list.

3 In the Settings window, locate the Upstream Properties section and type T_in in the T_{ustr} text field.

The node sequence in the Model Builder under the Heat Transfer in Porous Media interface should now match this figure:
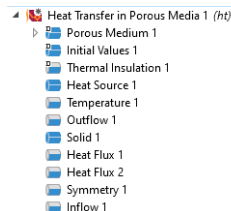
Darcy's Law Interface

Follow these steps to set up the Darcy's Law interface that describes the fluid flow through the reactor.

1 In the Model Builder window, under 3D Model (comp2), click the Darcy's Law 1 (dl) node 🔷 .

2 In the Settings window, locate the Domain Selection and choose Channel blocks from the Selection list.

POROUS MATRIX 1

1 Expand the Darcy's Law (dl)>Porous Medium 1, click Porous Matrix 1 .

2 Locate the Matrix Properties section, from the Permeability κ list, choose User defined and Diagonal.

3 In the κ table, enter the following settings:
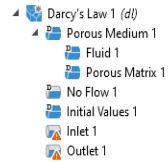
3.3e-7	0	0
0	0	0
0	0	0

SETTING THE BOUNDARY CONDITIONS

Now specify the boundary conditions for the Inlet, Pressure, and Outlet features.

1 In the Model Builder window, click Inlet 1 .

2 Locate the Boundary Selection section and choose Inlet from the Selection list.

3 Locate the Boundary Condition section and choose Mass flow from the list.

4 In the Mass flow section, type M0_in in the M_0 text field.

1 In the Model Builder window, click Outlet 1 .

2 Locate the Boundary Selection section and choose Outlet from the Selection list.

3 Locate the Boundary Condition section and choose Pressure from the list. Leave the default pressure value as zero.

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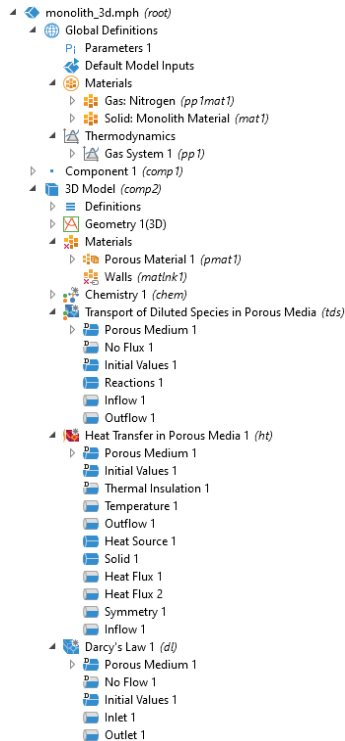
Before solving the problem numerically, the geometry needs to be discretized with a mesh.

Mesh

First create a Free Triangular mesh at the reactor inlet face and along two edges in the Symmetry boundary. Then complete the mesh by sweeping in the axial direction of the reactor.

FREE TRIANGULAR

1 In the Mesh toolbar from the Boundary ◬ menu, choose Free Triangular ◭ .

2 In the Settings window for Free Triangular, locate the Boundary Selection section and choose Inlet end from the Selection list.

Size 1

1 Right-click Free Triangular 1 �«◊ and choose Size ◭.

2 In the Settings window for Size, locate the Geometric Entity Selection section and choose Inlet walls from the Selection list.

3 Click the Custom button in the Element Size section.

4 Locate the Element Size Parameters section, select the Maximum element size check box and type 2.2 in the associated text field.

5 Select the Resolution of narrow regions check box and type 0.85 in the associated text field.

6 Click Build All ▦ .
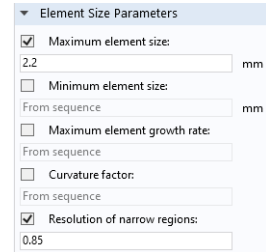
Now add a second Size feature to improve the mesh along two of the edges in the Symmetry boundary.

Size 2

1 In the Model Builder window, right-click Free Triangular 1 �«◊ and choose Size ◭.

2 In the Settings window for Size, locate the Geometric Entity Selection section and choose Edge from the Geometric entity level list.

3 Select Edges 5 and 17 only.

4 Locate the Element Size section and click the Custom button.

5 Locate the Element Size Parameters section, select the Maximum element size check box and type 5 in the associated text field.

6 Click Build All ▦ .

Now complete the mesh using the Swept feature.

SWEPT

1 In the Model Builder window, right-click Mesh 1 ◭ and choose Swept ◭.

2 Right-click Swept 1 ◭ and choose Distribution ▦ .

3 In the Settings window, locate the Distribution section and type 50 in the Number of elements text field.
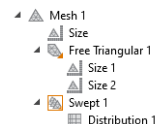
4 Click Build All ▦ , then click the Zoom Extents button ✛ in the Graphics toolbar to view the entire geometry.
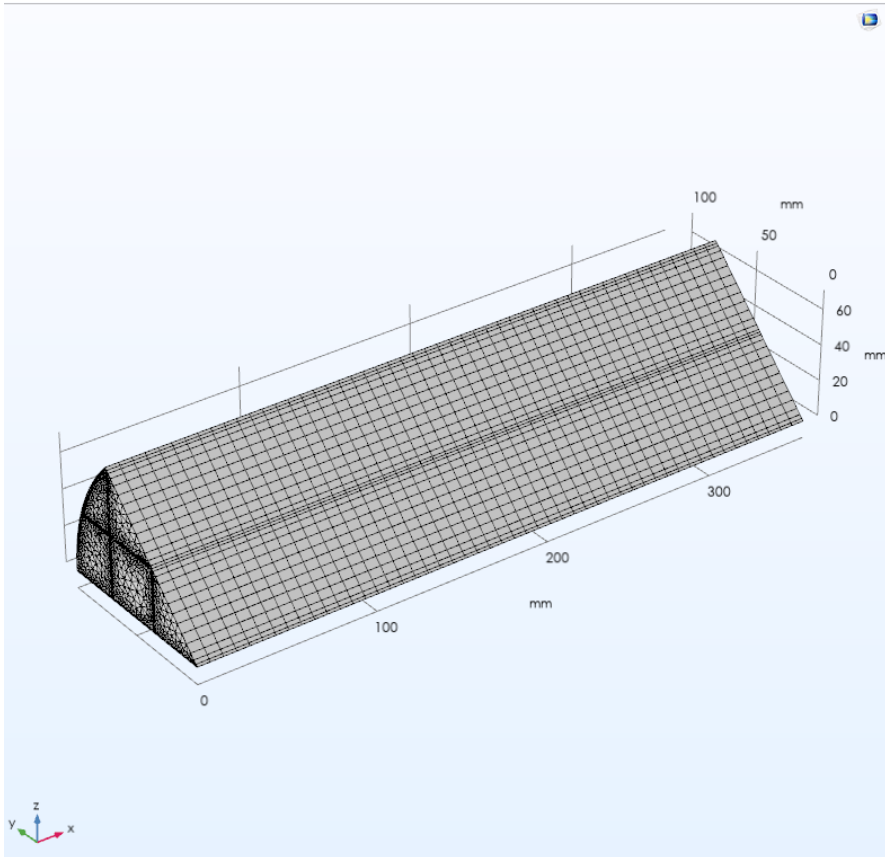
Study 2

It is time to solve the 3D 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 for Study 1.

1 In the Model Builder window, click Study 2 ⚬.

2 In the Settings window, locate the Study Settings section and clear the Generate default plots check box.

3 In the Home toolbar, click Compute ＝ .

Results — 3D Model

Follow these steps to create Figure 9, Figure 10, and Figure 11 for the 3D monolith model.

CONVERSION 3D MODEL - FIGURE 9

1 In the Home toolbar, click Add Plot Group and choose 3D Plot Group .

2 In the Settings window, type `Conversion 3D Model` in the Label text field.

3 Locate the Color Legend section and choose Left from the Position list.

4 Right-click the Conversion 3D Model node and choose Isosurface .

5 In settings window locate the Expression section and type `(F_NO_in/vrate-cNO)/(F_NO_in/vrate)` in the Expression text field. This plots the conversion of NO in the reactor.
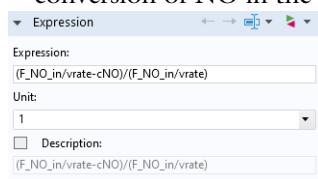
6 Locate the Levels section and type `20` in the Total levels text field.

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

8 In the Conversion 3D Model toolbar, click Plot .

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

TEMPERATURE 3D MODEL - FIGURE 10

1 In the Home toolbar, click Add Plot Group and choose 3D Plot Group .

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

3 Locate the Color Legend section and choose Left from the Position list.

4 Right-click the Temperature 3D Model node and choose Slice .

5 Locate the Expression section and type `T` in the Expression text field.

6 Locate the Plane Data section and type `10` in the Planes text field.

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

8 In the Temperature 3D Model toolbar, click the Plot button .

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

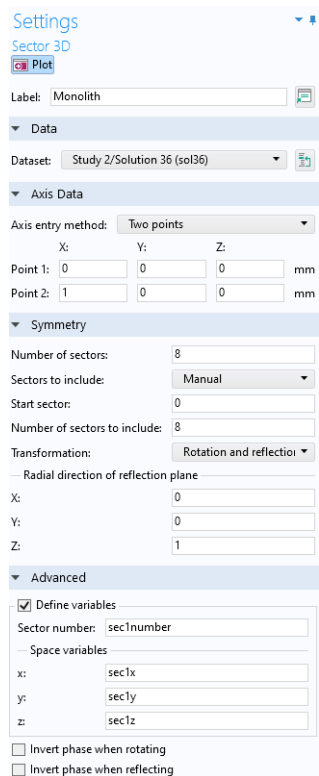In the last plot for this tutorial model, the full monolith structure is visualized (see Figure 11). This is accomplished by creating Sector 3D datasets, Slice plots, and using Filter.

In the first step, create the dataset for the selectivity data.

Sector 3D datasets

1 In the Results toolbar, click More Datasets ⚏ and choose Sector 3D 🌀.

2 In the Settings window, type `Monolith` in the Label text field.

3 Locate the Axis Data section and in row Point 2 set

- X to 1
- Z to 0

4 Locate the Symmetry section and type 8 in the Number of sectors text field.

5 From the Sectors to include list, choose Manual.

6 From the Transformation list, choose Rotation and reflection.

7 Find the Radial direction of reflection plane subsection and type

- 0 in the X text field and
- 1 in the Z text field.

8 Click to expand the Advanced section and select the Define variables check box. This setting is needed later by the Filter feature, used to exclude one sector from the Selectivity dataset.

9 Click Plot 🖼 in the Settings window to see the geometry of the created dataset.

In the next step, create the dataset that the temperature data will be added to. This is done by creating a Sector 3D dataset with only two sectors.

1 Right-click Monolith and choose Duplicate 🗐.

2 In the Settings window, type `Temperature sector` in the Label text field.

3 Locate the Symmetry section and type 2 in the Start sector text field.

4 Type 1 in the Number of sectors to include text field.

Now create a plot group that will use the created datasets.

3D Plot Group

1 In the Results toolbar, click 3D Plot Group 🔳 .

2 In the Settings window, type Monolith view in the Label text field.

3 Locate the Data section and choose Monolith from the Dataset list.

4 Locate the Plot Settings section and clear the Plot dataset edges check box.

5 Select the Show units check box in the Color Legend section.

Now add plots to the created plot group. The plots will use the sector 3D datasets. Begin with the selectivity data.

Slice Plot Selectivity

1 Right-click Monolith view and choose Slice 🔳 .

2 In the Settings window for Slice, type `Selectivity` in the Label text field.

3 Locate the Expression section. In the Expression text field, type `S`.

4 Select the Description check box.

5 Locate the Plane Data section and choose Coordinates from the Entry method list.

6 Click Range 🔳 and choose Number of values from the Entry method list in the Range dialog box.

7 In the Start text field, type `0` and in the Stop text field type `L` (the parameter for reactor length).

8 In the Number of values text field, type `5`. Click Replace.

9 In the Monolith view toolbar, click Plot 🔳 .

Now add the plot for the temperature data.

Slice Plot Temperature

1 Right-click Selectivity and choose Duplicate 🔳 .

2 In the Settings window, type `Temperature` in the Label text field.

3 Locate the Data section and choose Temperature sector from the Dataset list.

4 Locate the Expression section and type `T` in the Expression text field.

5 In the Description text field, type `Temperature`.

6 Locate the Coloring and Style section and choose HeatCameraLight from the Color table list.

By looking at the plot in the Graphics window we notice that the selectivity data is plotted on top of the temperature data. Use Filter to exclude the selectivity data from the temperature sector.

Filter

1 In the Model Builder window, click Selectivity.

2 In the Settings window, click to expand the Quality section and choose None from the Smoothing list.

3 Right-click Selectivity and choose Filter ▼ .

4 In the Settings window for Filter, locate the Element Selection section and type sec1number!=2 in the Logical expression for inclusion text field.

5 In the Monolith view toolbar, click Plot ▣ .

The plot in Figure 11 contains an arrow surface displaying the Darcy's velocity field. Create that plot using a Cut Plane dataset and an Arrow Surface plot.

Cut Plane

1 In the Results toolbar, click Cut Plane ▣ . This adds a Cut Plane dataset.

2 In the Settings window, locate the Data section and choose Monolith from the Dataset list.

3 Locate the Plane Data section and choose YX-planes from the Plane list.

4 In the Z-coordinate text field, type 2. Click Plot ▣ .

5 In the Model Builder window, right-click Monolith view and choose Arrow Surface ▣ .

6 In the Settings window for Arrow Surface, locate the Data section and choose Cut Plane 1 from the list.

7 Click Replace Expression ▶▼ in the upper -right corner of the Expression section. From the Menu, choose 3D Model (comp2)>Darcy's Law 1>Velocity and pressure>dl.u,dl.v,dl.w -Darcy's velocity field.

8 Locate the Coloring and Style section and choose Cone from the Arrow type list. Select the Scale factor check box and type 80 in the corresponding text field.

9 In the Monolith view toolbar, click Plot ▣ .

10 Click the Go to Default View ⬎ button in the Graphics toolbar.

The final step is to derive values for the outlet average conversion, as well as the highest temperature reached in the reactor.

Average Conversion and Maximum Temperature

1 In the Results toolbar, click More Derived Values ▦ and choose Average>Surface Average ᴬⱽ .

2 In the Settings window, locate the Selection section and choose Outlet from the Selection list.

3 Locate the Expression section. Click Clear Table ✎ .

4 In the table, enter the following settings:

EXPRESSION	UNIT	DESCRIPTION
(F_NO_in/vrate-chem.c_NO)/(F_NO_in/vrate)	1	Conversion

5 Click Evaluate = .

6 In the Results toolbar, click More Derived Values and choose Maximum>Volume Maximum MAX .

7 In the Settings window, locate the Selection section and choose All domains from the Selection list.

8 Click Evaluate AV .